

De: [Carlos Suarez](#)
A: [normacov](#)
Asunto: U.S. Grains Council: Antecedentes anteproyecto norma primaria de calidad del aire para COVs
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Señores
Oficina de Partes
Ministerio de Ambiente

Estimados señores,

El Consejo de Granos de los Estados Unidos tiene el gusto de presentar sus comentarios para contribuir con antecedentes para la elaboración del anteproyecto de norma primaria de calidad del aire para compuestos orgánicos volátiles (COVs).

Remitimos en el presente correo un archivo en PDF integrando todos los recursos referenciados y aportados, así como [este link a la carpeta](#) que contiene todos los recursos de manera individual y numerada para su acceso.

Agradecemos confirmación de recibo del material y quedamos completamente a su disposición para profundizar sobre cualquiera de los recursos aportados, así como para apoyar el desarrollo de la norma primaria de calidad del aire para COVs.

Un cordial saludo,



Carlos F. Suárez Isaacs
Regional Ethanol Trade Specialist
Latin America





Agosto 13 de 2020

Señores
Oficina de Partes
MINISTERIO DE MEDIO AMBIENTE DE LA REPÚBLICA DE CHILE
Santiago de Chile

REF: Contribución de antecedentes para anteproyecto de norma primaria de calidad del aire para compuestos orgánicos volátiles (COVs)

Respetados señores,

Reciban un muy cordial saludo.

Por medio de la presente comunicación, el Consejo de Granos de los Estados Unidos (el Consejo), en desarrollo de su objetivo de promover el uso del etanol combustible como herramienta para reducir las emisiones tóxicas asociadas a los combustibles que afectan la calidad del aire y las emisiones de gases de efecto invernadero asociadas al sector transporte, desea formalmente aportar antecedentes para el expediente relacionado con el anteproyecto de norma primaria de calidad del aire para compuestos orgánicos volátiles (COVs) en Chile.

El Consejo de Granos de los Estados Unidos es una organización sin ánimo de lucro, dedicada a desarrollar mercados, facilitar el comercio, y mejorar la calidad de vida, por medio del fomento a la demanda y fortalecimiento de las capacidades de los socios comerciales de varios productos de origen agrícola de los Estados Unidos, dentro de los cuales se encuentra el etanol.

En América Latina, nuestra organización trabaja directamente con formuladores de política (ministerios, reguladores, legisladores, etc.) y los diferentes miembros de la cadena de suministro de combustibles, para: 1) resaltar los beneficios ambientales, económicos y de salud del etanol; 2) Implementar políticas locales exitosas de biocombustibles; 3) asegurar el rol del comercio en el cumplimiento de los objetivos nacionales asociados a los biocombustibles; y 4) fomentar el intercambio de información técnica y académica.

En el desarrollo de su actividad, el Consejo ha recopilado y apoyado el desarrollo de múltiples recursos técnicos y académicos que sustentan y validan los beneficios del uso del etanol en materia económica, ambiental y de calidad del aire. En ese sentido, **por medio de la presente nos permitimos señalar y compartir los elementos y conclusiones de múltiples estudios que identificamos como más relevantes para el anteproyecto de norma primaria de calidad del aire para compuestos orgánicos volátiles (COVs), la cual creemos que podría enriquecerse enormemente al incorporar la mezcla del etanol con la gasolina como herramienta para reducir las emisiones e impactos de los COVs en Chile.**

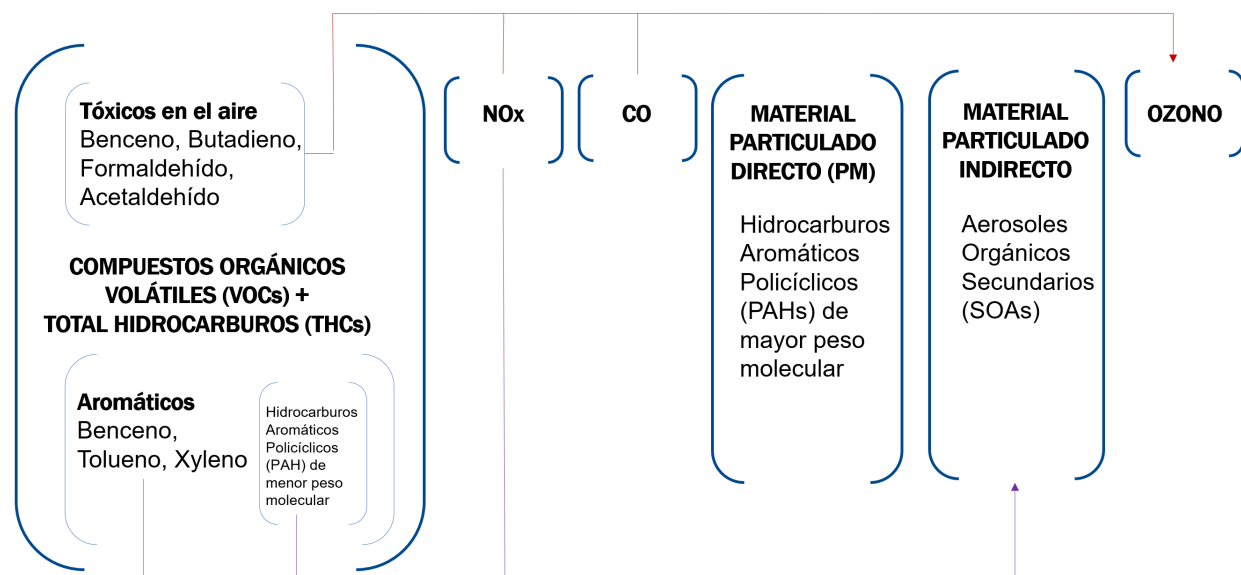
Una parte importante de los recursos aquí compartidos, hacen parte del trabajo de investigación de la Universidad de Illinois en Chicago, la cual ha dedicado importantes esfuerzos a su desarrollo y es considerada un referente en el tema.

Quedamos a su entera disposición para profundizar más sobre el material compartido, así como para facilitar la profundización en cualquiera de los temas que consideren pertinentes.

Contexto

Según la Agencia para la Protección Ambiental de los Estados Unidos (EPA, por sus siglas en inglés), los compuestos orgánicos volátiles (COVs) son compuestos de carbono “que tienen una alta presión de vapor y baja solubilidad en agua”¹. Los compuestos orgánicos se dividen en gases o aerosoles en función de sus propiedades químicas y vapor presión, donde aquellos que tienen baja vapor de presión ($<10^{-11}$ atm) a temperatura ambiente existen como aerosoles, mientras que los que cuentan con una alta vapor de presión ($>10^{-5}$ atm) existen en una fase gaseosa y se denominan comúnmente como compuestos orgánicos volátiles².

Los compuestos orgánicos volátiles incluyen algunos de los principales contaminantes para la salud humana como el benceno, el tolueno, el etilbenceno, el xileno y los hidrocarburos aromáticos policíclicos, los cuales fomentan además la formación de ozono y aerosoles orgánicos secundarios³. **Del total de COVs presentes en la atmósfera urbana, se ha demostrado que los compuestos aromáticos pueden llegar a constituir hasta entre un 20-30% de los compuestos orgánicos volátiles⁴, razón por la cual resulta fundamental revisar y controlar su presencia en los combustibles en el sector transporte.**



Adaptado de Steffen Mueller, University of Illinois at Chicago

El uso de hidrocarburos aromáticos en la gasolina es una práctica común en la refinación de combustibles, por cuenta de su alto aporte de octanaje y consecuente efecto antidetonante. Sin embargo, muchos de los aromáticos son considerados como compuestos tóxicos para el aire,

¹ “What are volatile organic compounds (VOCs)?”; EPA, , <https://bit.ly/3i5Cr1S>

² “Air Pollution from Gasoline Powered Vehicles and the Potential Benefits of Ethanol Blending”; Sobhani, Sadaf, <https://bit.ly/31xnti3>

³ “Public health impacts of secondary particulate formation from aromatic hydrocarbons in gasoline”, Katherine von Stackelberg, Jonathan Buonocore, Prakash V Bhavé & Joel A Schwartz; Environmental Health Volume 12, Article number: 19 (2013), <https://ehjournal.biomedcentral.com/articles/10.1186/1476-069X-12-19>

⁴ “The Mechanisms of Atmospheric Oxidation of the Aromatic Hydrocarbons”; J.G. Calvert, R. Atkinson, K.H. Becker, R.M. Kamens, J.H. Seinfeld, T.H. Wallington, and G. Yarwood. Oxford University Press, 2002.



entendidos como aquellos respecto a los cuales se ha comprobado o se sospecha que causan cáncer u otros efectos nocivos para la salud.

De acuerdo con el Centro de Estudios Energéticos de la Universidad de Illinois en Chicago, **dentro de “los compuestos atmosféricos más tóxicos asociados a las emisiones de los vehículos están el benceno, el 1,3 butadieno, el formaldehído, el acetaldehído y un grupo de compuestos llamados hidrocarburos aromáticos policíclicos (HAP)”**⁵. El impacto sobre la salud de los tóxicos más relevantes para el anteproyecto de norma primaria de calidad del aire para compuestos orgánicos volátiles (COVs) presenta a continuación⁶:

Benceno. El benceno ha sido clasificado como cancerígeno para los humanos (Grupo 1) por la Agencia Internacional para la Investigación del Cáncer. El benceno causa leucemia mieloide aguda (leucemia aguda no linfocítica) y se ha asociado positivamente con leucemia linfocítica aguda, leucemia linfocítica crónica, mieloma múltiple y linfoma no Hodgkin.

Butadieno. El 1,3-butadieno ha sido clasificado como cancerígeno para los humanos (Grupo 1) por la Agencia Internacional para la Investigación del Cáncer. El 1,3-butadieno se ha asociado con el cáncer de los órganos hematolinfáticos, como la leucemia.

Etanol: herramienta efectiva para el control de COVs

El uso de mezclas de etanol con gasolina se remonta a la década de 1970, cuando en Estados Unidos y Brasil se buscó reducir la dependencia en el crudo de los países del medio oriente, y la industria del petróleo tuvo que sustituir el aporte de octano del tetraetilo de plomo (plomo) en los procesos de refinación de gasolina, por cuenta de su prohibición a causa de sus efectos nocivos sobre la salud⁷. Sin embargo, hasta la década de los 90, no fue el etanol sino el el metil terbutil éter (MTBE) quien aportó el octanaje perdido por la prohibición del plomo, ya que este era un producto propio de la industria petrolera.

En el principal mercado de combustibles del mundo, Estados Unidos, el uso del MTBE en la gasolina fue restringido por un gran número de estados por cuenta de múltiples estudios que señalaron su alto potencial de contaminación de acuíferos y fuentes de agua potable⁸. Sin embargo, fue un litigio contra la industria petrolera y una conciliación multimillonaria⁹ lo que llevó a que se descontinuara el uso del MTBE de manera generalizada.

El uso de etanol como oxigenante en los combustibles se prolongó en Brasil desde la década de los 70, pero incrementó de manera exponencial cuando a principios de la década de los 2000, Estados Unidos lo adoptó como principal fuente de octanaje apalancado en el Estándar de Combustibles Renovables implementado en 2005. Desde entonces, se han desarrollado un sinnúmero de estudios para analizar el impacto de las mezclas de gasolina con etanol en diferentes niveles, por medio de los cuales se ha podido profundizar y entender cada vez mejor los beneficios que se generan en términos de calidad del aire y el medio ambiente por estas mezclas.

⁵ “Cancer Reductions from the Use of High-Octane Ethanol-Blended Gasoline with a Focus on Toxic Air Compounds”, Steffen Mueller, PhD, Principal Economist, University of Illinois at Chicago Energy Resources Center, <https://bit.ly/2EUjowJ>

⁶ Ibid

⁷ “Etanol combustible: el futuro del octanaje limpio, hoy” U.S. Grains Council, <https://bit.ly/3fniGso>

⁸ “Methyl Tertiary Butyl Ether (MTBE)”, U.S. Environmental Protection Agency, <https://bit.ly/30qHo2A>

⁹ “Groundwater Contamination Lawsuit Settlement- MTBE Factsheet”, <https://bit.ly/2DphmE7>

De manera muy concreta, la incorporación del etanol en los combustibles permite reducir el volumen de aromáticos en la gasolina, y, en consecuencia, la emisión de COVs. En la medida en que el etanol no contiene moléculas de aromáticos u olefinas, su incorporación en la gasolina permite diluir los aromáticos presentes en cada galón, mientras que el alto aporte de octanaje del etanol a la gasolina permite disminuir el volumen de aromáticos necesarios para cumplir con las especificaciones de octano. Este efecto ha sido ampliamente documentado en los Estados Unidos, donde el volumen de aromáticos disminuyó en un 7% entre 2000 y 2016, habilitado por el aumento en el volumen de etanol de cerca del 1% al 10% para el mismo periodo¹⁰.

En los Estados Unidos, la mezcla de etanol con el combustible permitió a las refinerías reducir su uso de aromáticos



Property	1990	2000		2016 RFG		2016 CG	
	Baseline	RFG Average	CG Average	Average	95%	Average	95%
Sulfur (ppm)	339	126	324	23.1	48.2	22.5	51.0
Benzene (vol%)	1.53	0.59	1.15	0.51	0.86	0.63	1.27
RVP (psi)	8.7	6.78	8.27	7.1	7.47	9.08	10.0
Aromatics (vol%)	32	19.3	28.5	17.12	27.3	21.76	32.1
E200 (vol%)	41	47.6	45.2	47.9	54.8	53.0	61.4
E300 (vol%)	83	84.7	80.7	85.6	92.0	84.8	91.1
Olefins (vol%)	13.1	10.6	11.8	10.5	18.7	8.38	16.4
Ethanol (vol%)	0.6	1.14	0.84	9.61	9.97	9.28	9.8

RFG: Gasolina reformulada | CG: Gasolina convencional

United States Environmental Protection Agency (EPA), Fuel Trends Report, 2017,

<https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100T5I6.pdf>

La norma primaria de calidad del aire para compuestos orgánicos volátiles (COVs) que Chile está en proceso de desarrollar ofrece una oportunidad muy valiosa para revisar la composición de sus gasolinas y en particular el volumen de aromáticos presente en las mismas, donde implementar las mezclas de etanol con gasolina en el país podría impactar de manera inmediata y costo-efectiva el efecto nocivo de los COVs tóxicos provenientes de los combustibles, tales como el benceno y el butadieno.

Desde el Consejo de Granos de los Estados Unidos aplaudimos los esfuerzos de Chile por buscar mejorar la calidad del aire para su población, donde la regulación de los compuestos orgánicos volátiles en los combustibles es un elemento fundamental. De igual forma, estamos seguros de que la mezcla de etanol con gasolina en Chile no sólo permitiría impactar positivamente las emisiones de COVs en el país, sino que podría además favorecer enormemente las emisiones de material particulado, las concentraciones de ozono y aerosol orgánico secundario, además de reducir las emisiones de efecto invernadero¹¹ e impactar positivamente el medio ambiente. En los estudios de Katherine Von Stackelberg se afirma que¹²:

“En los Estados Unidos, los vehículos que funcionan con gasolina son la mayor fuente de aromáticos hidrocarburos a la atmósfera. La mayoría de las formulaciones de gasolina

¹⁰ “Fuel Trends Report, 2017” U.S. Environmental Protection Agency (EPA), <https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100T5I6.pdf>

¹¹ “The greenhouse gas benefits of corn ethanol assessing recent evidence”, Lewandrowski et al, Biofuels, 2019

¹² Stackelberg et al, <https://ehjournal.biomedcentral.com/articles/10.1186/1476-069X-12-19>



consisten en aproximadamente 20% hidrocarburos aromáticos, que se utilizan en lugar de plomo para aumentar el octano. Por lo tanto, ha sido sugerido que la eliminación de compuestos aromáticos podría reducir las concentraciones de SOA y producir un considerable beneficio de salud pública"

A continuación, nos permitimos a compartir un resumen de la literatura relacionada con el impacto de las mezclas de etanol con gasolina en las emisiones vehiculares pertinentes, así como varios recursos y material que consideramos que puede servir como antecedente para enriquecer el ejercicio del Ministerio del Medio Ambiente en el desarrollo de la norma.

Listado de recursos compartidos por medio electrónico

1. "Summary of literature of vehicle emissions studies E10 and E20." University of Illinois at Chicago; Energy Resources Center, 2019.
2. "The Impact of Higher Ethanol Blend Levels on Vehicle Emissions in Five Global Cities"; University of Illinois at Chicago, Energy Resource Center; 2018
3. "Cancer Reductions from the Use of High-Octane Ethanol-Blended Gasoline with a Focus on Toxic Air Compounds"; University of Illinois at Chicago, Energy Resource Center ; 2019
4. "Avoided Mortalities from the Substitution of Ethanol for Aromatics in Gasoline with a Focus on Secondary Particulate Formation"; University of Illinois at Chicago, Energy Resource Center;; 2019
5. Presentation: "Environmental Benefits of Ethanol Blended Fuels"; Dr. Steffen Mueller, University of Illinois at Chicago, Energy Resource Center; September, 2019.
6. Presentation: "5 Cities Study"; Dr. Steffen Mueller, University of Illinois at Chicago, Energy Resource Center; March, 2019.
7. "Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles"; University of California, Karavalakis et al, Fuel, 2011
8. "Bioethanol Blending Reduces Nanoparticle, PAH, and Alkyl- and Nitro-PAH Emissions and the Genotoxic Potential of Exhaust from a Gasoline Direct Injection Flex-Fuel Vehicle"; Laboratory for Advanced Analytical Technologies, Laboratory for Air Pollution/Environmental Technology, EMPA, Swiss Federal Laboratories for Materials Science and Technology; Muñoz et al, Environmental Science and Technology, 2016
9. "An Overview of the Effects of Ethanol-Gasoline Blends on SI Engine Performance, Fuel Efficiency, and Emissions"; AVL Powertrain Engineering and Ford Motor Company; Stein et Al, SAE International, 2013.
10. "The greenhouse gas benefits of corn ethanol assessing recent evidence"; Lewandrowski et al, Biofuels, 2019; and USDA Factsheet: Lifecycle GHG emissions of corn-based ethanol.
11. "Air Pollution from Gasoline Powered Vehicles and the Potential Benefits of Ethanol Blending"; Sobhani Sadaf, <https://bit.ly/31xnti3>



12. "Public health impacts of secondary particulate formation from aromatic hydrocarbons in gasoline", Katherine von Stackelberg, Jonathan Buonocore, Prakash V Bhave & Joel A Schwartz; Environmental Health Volume 12, Article number: 19 (2013), <https://ehjournal.biomedcentral.com/articles/10.1186/1476-069X-12-19>

Resumen de literatura de los estudios de emisiones de vehículos E10 y E20

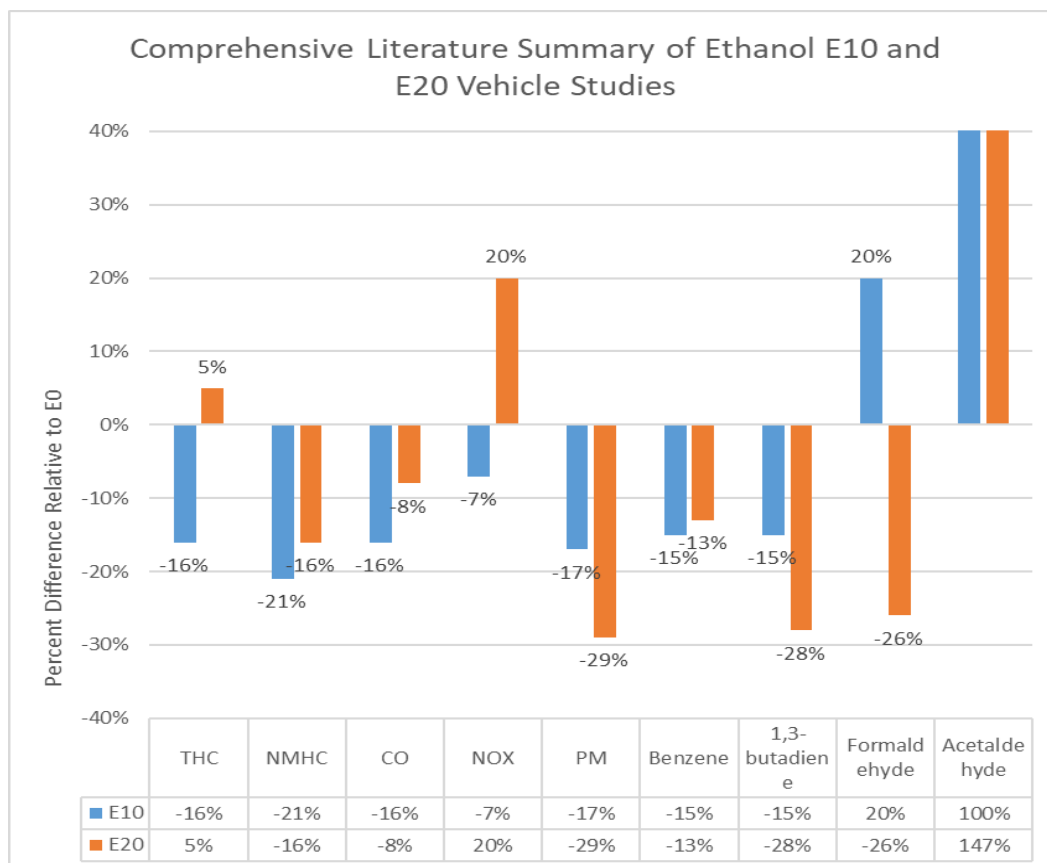
Steffen Mueller; PhD* y Sudheer Ballare**

*Energy Resources Center, University of Illinois at Chicago

**Department of Civil and Materials Engineering, University of Illinois at Chicago

Resumen:

Este documento sirve como suplemento al Estudio de 5 Ciudades de la UIC. Proporciona una actualización del resumen de la literatura mediante la inclusión de estudios recientemente publicados, así como de estudios adicionales de emisiones de vehículos que se han puesto en conocimiento de los autores. Tenga en cuenta que el estudio bibliográfico se llevó a cabo en apoyo del Estudio de 5 Ciudades de la UIC y los niveles de mezcla evaluados en el mismo, por lo tanto este cubre sólo aquellos niveles que incluyen mezclas de etanol en un 10% y un 20% en volumen. Los estudios revisados normalmente incluyen motores habilitados para etanol, pero no se centran en motores de alto octanaje que están optimizados para mezclas de etanol. El gráfico resumido a continuación muestra los ajustes medios de emisiones de las mezclas de etanol en todos los estudios por contaminantes. **Como se puede observar, las mezclas de etanol en un 10% en volumen proporcionan reducciones sustanciales de emisiones en todos los contaminantes estudiados (excepto en los aldehídos).** Esto es también el caso para las mezclas E20, excepto por una amplia variación en los resultados de las emisiones de NOx. Consulte la hoja de cálculo de Excel suplementaria a este documento para conocer los tipos de vehículos, los ciclos de prueba y el origen del estudio.



Tablas de resumen anotadas:

Las emisiones consideradas en esta sección incluyen Hidrocarburos Totales (THC), Hidrocarburos no metano (NMHC), Monóxido de carbono (CO), Óxidos de Nitrógeno (NOx) y Material Particulado (PM). Además, también se consideran los cuatro contaminantes tóxicos del aire (1,3 butadieno, benceno, formaldehído y acetaldehído) según lo requerido por el Procedimiento de Prueba de California para evaluar combustibles sustitutos y combustibles limpios.

Los cuadros 1 y 2 presentan los factores de emisión de etanol basados en el cambio porcentual de los factores de emisión de gasolina para los diversos contaminantes para las mezclas E10 y E20, obtenidos de la literatura publicada. El aumento de la mezcla de etanol da como resultado menor quema de combustible y temperaturas de exhosto. Las mezclas de etanol más altas proporcionan un alto octanaje cuando no hay ajuste de la gravedad de la unidad de reforma catalítica. Si la gravedad de la unidad de reforma catalítica se ajusta para mantener constante el octanaje de gasolina, las mezclas de etanol más altas dan como resultado un mayor volumen de gasolina. En las formulaciones de combustible, el etanol sustituye y diluye otros potenciadores de octanaje como el benceno, el tolueno y el xileno, causando una reducción de las toxinas clave asociadas a la combustión.

La literatura publicada muestra que la menor densidad energética del etanol probablemente no será un perjuicio significativo para la economía de combustible en combustibles correctamente diseñados y motores modernos, e incluso puede ser una ventaja en futuros diseños de motores dedicados de alto octanaje. En iBEAM, todos los cálculos de emisiones vuelven a una base por distancia y, por lo tanto, son independientes del ahorro de combustible.¹

Tabla 1: Factores medios de emisión de etanol (cambio relativo porcentual w.r.t. gasolina) obtenidos en la literatura para E10

Nombre del estudio	E 10 (% de cambio w.r.t. E0)								
	THC	NMHC	CO	NOx	PM	Benceno	1,3-butadieno	Formaldehído	Acetaldehído
Karavalakis et al., 2012	-12.80			13.60		-29	-30	-44	16
Bertoa et al., 2015	-65	-68	13			-56		-50	133
SAE, 1992	-4.90	-5.90	-13.40	5.10		-11.50	-5.80	19.30	159.00
NREL, 2009		-12	-15	-5.50				-85	9
Storey et al., 2010		-20	3	-42	-6			-29	95
ORNL 2012		-7.02	-2.36	34.26				-96	17
Promedio	-28	-23	-3	-3	-6	-32	-18	-47	72

Tabla 2: Factores medios de emisión de etanol (cambio relativo porcentual w.r.t. gasolina) obtenidos en la literatura para E20

Nombre del estudio	E 20 (% de cambio w.r.t. E0)								
	Thc	NMHC	Co	NO _x	PM	Benceno	1,3-butadieno	Formaldehído	Acetaldehído
Hilton y Duddy, 2009	-13.70	-19.10	-23.20	-2.40					

¹ Nota: Ibeam (Modelo Internacional de Análisis de Emisiones de Biocombustibles) es el término utilizado para el modelo de resumen de emisiones basado en hojas de cálculo desarrollado para el Estudio de 5 Ciudades.

Karavalakis et al., 2012	-22.9		-47.10	22.10			-36	-56	-36	101
NREL, 2009		-15	-12	12.23					-85	131
Storey et al., 2010			-14	-71	-29				-31	250
ORNL 2012		-17.05	-20.40	12.32					-81	161
Promedio	-18	-17	-23	-5	-29		-36	-56	-58	161

Tenga en cuenta que los hallazgos de la literatura muestran disminuciones generalmente consistentes para THC/NMHC, disminuciones constantes de CO para las mezclas de etanol más altas, disminuciones de PM con mezclas más altas de etanol, disminuciones para el benceno y el butadieno, pero mayor incertidumbre para NO_x y aldehídos.

Los resultados de las emisiones de iBEAM se comparan con los resultados de estudios adicionales en la literatura con respecto a los factores de emisión de etanol. Los resultados de esta validación se presentan a continuación:

Tabla 3: Factores medios de emisión de etanol (cambio relativo porcentual w.r.t. gasolina) obtenidos en literatura adicional para E10

Nombre del estudio	E 10 (% de cambio w.r.t. E0)								
	Thc	NMHC	Co	NO _x	PM	Benceno	1,3-butadieno	Formaldehído	Acetaldehído
Jin et al., 2017	15		6.18		-29.72	-67.27	-8	-14.00	
2011	-14		-2.60	-1.30					
Schifter et al., 2011	-5		-13.70	-2.70		-10	7	0	19
Zhu et al., 2017	-6		-22.70	-5.55					
Graham et al., 2008	9		-10	3		15	16	5	108
Bielaczyc et al., 2013	23		13.30	7.80	-19.70	-20.80		75	5.90
1998	-6.50		-8.30	-0.70		-20.10	-14	-40.00	
Canakci et al., 2013	-41		-24.20	-18.50					
Yao et al., 2011	-13	-11.50	-10	-4.40		-18		11.20	20.60
Czerwinski et al., 2016	-1		-16	-25				-17.20	
Martini et al., 2009	-49		-77	1	-26	17.90	-63.60	-5	149
Truyen et al., 2012	-4		-8	10.70					
Muñoz et al., 2019	-53		-75	-71.23					
Promedio	-13	-12	-21	-9	-23	-6	-14	-4	-128

Tabla 4: Factores medios de emisión de etanol (cambio relativo porcentual w.r.t. gasolina) obtenidos en literatura adicional para E20

Nombre del estudio	E 20 (% de cambio wrt E0)							
	THC	NMHC	Co	Nox	Benceno	1,3-butadieno	Formaldehído	Acetaldehído
Martins et al., 2014	84.6	0.0	78.0	153.0	0.0	0.0	0.0	0.0
Graham et al., 2008	0.0	-6.7	-31.8	78.6	26.3	0.0	61.5	200.0
Yao et al., 2011	-26.0	-21.8	-27.7	-12.0	-28.9	0.0	16.6	37.5
Truyen et al., 2012	3.1	0.0	22.3	-10.6	0.0	0.0	0.0	0.0

Promedio	20.6	-14.3	10.2	52.3	-1.3	0.0	39.1	118.8
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La revisión de la literatura adicional (cuadros 3 y 4) sobre los factores de emisión de etanol demuestra que los factores de emisión de etanol considerados en el modelo iBEAM están en línea con los resultados de otros estudios bibliológicos disponibles sobre mezclas más altas de etanol.

El Cuadro 5 presenta la media combinada de los factores de emisión de etanol para todos los estudios considerados aquí:

Tabla 5: Factores medios combinados de emisión de etanol (cambio relativo porcentual w.r.t. gasolina) obtenidos en literatura adicional para E10 y E20

	THC	NMHC	Co	NO _x	PM	Benceno	1,3-butadieno	Formaldehído	Acetaldehído
E10	-16	-21	-16	-7	-17	-15	-15	20	100
E20	5	-16	-8	20	-29	-13	-28	-26	147

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The Impact of Higher Ethanol Blend Levels on Vehicle Emissions in Five Global Cities

Update November 12, 2018



The Impact of Higher Ethanol Blend Levels on
Vehicle Emissions in Five Global Cities
University of Illinois at Chicago Energy Resources Center
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The Impact of Higher Ethanol Blend Levels on Vehicle Emissions in Five Global Cities

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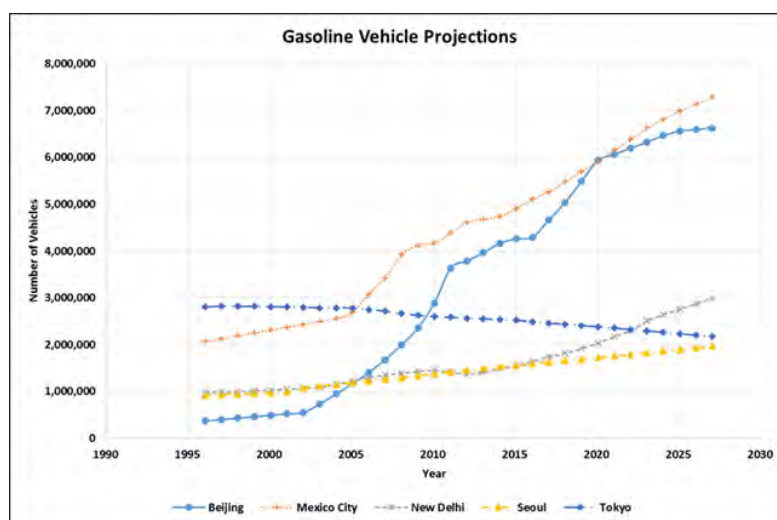
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Executive Summary

This study examines the tailpipe and greenhouse gas emissions savings from the use of ten and twenty percent ethanol blends in five mega cities around the world including Beijing, Delhi, Seoul, Tokyo, and Mexico City. The unique feature of the study is that it explores the comprehensive environmental linkages from fuel production through health impact. It takes into account: a) the regionally specific fuel blending requirements to meet local fuel specification, b) the calculated tailpipe emissions reductions in the local vehicle fleet and the local vehicle technology, c) the concentration reductions in the local atmosphere from the reduced tailpipe emissions, d) the localized health impact and treatment cost.

The model results indicate that ethanol added to gasoline will alter the gasoline formulation towards lower aromatic fuels and lower tailpipe emissions resulting in health benefits such as reduced cancer rates and health care costs. The benefits of such policies can be explored in conjunction with other clean transportation policies such as stricter fuel economy standards or electrification deployed separately or in combination.

The results of the study are based on a spreadsheet based model termed the International Biofuels Emissions Analysis Model (iBEAM). This model was developed in order to facilitate the exploration of many likely blending, emissions, and electric vehicle (EV) adoption scenarios in an open and transparent way while incorporating data from the latest ethanol-gasoline blend vehicle emissions studies.

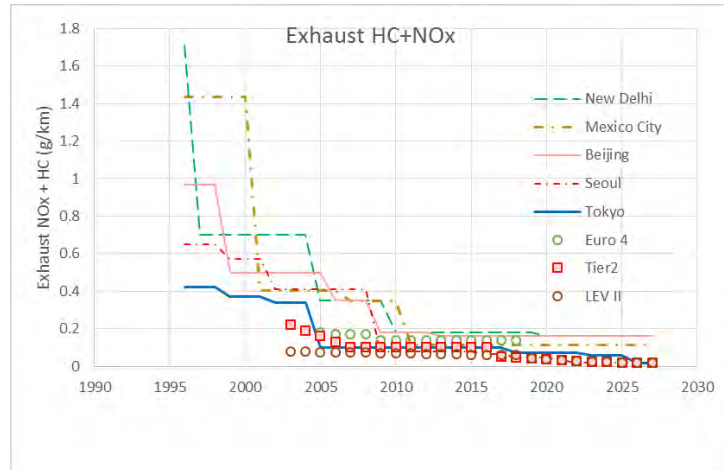


Tailpipe Emissions

The iBEAM model consists of a vehicle characterization module which is combined with an emission factor assessment for both gasoline and ethanol to derive total emissions adjustments from ethanol blended gasoline. In the model the projected passenger car population takes into account a) the projected electric vehicle share and b) the annual new car additions and replacement of retired vehicles.

The emissions factors for both gasoline and ethanol are assessed in two different ways:

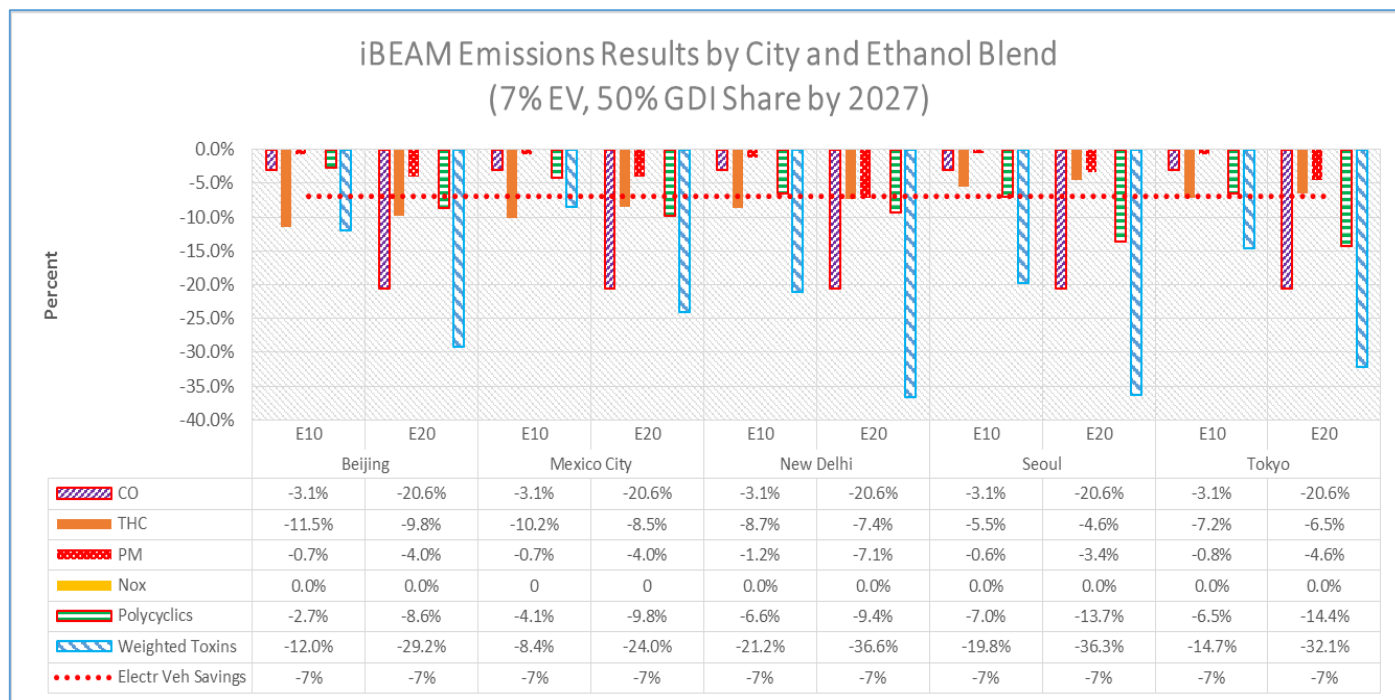
- Emissions Factors for Gasoline from Complex Model. In this case we ran the US EPA Complex Model with country specific gasoline samples to derive emissions factors for gasoline.



- Emissions Factors for Ethanol from Complex Model. A base gasoline was established for each city that met the properties of the gasoline samples followed by a modeled adjustment of the gasoline blend stocks from ethanol blending.
- Emissions Factors for Gasoline from past and future emissions standards. The past, current, and future emissions standards governing each city was surveyed for each city. The standards specify the emissions limits set for gasoline passenger vehicles for the applicable test protocols.
- Emissions Factors for Ethanol from published vehicle emissions studies. We surveyed the literature for substantially all major gasoline-ethanol vehicle emissions studies (for E10 and E20) and summarized the expected impact from ethanol on combustion emissions.
- For hydrocarbon emissions from gasoline and ethanol the effects of altitude and Reid vapor pressure on evaporative emissions were added as well as an explicit representation of refueling losses, permeation, spillage, and onboard refueling vapor recovery (ORVR) technologies.

On a total tonnage and percentage basis through the year 2027 the results show hydrocarbon (THC, VOC) reductions across all cities from E10 and E20 blends which should result in reduced risk for ozone formation in these cities. Furthermore, the study finds significant polycyclics and weighted toxins reductions (often correlated with cancer) and reduced CO emissions which reduces heart disease and other health effects. The study also shows that NOx emissions remain unaffected by ethanol blends.

The results are also particularly relevant in light of the current debate on electric vehicle deployment. Since iBEAM enables a selection of different EV adoption scenarios we can compare the emissions savings from ethanol blends to the emissions savings expected with EVs. Note that these are tailpipe emissions only and do not include any upstream emissions from electricity production which, in many of the studied countries, may come from coal fired power plants. The comparison between ethanol and EV (dashed red line in graph below) shows that EV vehicles through 2027 will just barely save the same amount of THC/VOC emissions as a fleet change to E10 and E20 would produce and that EV vehicles will provide significantly less savings for carbon monoxides and weighted toxins through 2027.



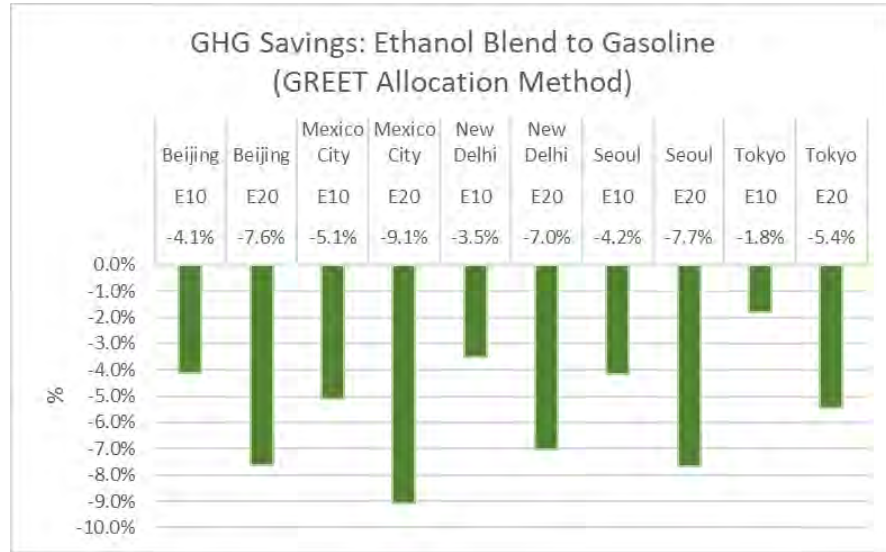
	Beijing		Mexico City		New Delhi		Seoul		Tokyo	
	E10	E20	E10	E20	E10	E20	E10	E20	E10	E20
CO	-69,613	-462,832	-94,806	-630,332	-21,844	-145,236	-15,004	-99,754	-21,480	-142,811
THC	-29,238	-24,866	-25,953	-21,593	-9,842	-8,353	-3,562	-2,968	-5,137	-4,581
PM	-10	-58	-11	-69	-6	-35	-1	-8	-4	-23

Greenhouse Gas Emissions

The GHG module in iBEAM calculates the GHG emissions based on data from two life cycle models:

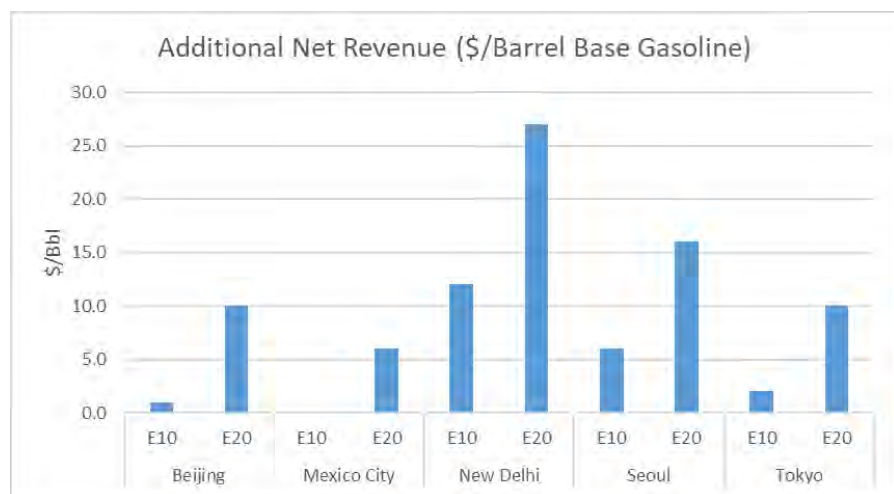
- 1) The GREET model developed by Argonne National Laboratory which is the gold standard for U.S. based life cycle analysis and contains the most up to date information on corn ethanol production. A California version of the GREET model is used for the Low Carbon Fuel Standard. An earlier version was used by the US Environmental Protection Agency for the Renewable Fuel Standard modeling.
- 2) The Biograce Model is a European life cycle model that evaluates European fuel pathways under the Renewable Energy Directive (RED). Current Japanese modeling efforts are also closely aligned with the EU RED methodology.

On a total tonnage and percentage basis the study shows sizable greenhouse gas reductions for all cities and ethanol blends. Cities with high fuel demand and current MTBE use can realize large GHG savings due to the high GHG intensity of the MTBE production pathway. Beijing and Mexico City, for example, can save 10 and 15 million metric tonnes of CO₂ emissions, respectively, from E10 blends through 2027.



Refinery Profitability

We assessed the financial impact on refiners serving our studied cities from accommodating E10 and E20 in their blend stocks. When oxygenates (like ethanol in E10 or E20) are added in gasoline blending, there is less need for octane from the catalytic reforming unit within a refinery and more hydrotreated naphtha feed to the catalytic reforming unit can be bypassed and blended directly to gasoline. The result is more gasoline production. However, as a result of operating at lower severity and processing less feed, there is less hydrogen produced from this unit for use in other plant processes. Based on our assessment of each country's refinery profile we determined the incremental hydrogen and incremental gasoline production and net revenue impact resulting from accommodating E10 and E20 in the blends. The net revenue was calculated on the basis of dollar per barrels of base case gasoline for each city. The results show that all ethanol blended fuels return equal or increased revenue for refiners.

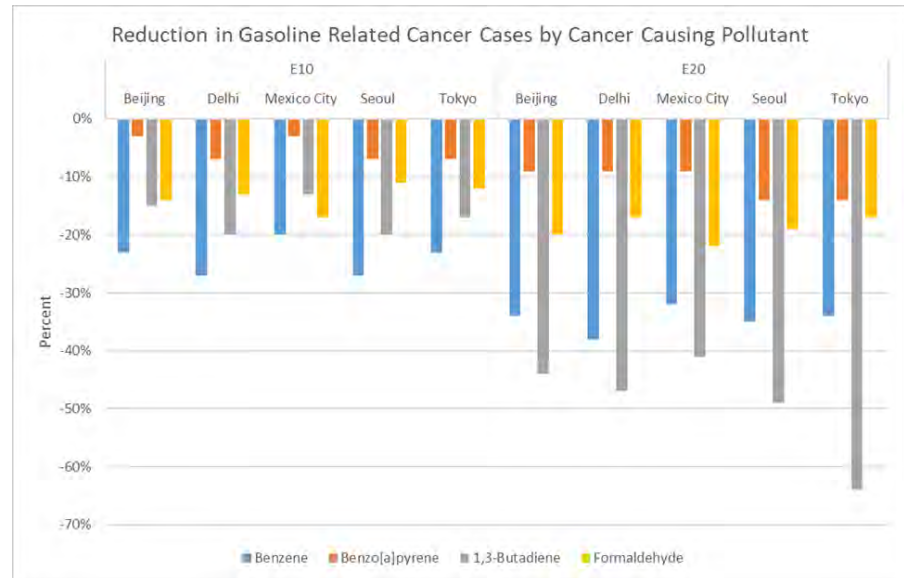


The net revenue was calculated on the basis of dollar per barrels of base case gasoline for each city. The results show that all ethanol blended fuels return equal or increased revenue for refiners.

Health Impact

The introduction of ethanol fuels was estimated to yield a net reduction of approximately 200-300 cancers per city, associated with several of the key pollutants in vehicle exhaust relative to continued use in gasoline, and varying among cities and between ethanol fuel blends. Avoiding these cancers will save several thousand years of potential life lost in each city and an additional tens of millions of

dollars of direct healthcare costs for cancer treatment. The impact of cancer, however, is much greater than these metrics, as cancer adversely impacts the quality of life, can lead to loss of income, and devastates families. For example, in the US, a person-year of life lost has been valued at \$150,000 which leads our assessment to show several hundred million dollars of savings from ethanol blends.



In summary adding E10 or E20 to the fuel supply in each of studied city significantly reduces key pollutants and especially air toxins and polycyclic hydrocarbons with quantifiable positive health impacts. Linear Refinery Programming showed that these ethanol blends given each country's refinery structure can be produced with additional profits to the refining sector.

1 Introduction

The purpose of this study coauthored by the University of Illinois at Chicago (UIC) Energy Resources Center is to assess the cumulative future tailpipe and greenhouse gas emissions benefits from adopting higher ethanol blends for the light duty vehicle market in light of current and predicted fuel demand for five major global cities. The study also assesses refinery profitability considerations associated with producing these fuels. The five cities of interest are Beijing, Mexico City, New Delhi, Seoul, and Tokyo, all of which face major air quality challenges.

In the United States the blending of ethanol at 10% and 15% (E10 and E15) in conventional vehicles and at higher blends (in flex fuel vehicles) has been accompanied by a dramatic reduction in air emissions across altitudes and throughout all driving seasons [1]. Together with Brazil and Europe a large amount of experience and data has been accumulated to document the benefits of introducing ethanol into the fuel supply.

The scenarios in the present study include the quantification of emissions differences between current gasoline use without ethanol compared to higher ethanol blends including E10 and E20. It is expected that the growing use of hybrid electric vehicles and fully electric vehicles (EVs) will eventually impact the demand for gasoline and ethanol, and therefore this trend will also be forecasted here through 2027.

Models that assess the contributions of vehicle tailpipe emissions from different ethanol gasoline blends would ideally incorporate emissions factors for different regional driving and traffic conditions, different vehicle vintages and market shares, altitude and climate effects, and the respective baseline fuel compositions. One such model, the US Environmental Protection Agency's MOtor Vehicle Emission Simulator (MOVES) is an emission modeling system that estimates emissions for mobile sources at the national, county, and project level for pollutants. However, MOVES is not set up to assess emissions from ethanol blends greater than E15 and its handling of ethanol blends E10 and E15 has received criticism [2] [3] [4] [5].

While MOVES has powerful databases the calculation of the data in a "black box" makes the interpretation of the results often difficult. Moreover, while a recent effort was made to adjust MOVES for Mexico the country-specific adjustment resorts often to basic recalibration factors which adds another level of uncertainty to the results.

In order to facilitate the exploration of many likely blending, emissions, and EV adoption scenarios in an open and transparent way we have developed a spreadsheet based model termed the International Biofuels Emissions Analysis Model (iBEAM).

For tailpipe emissions assessments this model allows us to incorporate data from the latest ethanol-gasoline blend vehicle emissions studies, while still taking key emissions aspects such as vehicle retirement and emissions control deterioration effects over time into account. Compared to MOVES we note that iBEAM is limited in its analysis to passenger cars and light trucks. Furthermore, we employ simplified vehicle activity data and rely on compliance with vehicle emissions standards.

For greenhouse gas emissions assessments, we rely on data from the GREET model developed by Argonne National Laboratory which is the gold standard for U.S. based life cycle analysis and contains the most up to date information on corn ethanol production. We also utilize the Biograce Model which is a European life cycle model that evaluates European fuel pathways under the Renewable Energy Directive (RED). Current Japanese modeling efforts are closely aligned with the EU RED methodology.

2 Structure of the iBEAM Emissions Model

This section provides an overview of the iBEAM structure. Each module will be further explained in the following sections.

The iBEAM model consists of a vehicle characterization module which is combined with an emission factor assessment for both gasoline and ethanol to derive total emissions adjustments from ethanol blended gasoline. Separately, the impact from the production of E10 and E20 fuels on refinery revenue is being assessed.

The vehicle characterization includes a projection of annual gasoline passenger car population multiplied by the distance travelled annually by each car to derive the total driven passenger distance (total kilometers) in each city. The passenger car population is a) also corrected for projected electric vehicle share and b) broken out by annual new car additions including replacement of retired vehicles.

The emissions factors for both gasoline and ethanol are assessed in two different ways:

- Emissions Factors for Gasoline from Complex Model. In this case we ran the US EPA Complex Model with country specific gasoline samples to derive emissions factors for gasoline.
- Emissions Factors for Ethanol from Complex Model. A base gasoline was established for each city that met the properties of the gasoline samples followed by a modeled adjustment of the gasoline blend stocks from ethanol blending.
- Emissions Factors for Gasoline from past and future emissions standards. The past, current, and future emissions standards governing each city was surveyed for each city. The standards specify the emissions limits set for gasoline passenger vehicles for the applicable test protocols.
- Emissions Factors for Ethanol from published vehicle emissions studies. We surveyed the literature for substantially all major gasoline-ethanol vehicle emissions studies (for E10 and E20) and summarized the expected impact from ethanol on combustion emissions.

Since emissions factors for gasoline and ethanol are only representative for the underlying vehicle fleet and control technology a correction of emissions factors by vehicle age was introduced. Finally, for hydrocarbon emissions the effects of altitude and Reid vapor pressure on evaporative emissions were added as well as an explicit representation of refueling losses, permeation, spillage, and onboard refueling vapor recovery (ORVR) technologies.

In most scenarios the blending of E10, E20 will enable refineries to produce more gasoline volume which will overall increase revenue. That revenue addition is compared against the need to add hydrogen production capacity to offset reduced production from the reforming unit within the refinery. The figure below provides a representation of the model structure. Appendix B provides a Quickstart to the iBEAM Excel spreadsheet.

iBEAM Structure

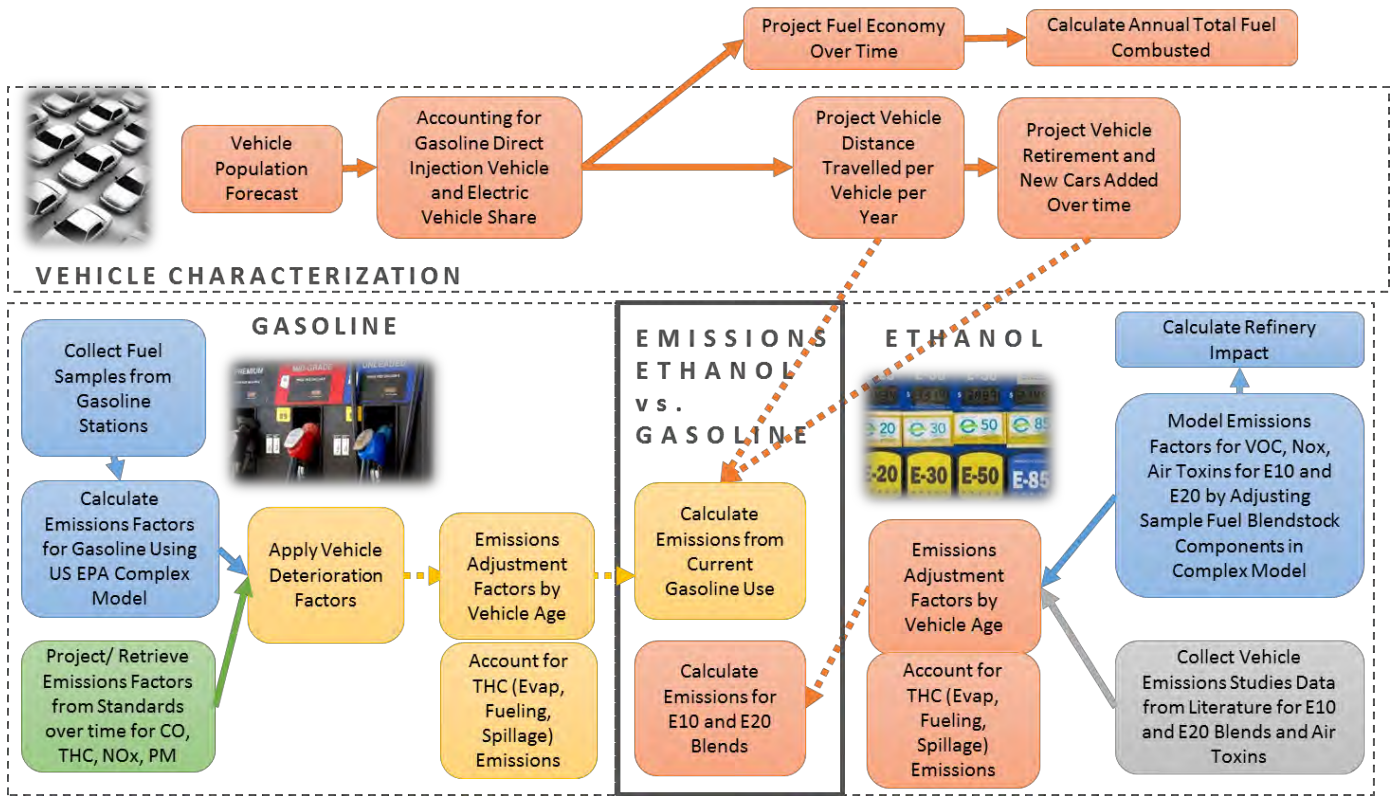


Figure 1: iBEAM Flow Diagram

3 Vehicle Characterization

3.1 Vehicle Population, Distance Travelled, and Fuel Economy

The vehicle characterization includes a projection of the annual gasoline passenger car population multiplied by the distance travelled by each car to derive the total driven passenger distance (total kilometers) in each city. This number is relevant since it can be multiplied by the emissions factors which are assessed in grams of pollutant per distance (e.g. kilometer) traveled to derive the total emissions from gasoline vehicles in a year.

The passenger car population in iBEAM is assessed for each city according to two separate methods: a) by extrapolating historic data on vehicle saturation levels (customarily stated in vehicles per 1000 people multiplied by projected population levels for each city and b) by reviewing existing vehicle studies for the respective country and city. For example, the figure below shows the extrapolation of vehicle data for Beijing. This data was then triangulated with published studies including an announcement that Beijing will limit vehicle sales to 6.3 million vehicles by to end of 2020.

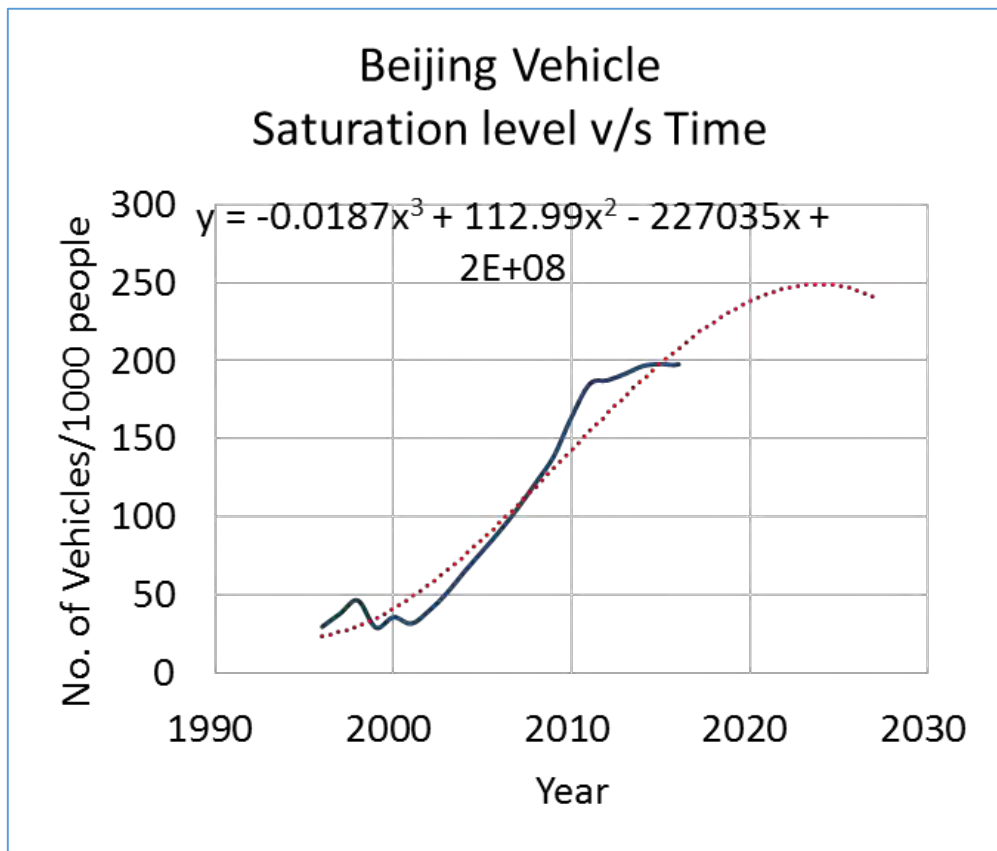


Figure 2: Example of Vehicle Population Estimation

Based on this approach we derived the vehicle populations for our cities shown in the graph below.

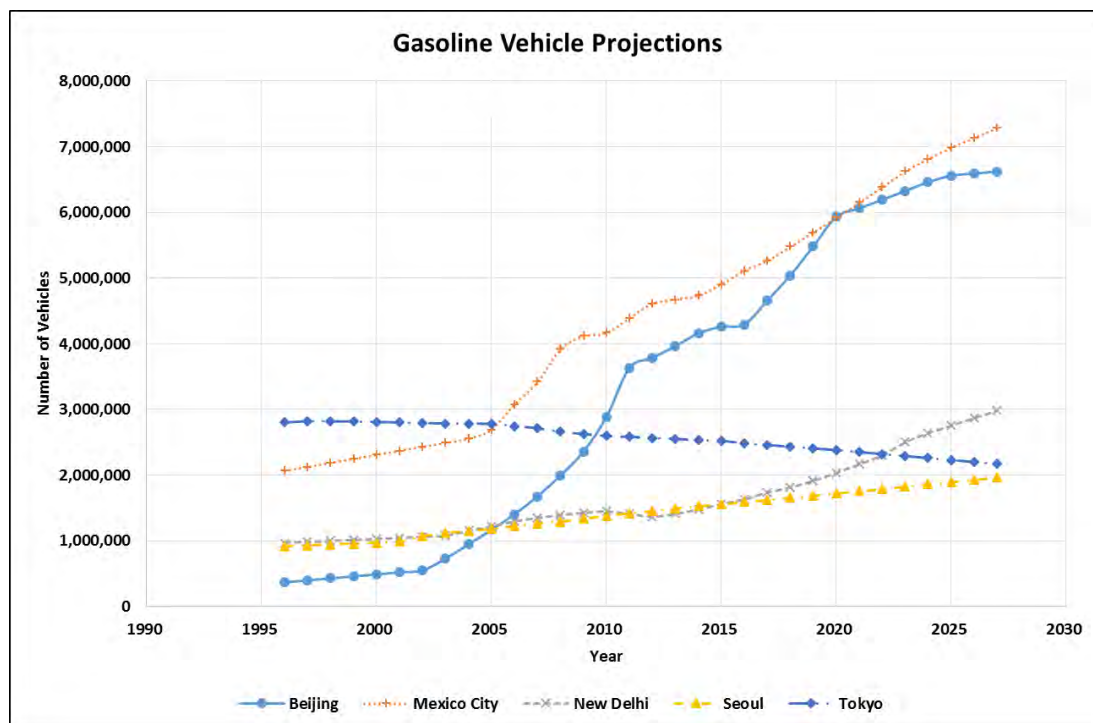


Figure 3: Summary of Gasoline Vehicle Projections by City

The tables below detail the citations used in iBEAM to characterize passenger car population and vehicle distance travelled.

Table 1: Sources for Gasoline Car Population

City	Citation	Notes
Beijing	<ul style="list-style-type: none"> National Bureau of Statistics of China http://www.stats.gov.cn/english/statisticaldata/AnnualData/ 	The data has been obtained by accessing the data sheet of every year and populating it into the excel file. China has banned all Diesel vehicles from the year 2000, thus all vehicle data is Gasoline only.
Mexico City	<ul style="list-style-type: none"> National Statistical and Geographic Information System "INEGI," [Online]. Available: http://www.inegi.org.mx/ 	Filters for Mexico City Metropolitan Area are applied, and the values for Passenger Vehicles are taken. The number of Diesel vehicles make up less than 0.1% of the data shown, thus all data provided are taken as Gasoline vehicles.
New Delhi	<ul style="list-style-type: none"> "Economic survey of Delhi," [Online]. Available: http://delhi.gov.in/wps/wcm/connect/DoI 	First citation gives the total population of passenger vehicles in Delhi. Second citation's appendix gives the

	<p>T Planning/planning/our+services1/economic+survey+of+delhi . [Accessed 22 June 2017].</p> <ul style="list-style-type: none"> • S. G. Rahul Goel, "Evolution of on-road vehicle exhaust emissions in Delhi," <i>Atmospheric Environment</i>, vol. 105, pp. 78-90, March 2015. 	split and projection between the gasoline and diesel vehicles.
Seoul	<ul style="list-style-type: none"> • "Number of Registered Motor Vehicles and Emission Quantity," 2013. [Online]. Available: http://eng.me.go.kr/eng/web/index.do?menuId=254 . [Accessed 24 July 2017] . • KAMA, 2016. [Online]. Available: http://stat.molit.go.kr/portal/cate/engStatListPopup.do. [Accessed 24 July 2017]. 	<p>The first citation gives the data of number of vehicles in South Korea. The second citation gives the data of number of gasoline vehicles in Seoul, for few years.</p> <p>The same percentage has been applied throughout the study as Seoul has incremental increase in vehicle population over the years.</p>
Tokyo	<ul style="list-style-type: none"> • http://www.toukei.metro.tokyo.jp/homepage/ENGLISH.htm • "Diesels may return to Japan roads," NY Times, 3 March 2006. [Online]. Available: http://www.nytimes.com/2006/03/03/business/worldbusiness/diesels-may-return-to-japan-roads.html . [Accessed 24 July 2017]. 	<p>The first citation gives the data of number of vehicles in Tokyo from the statistical year book. The second citation gives the data of number of gasoline vehicles in Japan as a split with Diesel, for few years.</p> <p>5% has been applied as the diesel share throughout the study as Tokyo has little changes in vehicle population over the years.</p>

The vehicle distance travelled by each car differs by city based on several factors including the geographic expansion of the city boundaries and the development of public transportation systems. For example, Guerra shows that the average vehicle distance travelled for Mexico City has increased over the past years, and that this trend will likely continue with outward urban sprawl. [6] . Conversely, for Seoul Myung-JinJun et. all, argue that with the “greenbelt and newtown development” in Seoul, commuting costs and travel distances would be significantly reduced. The table below lists the citations used in iBEAM for vehicle distance travelled per car followed by a summary graph.

Table 2: Sources for Vehicle Distance Travelled

City	Citation	Notes
Beijing	<ul style="list-style-type: none"> • He, "Oil consumption and CO2 emissions in China's road transport: Current status, future trends, and policy implications," <i>Energy policy</i>, vol. 33, no. 12, pp. 1499-1507, August 2015. • Huo, "Projection of Chinese motor vehicle growth, oil demand, and CO2 emissions through 2050," <i>Transportation research record</i>, no. 2038, pp. 69-77, 2007 	The data has been obtained by the two research papers. Values have been projected for future years. The missing middle data has been interpolated
Mexico City	<ul style="list-style-type: none"> • C. S.-P. Carlos Chavez-Baeza, "Sustainable passenger road transport scenarios to reduce fuel consumption, air pollutants and GHG (greenhouse gas) emissions in the Mexico City Metropolitan Area," <i>Energy</i>, vol. 66, pp. 624-634, March 2014. • http://journals.sagepub.com/doi/pdf/10.1177/0739456X14545170 * 	The data has been obtained from the first research paper. The second paper argues for an ever increasing VDT in Mexico City, owing to its geographic expansion.
New Delhi	<ul style="list-style-type: none"> • S. G. Rahul Goel, "Evolution of on-road vehicle exhaust emissions in Delhi," <i>Atmospheric Environment</i>, vol. 105, pp. 78-90, March 2015. 	Data has been obtained from the appendix of the citation.
Seoul	<ul style="list-style-type: none"> • http://kosis.kr/eng/statisticsList/statisticsList_01List.jsp#SubCont • http://www.sciencedirect.com/science/article/pii/S0264275101000075 ** 	Data from the citation gives the annual VDT for the years 2011-16. The second citation gives the city VKT trend for the remaining years.
Tokyo	<ul style="list-style-type: none"> • http://www.toukei.metro.tokyo.jp/homepage/ENGLISH.htm 	Citation gives the statistical year book of Tokyo. VDT is in terms of annual kilometers driven. Data has been calculated per vehicle from vehicle population data.

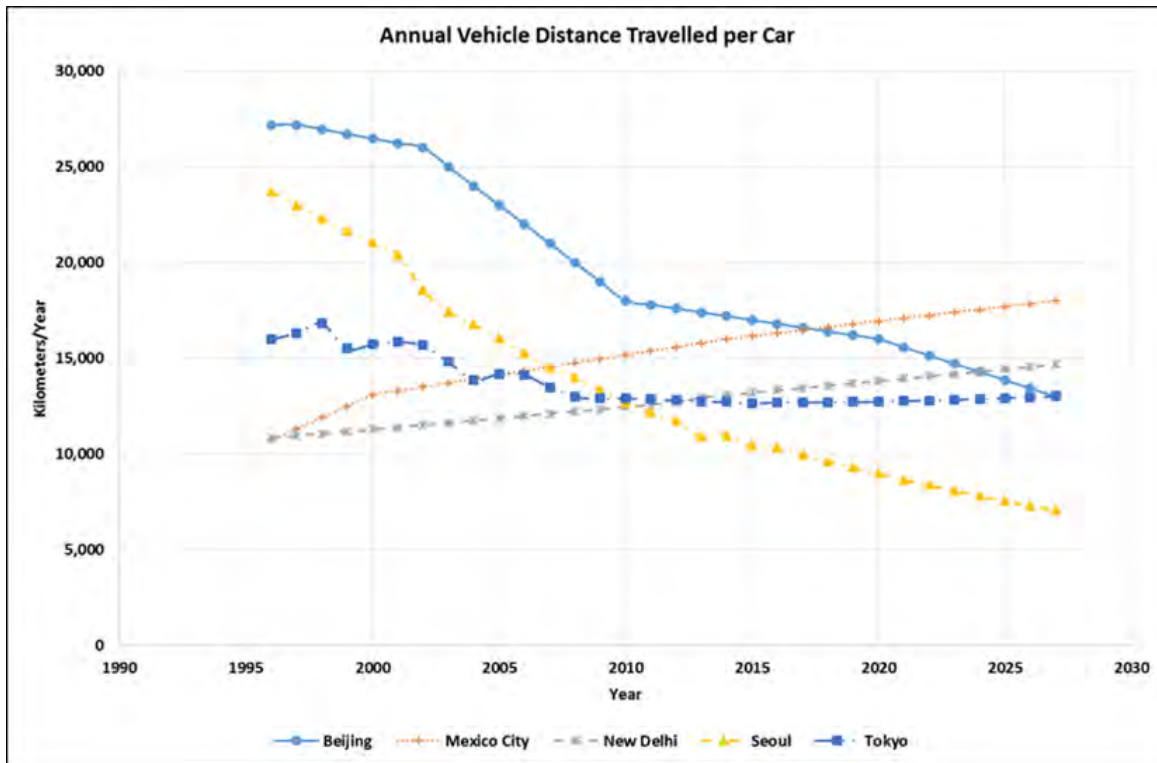


Figure 4: Summary of Annual Vehicle Distance Travelled by City

Fuel economy factors were developed for each of the cities. These factors are necessary for the fuelage, spillage, and permeation emissions calculations discussed in the respective section of this report. The table below lists the citations for the employed fuel economy values in iBEAM followed by a summary graph.

Table 3: Sources for Fuel Economy

City	Citation	Notes
Beijing	<ul style="list-style-type: none"> He, "Oil consumption and CO2 emissions in China's road transport: Current status, future trends, and policy implications," <i>Energy policy</i>, vol. 33, no. 12, pp. 1499-1507, August 2015. Han Haoa, "Comparison of policies on vehicle ownership and use between Beijing and Shanghai and their impacts on fuel consumption by passenger vehicles," <i>Energy policy</i>, vol. 39, no. 2, pp. 1016-1021, February 2011 	The data has been obtained by the two research papers. Values have been projected for future years. The missing middle data has been interpolated.

Mexico City	<ul style="list-style-type: none"> • http://dof.gob.mx/nota_detalle.php?codigo=2091196&fecha=07/09/2005. • C. S.-P. Carlos Chávez-Baeza, "Fuel economy of new passenger cars in Mexico: Trends from 1988 to 2008 and prospects," <i>Energy Policy</i>, vol. 39, no. 12, pp. 8153-8162, December 2011. 	The data has been obtained by the two research papers. Values have been projected for future years. The missing middle data has been interpolated.
New Delhi	<ul style="list-style-type: none"> • M. M. a. J. S. Stephane de la Rue du Can, "India Energy Outlook: End Use Demand in India to 2020," <i>ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY</i>, January 2009. 	Data has been obtained from the citation. Missing data has been interpolated.
Seoul	<ul style="list-style-type: none"> • "South Korea: Light-duty: Fuel Economy and GHG," 26 February 2016. [Online]. Available: http://transportpolicy.net/index.php?title=South Korea: Light-duty: Fuel Economy and GHG . [Accessed 24 Jul4 2017]. 	Seoul has defined a series of targets for manufacturers to achieve over the next few years.
Tokyo	<ul style="list-style-type: none"> • "Japan: Light-duty: Fuel Economy," icct and DieselNet, 3 January 2017. [Online]. Available: http://transportpolicy.net/index.php?title=Japan: Light-duty: Fuel Economy . [Accessed 25 July 2017]. 	Tokyo has defined a series of targets for manufacturers to achieve over the next few years.

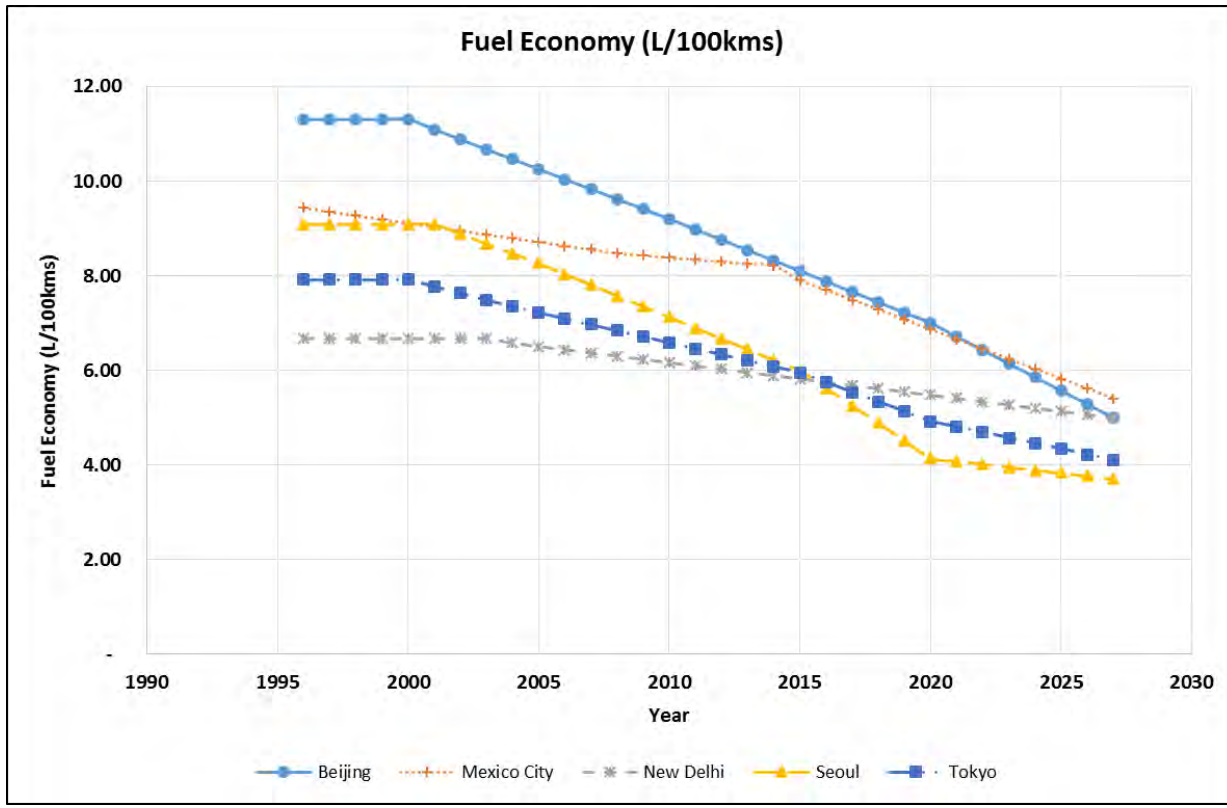


Figure 5: Summary of Fuel Economy by City

3.2 Electric Vehicle Share

In iBEAM we correct the vehicle population for the projected adoption of electric vehicles. Increased interest in EV power trains has been widely discussed in recent articles including a recent announcement by Volvo to manufacture solely battery-only and battery-hybrid vehicles by 2019 [7]. Estimates regarding the future adoption rate of this technology vary widely. A recent study by ReThinkX asserts that purely by economic factors, 95% of vehicle miles driven will be by electric vehicles by the year 2030 [8]. By contrast, a comment by Reg Modlin, former Director of Regulatory Affairs at Fiat Chrysler Automotive and a present Senior Advisor to the Ag-Auto-Ethanol Working Group, speaks more cautionary about the projected EV influence. He shows that recent aggressive electrification announcements by Volvo and Daimler still include provisions that internal combustion engines are included in mild-hybrid (Start/Stop), hybrid and plug-in hybrid systems [9].

Here are some regional positions from our areas of interest.

New Delhi, India

India has taken an aggressive stance to manufacture and sell only electric vehicles by the end of 2030. The energy minister has stated the intention to facilitate growth of the EV effort by subsidizing the cost of EVs for a couple of years until they become economically viable. With their target of 6-7 million EVs by the end of 2020, New Delhi could be a considerable adopter of EV technologies [10].

Beijing, China

China recently introduced a new vehicle energy score with aggressive targets of 10 percent of low or zero emissions vehicle sales per auto manufacturer starting in 2019, rising to 12 percent in 2020. [11] [12, 13].

Tokyo, Japan

A recent study by Nissan showed that Japan has more EV charging stations than gas fueling stations. Japan has been ahead of the curve in their interest in EVs, and started about a decade ago with infrastructure build out. Japan has set up subsidies for charging station installations, provided tax incentives, and permits lanes used by buses and taxis to be used by EVs. Japan is likely a strong adopter of EV technologies [14, 15, 16].

Seoul, South Korea

South Korea offers a subsidy of up to 26 million won (~\$23,000) per vehicle for the purchase of EVs. This provides an edge for small compact EVs to enter the market much sooner, which is the major target for South Korea in easing up congestion. Sale of EVs in Korea doubled in 2016 from 2015. The nation is setting up targets for EV companies to meet charging driving range targets [17, 18].

Mexico City, Mexico

Mexico has not made any significant efforts with its development of an electric vehicle market. However, there have been some talks about collaborations within companies to start a locally-made electric car company and Mexico is certainly a leader in vehicle manufacturing [19]. Nevertheless we expect Mexico to be a slower adopter of EV technologies.

We searched the literature for global EV adoption rate projections. Whitmore developed a global EV adoption model which projects EV stock for three cases reflective of a slower, moderate, and strong

policy scenario [20]. The study shows that annual EV vehicle sales will account for between 20% to 60% by the year 2030 converting to 7% and 22% of total vehicle stock depending on the policy scenario. A Roland Berger report cites annual new vehicle sales (Figure 21 of that report) of EVs by 2030 of 19% (3% Battery Hybrid plus 3% Plug-in Electric Vehicle plus 1% Full Hybrid and 11% Mild Hybrid) which would correspond more closely with the slower adoption scenario by Whitmore [21]. In the Whitmore article we read the graphs for 2027 and derive stock shares of 4%, 7%, and 11% for the slower, moderate, and strong policy, respectively. We believe that these adoption rates may be realistic and we have therefore incorporated these rates into our modeling.

3.3 Vehicle Retirement

We consider vehicle retirement in our model. The retirement of vehicles increases the amount of new vehicles brought into the vehicle pool which reduces overall emissions due to their compliance with the newest standards.

We adopted the retirement matrix in Argonne's Vision model [22]. The Vision model lists year over year survival factors which represent the fraction of cars on the road for each model year compared to the subsequent year. The adopted retirement matrix from Vision in iBEAM calculates the number of vehicles for each model year in a given calendar year. New vehicle purchases are determined from the projection of on road vehicles minus the calculation of surviving vehicles from prior years. The surviving vehicles in each year is determined from the year over year survival rate. Surviving cars are calculated for subsequent years. The iBEAM model tracks vehicle introductions since 1996.

4 Emissions Factors for Gasoline and Ethanol Based on the Complex Model

4.1 Gasoline Sampling

To get a baseline for blending, three gasoline samples were taken in each city and their compositions analyzed to determine what gasoline properties were prevalent. The samples were taken and analyzed by local Intertek Laboratories affiliates. Three samples were collected in each city, generally from different fuel providers and random geographic locations. The table below summarizes averages for some of the major properties from sampling gasoline in each city.

Table 4: Properties of Sampled Gasolines

		Beijing	Seoul	Tokyo	New Delhi	Mexico City
RON		88.2				88.6
MON						80.6
Specific Gravity		0.679				0.721
Sulfur	mg/kg	6.3	5.7	6.7	16.7	
RVP	psi	5.84	8.54	9.43	7.92	7.63
RVP	kPa	40.3	58.9	65.0	51.7	52.6
Benzene	vol%	0.62	0.46	0.59	1.17	0.46
Aromatics	vol%	25.2	10.4	22.5	31.6	17.8
Olefins	vol%	12.3	13.0	15.1	13.8	6.0
Oxygenate						
MTBE	vol%	6.98	0	0		11.13
ETBE	vol%	0	0	6.42	0	0.00
MTBE	wt%				1.97	

4.2 Methodology for Estimating Impact of Blending Ethanol vs. MTBE and ETBE

While gasoline sampling provided many of the major gasoline properties it was not sufficient to determine the recipe for gasoline blending – i.e. how much reformat, alkylate, butane, isomerate, FCC naphtha, etc. was used to produce the particular gasoline. This makes it difficult to determine the change in recipe from adding ethanol or replacing MTBE or ETBE with ethanol.

To get around this limitation and show the change in gasoline properties from ethanol blending, a base gasoline was first established for each city that met the properties of the gasoline samples shown in Table x-1. Next the recipe was adjusted by blending ethanol while keeping the gasoline octane and RVP at the same values as in the base gasoline.

The impact of ethanol blending in gasoline used in each city was estimated by looking at the change in gasoline properties and change in toxics emissions from gasoline use. The EPA Complex Model was used to estimate emissions of exhaust benzene, acetaldehyde, formaldehyde, 1,3 butadiene, and polycyclics as well as nonexhaust benzene emissions from using each gasoline in a vehicle. Emissions are estimated based on the following gasoline composition parameters: vol% benzene, vol% aromatics, vol% olefins, vol% evaporated at 200 °F (E200), vol% evaporated at 300 °F (E300), weight parts per million (ppm) sulfur, RVP as psi, wt% oxygen, and vol% and type of oxygenate blended.

The EPA Complex Model was developed over twenty years ago and is still used by refiners today for compliance purposes and it can be used to estimate emissions from gasoline use in older vehicles. For the purpose of this study the relative change in emissions from one gasoline sample to another was used as an indicator of directional change in emissions from blending different oxygenates.

The first step in this analysis was to establish a gasoline recipe for each city from gasoline blend stocks produced from a hypothetical refinery having the refining capacity representative of the country in which the city was located. Next the gasoline recipe was adjusted by adding ethanol and replacing MTBE or ETBE if these oxygenates were used. Ethanol addition was at either 10 or 20 vol% in the final gasoline. Gasoline blends were also prepared with no oxygenate and with the oxygenate type and level reported in the city gasoline samples. If the city gasoline samples reported MTBE use, a blend was prepared with the same volume of ETBE and vice versa.

To meet gasoline octane and RVP specifications, the severity of the catalytic reforming unit was adjusted and butane and pentanes removed or butane added as needed. Feed to the catalytic reforming unit was allowed to bypass the unit to meet gasoline octane and maximize gasoline production. Reformate benzene and aromatics levels, volume and hydrogen yield changed with reforming unit severity. Gasoline olefins and distillation percent evaporated at 200 °F and 300 °F (E200 and E300) changed as a result of blending oxygenates and changing reforming unit operation. Gasoline blending, including changes in reforming unit yields, was done using a linear programming model. The properties for each gasoline produced for each city from the blending recipe were put into the EPA Complex Model to estimate toxics emissions. The relative change in emissions from the base gasoline were reported.

4.3 Gasoline Blend Specifications

Gasoline blending constraints were set by country level gasoline specifications shown in Table x-2. In many countries there is a range of RONs specified. For this study, the middle RON was chosen as the specification for blending. Mexico uses $(R+M)/2$ for its specifications and has a specification of $87 (R+M)/2$ for regular and $91 (R+M)/2$ for premium. It was decided to use the $87 (R+M)/2$ as the gasoline octane specification for Mexico in this study.

Most countries had an upper RVP specification for gasoline. Japan had a range, so it was decided to use 60 kPa as the upper limit, which is consistent with Korean gasoline. Japan did not set a limit on aromatics or olefins. It was decided to use 40 vol% as the upper limit on aromatics and 25 vol% as the upper limit on olefins for Japan.

Table 5: Gasoline Blend Specifications

		Beijing	Seoul	Tokyo	New Delhi	Mexico City
		China	South Korea	Japan	India	Mexico
RON	min	92.0	94.0	91.6	91.0	
MON	min				81.0	
(R+M)/2	min					87
RVP	psi max	9.43	8.70	8.70	8.70	7.80
RVP	kPa max	65	60	60	60	54
Benzene	vol% max	1	0.7	1	1	1
Aromatics	vol% max	40	24	40	35	25
Olefins	vol% max	24	18	25	21	10
Sulfur	ppm max	10	10	10	10	30
Oxygen	wt% max	2.7	2.3	1.3	2.7	2.7
MTBE	vol% max			7.0		

4.4 Gasoline Blending Results and Emissions Factor Results

Model results for each city with no oxygenate, with MTBE or ETBE at the average level in the gasoline sampled for each city, and with 10 and 20 vol% ethanol are shown in the following tables for each city. These results summarize the impact on catalytic reforming unit severity, change in gasoline volume and catalytic reforming unit hydrogen production from the base. The relative amount of gasoline blendstock used for each gasoline blend using 100 as the volume of gasoline in the base case for each city are shown. Gasoline properties are shown as are the relative change in toxics emissions relative to the base gasoline for each city.

Gasoline meets the RVP spec for each country. Gasoline octanes are the same for each blending case with the exception when blending 20 vol% ethanol. For this case, the RON was allowed to go to 95, which is a potential gasoline specification that will enable greater use of higher efficiency gasoline engines.

Table 6: Complex Model Emissions Results Beijing

		Beijing		
		MTBE	Ethanol-10	Ethanol-20
CHANGE FROM BASE		BASE-Beijing		
Gasoline Volume - Relative	BPD	100.0	104.1	119.2
Hydrogen from Catalytic Reformer - Relative	MM SCF/day	10.4	5.4	2.2
Gasoline Volume Change from Base		0.0%	4.1%	19.2%
Hydrogen Volume Change from Base		0.0%	-47.8%	-79.2%
Catalytic Reforming Unit Octane (Severity)	RON	98.5	88.0	88.0
OXYGENATE MIX				
MTBE	vol%	6.98%	0.0%	0.0%
ETBE	vol%	0.0%	0.0%	0.0%
ETHANOL	vol%	0.0%	10.0%	20.0%
TAME	vol%	0.0%	0.0%	0.0%
GASOLINE PROPERTIES				
RON		91.9	92.0	94.9
MON		83.0	82.0	81.8
(R+M)/2		87.5	87.0	88.4
Specific Gravity		0.7582	0.7499	0.7447
Oxygen	wt%	1.2	3.7	7.4
Sulfur	ppm	6.9	6.6	5.9
RVP	psi	9.4	9.4	9.4
E200	vol%	47.2	52.8	60.8
E300	vol%	79.7	79.3	83.6
Aromatics	vol%	27.1	26.2	23.3
Olefins	vol%	13.2	12.8	11.4
Benzene	vol%	0.66	0.64	0.57
GASOLINE BLENDSTOCKS				
Butane	vol%	3.81	2.30	2.13
MTBE	vol%	6.98	0.00	0.00
ETBE	vol%	0.00	0.00	0.00
Ethanol	vol%	0.00	10.00	20.00
Light Straight Run Naphtha	vol%	9.83	9.44	8.24
Penex	vol%	0.00	0.00	0.00
Pen_DIH	vol%	0.00	0.00	0.00
Pen_PSA	vol%	0.00	0.00	0.00
Light Hydrocracked Naphtha	vol%	6.43	6.18	5.40
Light Coker Naphtha	vol%	0.00	0.00	0.00
Alkylate	vol%	2.16	2.07	1.81
Natural Gasoline	vol%	0.00	0.00	0.00
Reformer Feed	vol%	0.00	4.61	14.09
Reformate	vol%	20.10	16.68	5.81
FCC_Naphtha	vol%	50.70	48.72	42.53
Gasoline Volume	vol%	100.00	100.00	100.00
EMISSIONS - EPA COMPLEX MODEL				
VOC				
Exhaust	mg/mile	840.93	818.61	768.40
Non-exhaust	mg/mile	722.87	722.87	722.87
Total VOC	mg/mile	1563.80	1541.48	1491.27
NOx	mg/mile	1197.12	1194.28	1176.65
TOXICS				
Exhaust				
Benzene	mg/mile	31.43	26.83	21.18
Acetaldehyde	mg/mile	4.22	11.14	27.24
Formaldehyde	mg/mile	10.28	9.88	9.88
Butadiene	mg/mile	10.31	9.07	7.00
Polycyclics	mg/mile	2.82	2.75	2.58
Subtotal	mg/mile	59.07	59.68	67.89
Non-Ehxaust				
Benzene	mg/mile	3.02	3.11	2.77
Total Toxics	mg/mile	62.09	62.79	70.65

Table 7: Complex Model Results Mexico City

		MTBE	Ethanol-10	Ethanol-20
CHANGE FROM BASE		BASE-Mexico City		
Gasoline Volume - Relative	BPD	100.0	100.3	112.3
Hydrogen from Catalytic Reformer - Relative	MM SCF/	51.8	43.0	28.4
Gasoline Volume Change from Base		0.0%	0.3%	12.3%
Hydrogen Volume Change from Base		0.0%	-17.0%	-45.2%
Catalytic Reforming Unit Octane (Severity)	RON	101.0	101.0	101.0
OXYGENATE MIX				
MTBE	vol%	11.13%	0.0%	0.0%
ETBE	vol%	0.0%	0.0%	0.0%
ETHANOL	vol%	0.0%	10.0%	20.0%
TAME	vol%	0.0%	0.0%	0.0%
GASOLINE PROPERTIES				
RON		91.0	91.5	95.0
MON		83.1	82.6	82.8
(R+M)/2		87.1	87.1	88.9
Specific Gravity		0.7671	0.7656	0.7609
Oxygen	wt%	2.0	3.6	7.3
Sulfur	ppm	11.3	11.4	10.2
RVP	psi	7.8	7.8	7.8
E200	vol%	38.2	43.1	52.0
E300	vol%	82.5	81.7	84.1
Aromatics	vol%	20.0	20.3	18.0
Olefins	vol%	6.7	6.8	6.0
Benzene	vol%	0.52	0.53	0.47
GASOLINE BLENDSTOCKS				
Butane	vol%	3.53	2.26	2.21
MTBE	vol%	11.13	0.00	0.00
ETBE	vol%	0.00	0.00	0.00
Ethanol	vol%	0.00	10.00	20.00
Light Straight Run Naphtha	vol%	0.37	2.15	0.11
Penex	vol%	0.00	0.00	0.00
Pen_DIH	vol%	0.00	0.00	0.00
Pen_PSA	vol%	0.00	0.00	0.00
Light Hydrocracked Naphtha	vol%	0.00	0.00	0.00
Light Coker Naphtha	vol%	0.00	0.00	0.00
Alkylate	vol%	17.95	17.90	15.99
Natural Gasoline	vol%	0.00	0.00	0.00
Reformer Feed	vol%	14.32	18.47	22.70
Reformate	vol%	19.73	16.34	9.62
FCC_Naphtha	vol%	32.97	32.88	29.36
Gasoline Volume	vol%	100.00	100.00	100.00
EMISSIONS - EPA COMPLEX MODEL				
VOC				
Exhaust	mg/mile	799.46	777.10	731.16
Non-exhaust	mg/mile	405.79	404.37	405.79
Total VOC	mg/mile	1205.26	1181.47	1136.95
NOx	mg/mile	1124.08	1128.92	1120.49
TOXICS				
Exhaust				
Benzene	mg/mile	26.60	24.24	19.17
Acetaldehyde	mg/mile	4.02	10.67	26.07
Formaldehyde	mg/mile	12.16	11.15	11.22
Butadiene	mg/mile	8.45	7.82	6.30
Polycyclics	mg/mile	2.68	2.61	2.45
Subtotal	mg/mile	53.91	56.49	65.22
Non-Ehxaust				
Benzene	mg/mile	1.56	1.71	1.52
Total Toxics	mg/mile	55.47	58.20	66.74

Table 8: Complex Model Results New Delhi

		New Delhi		
		MTBE	Ethanol-10	Ethanol-20
CHANGE FROM BASE		BASE- New Delhi		
Gasoline Volume - Relative	BPD	100.0	120.9	144.1
Hydrogen from Catalytic Reformer - Relative	MM SCF/day	5.4	0.0	0.0
Gasoline Volume Change from Base		0.0%	20.9%	44.1%
Hydrogen Volume Change from Base		0.0%	-99.9%	-99.9%
Catalytic Reforming Unit Octane (Severity)	RON	101.0	88.0	88.0
OXYGENATE MIX				
MTBE	vol%	1.95%	0.0%	0.0%
ETBE	vol%	0.0%	0.0%	0.0%
ETHANOL	vol%	0.0%	10.0%	20.0%
TAME	vol%	0.0%	0.0%	0.0%
GASOLINE PROPERTIES				
RON		91.0	91.1	95.5
MON		83.3	82.0	83.2
(R+M)/2		87.1	86.5	89.3
Specific Gravity		0.7423	0.7283	0.7321
Oxygen	wt%	0.4	3.8	7.5
Sulfur	ppm	17.0	15.6	13.9
RVP	psi	8.7	8.7	8.7
E200	vol%	47.6	57.0	67.0
E300	vol%	81.6	85.1	85.9
Aromatics	vol%	32.2	29.6	26.3
Olefins	vol%	14.1	12.9	11.5
Benzene	vol%	1.19	1.09	0.97
GASOLINE BLENDSTOCKS				
Butane	vol%	2.56	0.49	0.03
MTBE	vol%	1.95	0.00	0.00
ETBE	vol%	0.00	0.00	0.00
Ethanol	vol%	0.00	10.00	20.00
Light Straight Run Naphtha	vol%	1.82	7.06	5.92
Penex	vol%	0.00	0.00	0.00
Pen_DIH	vol%	0.00	0.00	0.00
Pen_PSA	vol%	0.00	0.00	0.00
Light Hydrocracked Naphtha	vol%	8.14	6.73	5.64
Light Coker Naphtha	vol%	0.00	0.00	0.00
Alkylate	vol%	16.70	13.81	11.59
Natural Gasoline	vol%	0.00	3.31	7.64
Reformer Feed	vol%	0.00	8.39	7.04
Reformate	vol%	8.11	0.01	0.01
FCC_Naphtha	vol%	60.73	50.21	42.13
Gasoline Volume	vol%	100.00	100.00	100.00
EMISSIONS - EPA COMPLEX MODEL				
VOC				
Exhaust	mg/mile	826.15	771.75	748.50
Non-exhaust	mg/mile	560.77	560.77	560.77
Total VOC	mg/mile	1386.92	1332.52	1309.26
NOx	mg/mile	1219.21	1208.05	1194.73
TOXICS				
Exhaust				
Benzene	mg/mile	41.34	32.40	24.53
Acetaldehyde	mg/mile	4.10	10.37	26.60
Formaldehyde	mg/mile	9.21	9.07	9.43
Butadiene	mg/mile	10.50	8.14	6.44
Polycyclics	mg/mile	2.77	2.59	2.51
Subtotal	mg/mile	67.92	62.57	69.51
Non-Ehxaust				
Benzene	mg/mile	4.78	4.46	3.97
Total Toxics	mg/mile	72.71	67.03	73.47

Table 9: Complex Model Emissions Factor Results – Seoul

			Seoul	
	Unit	MTBE	Ethanol-10	Ethanol-20
OXYGENATE MIX				
MTBE	vol%	10.0%	0.0%	0.0%
ETBE	vol%	0.0%	0.0%	0.0%
ETHANOL		0.0%	10.0%	20.0%
GASOLINE PROPERTIES				
RON		94.0	93.9	94.9
MON		85.0	84.0	82.1
(R+M)/2		89.5	89.0	88.5
Specific Gravity		0.7911	0.7828	0.7639
Oxygen	wt%	1.2	3.5	7.2
Sulfur	ppm	5.3	5.1	4.5
RVP	psi	8.7	8.7	8.7
E200	vol%	37.2	44.2	52.9
E300	vol%	75.9	73.4	80.0
Aromatics	vol%	9.7	9.4	8.3
Olefins	vol%	12.1	11.7	10.4
Benzene	vol%	0.43	0.42	0.37
GASOLINE BLENDSTOCKS				
Butane	vol%	4.35	2.91	2.70
MTBE	vol%	7.00	0.00	0.00
ETBE	vol%	0.00	0.00	0.00
Ethanol	vol%	0.00	10.00	20.00
Light Straight Run Naphtha	vol%	3.96	3.81	3.27
Light Hydrocracked Naphtha	vol%	8.84	8.51	7.31
Alkylate	vol%	6.51	6.27	5.38
Natural Gasoline	vol%	0.00	0.00	0.00
Reformer Feed	vol%	0.00	0.00	15.08
Reformate	vol%	43.30	43.46	24.76
FCC_Naphtha	vol%	26	25	22
Gasoline Volume	vol%	100	100	100

Steffen Mueller:
corrected to reflect
comments on MTBE use

Table 10: Complex Model Results Tokyo

		Tokyo		
		ETBE	Ethanol-10	Ethanol-20
CHANGE FROM BASE		BASE-Tokyo		
Gasoline Volume - Relative	BPD	100.0	104.3	119.1
Hydrogen from Catalytic Reformer - Relative	MM SCF/day	51.7	36.7	27.5
Gasoline Volume Change from Base		0.0%	4.3%	19.1%
Hydrogen Volume Change from Base		0.0%	-29.0%	-46.8%
Catalytic Reforming Unit Octane (Severity)	RON	90.4	88.0	88.0
OXYGENATE MIX				
MTBE	vol%	0.00%	0.0%	0.0%
ETBE	vol%	6.42%	0.0%	0.0%
ETHANOL	vol%	0.0%	10.0%	20.0%
TAME	vol%	0.0%	0.0%	0.0%
GASOLINE PROPERTIES				
RON		91.5	91.5	94.9
MON		82.6	81.6	81.8
(R+M)/2		87.0	86.5	88.4
Specific Gravity		0.7818	0.7727	0.7665
Oxygen	wt%	1.0	3.6	7.2
Sulfur	ppm	7.2	6.9	6.2
RVP	psi	8.7	8.7	8.7
E200	vol%	36.0	43.0	52.3
E300	vol%	74.5	75.9	79.4
Aromatics	vol%	24.1	23.1	20.6
Olefins	vol%	16.1	15.5	13.8
Benzene	vol%	0.63	0.61	0.54
GASOLINE BLENDSTOCKS				
Butane	vol%	5.21	3.39	3.06
MTBE	vol%	0.00	0.00	0.00
ETBE	vol%	6.42	0.00	0.00
Ethanol	vol%	0.00	10.00	20.00
Light Straight Run Naphtha	vol%	2.85	2.73	2.39
Penex	vol%	0.00	0.00	0.00
Pen_DIH	vol%	0.00	0.00	0.00
Pen_PSA	vol%	0.00	0.00	0.00
Light Hydrocracked Naphtha	vol%	2.76	2.65	2.32
Light Coker Naphtha	vol%	0.00	0.00	0.00
Alkylate	vol%	4.23	4.06	3.56
Natural Gasoline	vol%	0.00	0.00	0.00
Reformer Feed	vol%	0.00	9.66	16.71
Reformate	vol%	42.13	32.61	21.40
FCC_Naphtha	vol%	36.40	34.89	30.57
Gasoline Volume	vol%	100.00	100.00	100.00
EMISSIONS - EPA COMPLEX MODEL				
VOC				
Exhaust	mg/mile	889.58	831.37	761.67
Non-exhaust	mg/mile	560.77	560.77	560.77
Total VOC	mg/mile	1450.35	1392.14	1322.44
NOx				
Exhaust	mg/mile	1204.24	1197.66	1174.60
TOXICS				
Exhaust				
Benzene	mg/mile	29.48	25.17	20.01
Acetaldehyde	mg/mile	6.44	11.35	27.24
Formaldehyde	mg/mile	9.99	10.01	10.11
Butadiene	mg/mile	13.47	11.34	8.65
Polycyclics	mg/mile	2.98	2.79	2.56
Subtotal	mg/mile	62.35	60.66	68.57
Non-Ehxaust				
Benzene	mg/mile	2.59	2.49	2.21
Total Toxics	mg/mile	64.94	63.16	70.78

The graph below summarizes the relative trend in emissions factors from the Complex Model for E10 and E20. The trends are graphed in percent change relative to E0. These emissions can be interpreted as the model results that country specific refiners would derive by employing the US Complex Model and its underlying vehicle fleet. The air toxins (benzene, acetaldehyde, formaldehyde, 1,3 butadiene) derived from the Complex Model were multiplied by their respective cancer potency factors to derive weighted toxins (see Section 5.5 for more detail).

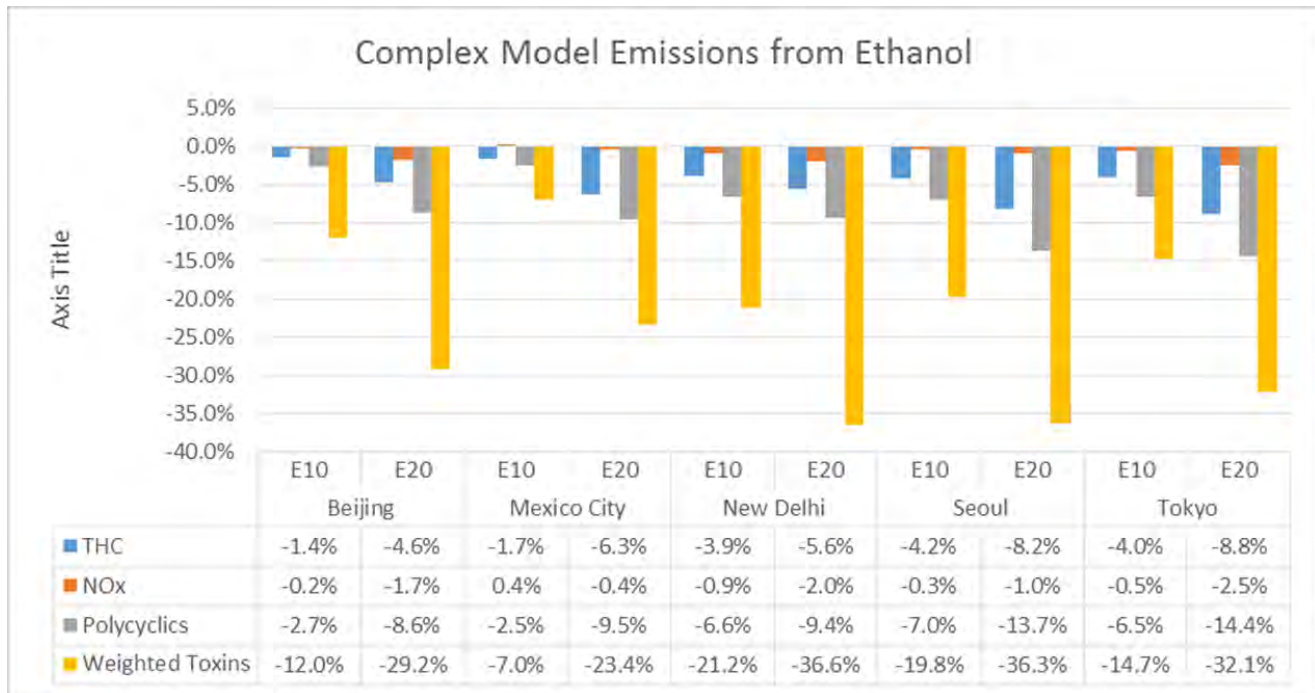


Figure 6: Summary of Complex Model Emissions Factor Results for Ethanol Blends by City

5 Emissions Factors for Ethanol Based on Published Emissions Studies

This section summarizes some of the key ethanol-gasoline vehicle emissions studies detailed in the literature.

5.1 The Impact of Ethanol on Fuel Economy

Stein et al point out that while the energy content of ethanol is approximately 33% less than gasoline the difference can be partially offset by improved thermal efficiency [23]. The authors state that increased ethanol enables redesigned engines to operate at higher compression ratios. The study cites Ford's Ecoboost direct injection engine tests that showed that 96 RON E20 at 11 .9: 1 CR provides comparable fuel economy. Stein restates that volumetric fuel economy can stay equal to gasoline for E20-E30 based on several efficiency effects including reduced enrichment with higher ethanol content, and improved efficiency at part loads due to reduced heat transfer losses with ethanol, as well as the above mentioned higher compression ratios.

In 2016 Oak Ridge National Laboratory conducted engine tests on different ethanol blends to demonstrate the fuel economy of different ethanol blends in dedicated engines with downsizing and down speeding [24]. Down speeding was achieved with larger drive wheels and a different differential. Downsizing was achieved with increased test weight. For E30 (101 RON) the results showed already a fuel economy gain of 5% for the unmodified vehicles and a fuel economy improvement of 10% for the modified (downsped/downsized vehicle) over the baseline E10. Furthermore, the results showed that a splash blended RON 97 with 15% ethanol already in an unmodified 2014 Ford Fiesta (non-FFV) vehicle with a small turbocharged direct-injection engine already showed quasi fuel economy parity for the US06 driving cycle. Also noteworthy is that these tests do not include further potential improvements from custom designed pistons to increase the compression ratio.

These recent research findings show that the lower energy density of ethanol will likely not be a significant detriment to fuel economy in properly designed fuels and modern engines and may even be an advantage in future high octane dedicated engine designs. In iBEAM all emissions calculations revert to a per distance driven basis and are therefore independent of fuel economy.

5.2 Emissions Factors for NO_x, THC, CO, and Selected Air Toxins

Hilton and Duddy (2009) studied criteria pollutant tailpipe emissions from running splash blended E20 versus gasoline using the FTP-75 federal test procedure in a fleet of vehicles ranging from model year 1998 to 2004. The study was funded by the U.S. Department of Transportation [25]. The emissions test results for the average fleet measurements are listed in the table below.

Table 11: Hilton and Duddy Emissions Factors

	E20
NOx	-2.4
THC	-13.7
CO	-23.2

A joint study between the National Renewable Energy Laboratory and Oak Ridge National Laboratory tested sixteen in-use, light-duty passenger vehicles [26]. All fuels were splash blended and vehicles were tested on the LA92 (unified) drive cycle. The vehicle model years ranged from 1999 through 2007 and corresponded to Tier 0, Tier 1, and Tier 2 models. The estimated change in emissions relative to E0 for the statistically significant observations is summarized in the table below. In this study oxides of nitrogen showed no significant change.

Table 12: NREL/ORNL Emissions Factors

		E10	E15	E20
NMHC	(%)	-12.04	-11.49	-15.13
CO	(%)	-14.98	-15.11	-12.31
Acetaldehyde	(mg/mi)	0.38	0.7	0.81
Formaldehyde	(mg/mi)	0.11	0.14	0.11
Fuel Economy	(%)	-3.68	-5.34	-7.71

A study by Suarez-Bertoa et al. (2015) conducted in the Vehicle Emission Laboratory (VELA) at the European Commission Joint Research Centre assessed regulated and unregulated emissions from a Euro 5a flex-fuel vehicle (model year 2012 with direct injection) tested with nine different hydrous and anhydrous ethanol containing fuel blends over the World harmonized Light-duty vehicle Test Cycle and the New European Driving Cycle [27]. Emissions trends were compared to a 5% ethanol baseline gasoline blend. The following emissions profiles were obtained:

Table 13: Suarez-Bertoa et al. Emissions Factors

	E5	E10	E15	E10 vs. E5	E15 vs. E5
	mg/km	mg/km	mg/km	%	%
THC	120	42	49.5	-65%	-59%
NMHC	104	33.5	39.5	-68%	-62%
CO	378.5	429	384	13%	1%
NOx	36	27.5	30.5	-24%	-15%
Formaldehyde	1	0.5	0.5	-50%	-50%
Acetaldehyde	2	3.5	4	75%	100%
Benzene	4.5	2	1.5	-56%	-67%
Toluene	16	5	4.5	-69%	-72%

Note: Emissions factors for E5, E10 and E15 averaged for the WLTC and NEDC.

A study by Karavalakis et al. (UC Riverside and Pacific Northwest Laboratory) also investigated the impact of ethanol blends on criteria and a suite of unregulated pollutants in a fleet of gasoline-powered light-duty vehicles. Model year vehicles ranging from 1984 to 2007 were tested on FTP protocols [28]. Emissions from the different ethanol blends (E10, E20, E50, and E85) were compared against CARB phase 2 certification fuel with 11% MTBE content (i.e. E0) and a CARB phase 3 certification fuel with a 5.7% ethanol content. The study found that in most test cases THC and NMHC emissions were lower with the ethanol blends. CO emissions were lower with ethanol blends for all vehicles. NO_x emissions results were mixed, with some older vehicles showing increases with increasing ethanol level, while other vehicles showed either no impact or a slight, but not statistically significant, decrease. Acetaldehyde emissions increased with increasing ethanol levels while BTEX and 1,3-butadiene emissions decreased with ethanol blends compared to the E0 fuel.

We extracted the following emissions factors from the paper:

Table 14: Karavalakis et al. Emissions Factors

	Vehicle	E10	E20	Additional Citations from Study
NO _x	1984 Toyota	+14%	+19.5%	
NO _x	1993 Ford Festiva	+13.2%	+24.6%	
Nox	Newer Vehicles (1996 Honda Accord, 2000 Toyota Camry, 2007 Chevrolet Silverado)			“did not show statistically significant trends in NO _x emissions, although ethanol blends generally had lower emissions than CARB 2.”
THC	1984 Toyota pickup.	-17.4%	-22.7%	
THC	1985 Nissan pickup	-8.1	-23%	
THC	Newer Vehicles			“Total THC/NMHC emissions are an order of magnitude lower for newer vehicles as compared to older vehicles for all fuels tested, as would be expected with the more advanced emission control technologies seen in new vehicles.”
CO	1984 Toyota		-72.2	
CO	1985 Nissan		-36.4	
CO	1996 Honda Accord		-32.8	
CO				“The general trend of decreasing CO emissions with increasing ethanol content is consistent with previous studies and reductions may be ascribed to the fuel-borne oxygen, which leans the air-fuel ratio and improves oxidation during combustion and over the catalyst.”
Benzene	1996 Honda Accord	-58%	-71%	

Benzene	2007 Chevy Silverado FFV	+1%	-1%	
1,3 Butadiene	1996 Honda Accord	-31%	-50%	
1,3 Butadiene	2007 Chevy Silverado FFV	-29%	-62%	
Acetaldehyde	1996 Honda Accord	71%	202%	
Acetaldehyde	2007 Chevy Silverado FFV	-39%	+/-0%	
Formaldehyde	2007 Chevy Silverado FFV	-44%	-36%	

Storey et al (2010) derived the following results for a 2007 Pontiac Solstice equipped with a 2.0 L, turbocharged across FTP and US06 driving cycles.

Table 15 Storey et al. Emissions Factors

	E0	E10	E20	E10	E20
	g/mile	g/mile	g/mile	% vs E0	% vs E0
NMHC	0.055	0.044	0.091	-20%	65%
Nox	0.031	0.018	0.009	-42%	-71%
CO	0.35	0.36	0.3	3%	-14%

For older vehicles the SAE 920326 study titled "Effects of Oxygenated Fuels and RVP on Automotive Emissions - Auto / Oil Air Quality Improvement Program" derives the results listed in the table below.

Table 16: SAE 920326 Emissions Factors

Tailpipe Toxins	% vs E0
THC Total	-4.9
NMHC	-5.9
CO	-13.4
NOx	5.1
Benzene	-11.5
1,3 -butadiene	-5.8
Formaldehyde	+19.3
Acetaldehyde	159

A relatively comprehensive study by Oak Ridge National Laboratory tested vehicles from six vehicle manufacturers and model years 2000 through 2009 including Tier 2 and pre-Tier 2 vehicles. Splash blended E10, E15 and E20 fuels were produced and emissions were compared against E0. Emissions were measured using the Federal Test Procedure (FTP) [29]. The findings are summarized below.

Table 17: ORNL 2012 Study Emissions Factors

	E10	E20
	median	median
CO (%)	-2.36%	-20.43%
NO _x (%)	34.26%	12.32%
NMHC (%)	-7.02%	-17.05%
NMOG (%)	-1.36%	-0.90%

5.3 Emissions Factors for PM Emissions

PM emissions in the past have not been regulated for gasoline engines. However, increasing fuel efficiency standards have spurred the deployment of direct injection (DI) engines over traditional port fuel injection engines (PFI). Reports show that all current gasoline engine development utilizes direct injection. GDI technology is currently used on Audi, BMW, GM, Ford, Hyundai, Lexus, Mazda, Mini, Nissan, Porsche, VW and other vehicles (<https://noln.net/2017/04/27/unintended-consequences-drive-gdi-engines-shops-part-7/>)

Storey et al confirm that DI gasoline engines can produce higher levels of PM emissions than port fuel injection engines and potentially even more than diesels equipped with diesel particulate filters [30]. The authors used a 2007 Pontiac Solstice equipped with a 2.0 L, turbocharged, direct injection engine. Storey et al showed that by increasing the ethanol blend level from E0 to E20, the average mass emissions declined 30% and 42% over the FTP and US06, respectively. Measurements during hot cycle transient operation demonstrated that E20 also lowered particle number concentrations. The table below summarizes the emissions results from Storey et al:

Table 18: Storey et al PM Emissions Factors

	E0	E10	E20	E10	E20
	mg/mile	mg/mile	mg/mile	% vs E0	% vs E0
FTP	3.65	3.43	2.58	-6%	-29%
US06	15.1	14.11	8.79	-7%	-42%
Average				-6%	-36%

Relatively large PM reductions were also reported for high ethanol blends by Mariq et al. [31]. That study shows a possibly small (<20%) benefit in PM mass and particle number emissions for ethanol blends between 0% to 20% but statistically significant 30%–45% reduction in PM mass and number emissions for high ethanol content fuel >30%.

Aikawa and Jetter (2014) showed that fuel components with high double bond values to more readily form particulate. The DBE value for ethanol and paraffins such as isooctane is zero, whereas for aromatics it is in the range of four to seven. Therefore, aromatic hydrocarbons (which tend to have high DBE values and low vapor pressure) disproportionately contribute to PM formation, and increasing paraffin or ethanol content of the fuel tends to decrease PM. This observation was found to

be true for both direct injection and port fuel injection engines. The studies used the FTP75 driving cycles [32].

In iBEAM we recognize the evolving research on PM emissions reductions with ethanol blends as follows: We apply the derived emissions reductions cited above from Storey et al to vehicles equipped with GDI engines. The GDI engine share of future vehicle populations can be changed within iBEAM.

5.4 Polycyclic Aromatic Hydrocarbons, PM_{2.5} and Ultrafine Particles

Increasingly, a subcategory of PM emissions, the fine particle pollution classes with particles less than 2.5 microns in diameter (PM_{2.5}) and ultrafine particles with particles less than 0.1 microns have received significant attention in emissions research due their large impact on mortality and health (<https://www.ncbi.nlm.nih.gov/pubmed/19590680>). Kawanaka et al argue in their study that while the contributions of ultrafine particles to total PM mass were only 2.3% (1.3% for suburban environments) the contributions of ultrafine particles to PAH deposition in the very sensitive alveolar region of the lung were about 10-fold higher than those to total PM mass for both the roadside and suburban atmospheres. The authors conclude that these results indicate that ultrafine particles are significant contributors to the deposition of PAHs in the alveolar region of the lung, although the concentrations of ultrafine particles in the atmosphere are very low. [33] The authors state that several PAHs are known to be strong mutagens and potential human carcinogens. In iBEAM polycyclic are assessed via the Complex Model results for each city.

According to the US EPA a major component of PM_{2.5} are secondary organic aerosols (SOA) (<https://www.epa.gov/air-research/secondary-organic-aerosol-soas-research>). SOAs are produced through the interaction of sunlight, volatile organic compounds from vehicles and industrial emissions, plants, and other airborne chemicals. Studies show significant lung and heart health impacts associated with SOAs. Importantly, Benzene is a major contributor to SOAs. Bruns et al showed that for wood combustion, in some cases, oxidation products of phenol, naphthalene and benzene alone can comprise up to 80% of the observed SOA [34]. The pathways of benzene emissions are extremely complex but important to understand. According to Stein et al. Benzene is formed from either unburned fuel-borne benzene or benzene formed during combustion of other compounds found in gasoline. Borrás et al studied the atmospheric transformations of VOCs with a focus on benzene. They showed two general aerosol formation routes of benzene photo oxidation: a) via the formation of phenol, promoting the formation of SOA intermediate and b) directed by nitrogen oxides, the production of a gaseous intermediate, perhaps a ring fragmentation product such as muconaldehyde which also induces the aerosol formation [35]. In iBEAM the effect of benzene is additionally counted towards its cancer potency (see section below).

5.5 Air Toxins and Cancer Risk Assessment

The California Test Procedure for Evaluating Substitute Fuels and Clean Fuels specifically requires a risk analysis for the four Toxic Air Contaminants (1,3 Butadiene, Benzene, formaldehyde, and acetaldehyde [36]. Lloyd and Denton compiled a report detailing all the cancer potency factors for many chemical compounds and the underlying cancer studies [37]. The relative potency factors for the four toxic air contaminants are listed below.

Table 19: Lloyd and Denton Cancer Potency Factors

Toxic Air Contaminant	Relative Potency
benzene	0.17
acetaldehyde	0.016
formaldehyde	0.035
1,3 butadiene	1

Unnasch et al. applied the cancer potency factors in their assessment of different fuel cycle pathways [38]. Stein et al state that combustion chemistry shows that the oxidation of ethanol does not produce 1,3 butadiene nor benzene. Therefore, higher levels of ethanol would reduce engine out emission of benzene and 1,3 butadiene but increase acetaldehyde and formaldehydes. However, when factoring in the relative toxicity levels (e.g. toxicity factors applied by the California Air Resource Board) 1,3 butadiene and benzene have much higher weights and therefore the weighted sum risk of all four compounds is lower with ethanol [23]. In iBEAM we apply the relative potency factors to the emissions from both gasoline and ethanol blends for the four toxic air contaminants.

5.6 Summary of Emissions Factors for Ethanol Blends

The table below summarizes the literature of vehicle studies with E10 and E20 ethanol blends. These derived emissions adjustments for ethanol blends are used in iBEAM. Note that the results show generally consistent decreases for THC/NMHC, consistent decreases for CO for the higher ethanol blends, with higher uncertainties for NOx reflected in the literature. For PM emissions adjustments from ethanol blends we show the data from Storey et al which is based on GDI engine tests. Therefore, iBEAM projects the GDI share of future vehicles and then applies the respective emissions adjustments for ethanol blends from that citation.

Table 20: Summary of Ethanol Emissions Factors

		E10	E20	
Hilton and Duddy	THC		-13.7%	
Karavalakis	THC	-12.8%	-22.9%	
Bertoa	THC	-65.0%	-59.0%	vs E5
SAE 1992	THC	-4.9%		
NREL	NMHC	-12.0%	-15.1%	
Storey	NMHC	-20.0%		
Bertoa	NMHC	-68.0%		vs E5
SAE 1992	NMHC	-5.9%		
ORNL 2012	NMHC	-7.0%	-17.1%	
ORNL 2012		-1.4%	-0.9%	
Average	THC/NMC	-21.9%	-21.5%	

		E10	E20	
Hilton and Duddy	CO		-23.2%	
Karavalakis	CO		-47.1%	
NREL	CO	-15.0%	-12.3%	
Storey	CO	3.0%	-14.0%	
Bertoa	CO	13.0%		vs E5
SAE 1992	CO	-13.4%		
ORNL 2012	CO	-2.4%	-20.4%	
Average	CO	-3.0%	-23.4%	

		E10	E20	
Hilton and Duddy	NOx		-2.4%	
Karavalakis	NOx	13.6%	22.1%	
Storey	Nox	-42.0%	-71.0%	
Bertoa	NOx	-24.0%		vs E5
SAE 1992	NOx	5.1%		
ORNL 2012	NOx	34.3%	12.3%	
Average	NOx	-11.8%	-17.1%	

Storey	PM	-6.0%	-36.0%	
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E10 E20

SAE 1992	Benzene	-11.5%		
Bertoa	Benzene	-56.0%		vs E5
Karavalakis	Benzene	-29.0%	-36.0%	
Average	Benzene	-32.0%	-36.0%	

Karavalakis	1,3 –butadiene	-30.0%	-56.0%	
SAE 1992	1,3 –butadiene	-5.8%		
Average	1,3 –butadiene	-18.0%	-56.0%	

SAE 1992	Formaldehyde	19.3%		
Bertoa	Formaldehyde	-50.0%		vs E5
Karavalakis	Formaldehyde	-44.0%	-36.0%	
Average	Formaldehyde	-24.9%	-36.0%	

SAE 1992	Acetaldehyde	159.0%		
Bertoa	Acetaldehyde	75.0%		vs E5
Karavalakis	Acetaldehyde	16.0%	101.0%	
Average	Acetaldehyde	83.3%	101.0%	

6 Ethanol Emissions Factor Adjustments by Vehicle Age

Based on our literature review we grouped the studies by their employed vehicle fleet. Different colored cells in the figure below indicate the vehicle fleet years covered by the respective study. This forms the basis for a function in iBEAM that allows to account for the fact that different vintages of vehicles derive more or less emissions benefits from ethanol blended fuels.

	EPA Complex Model	SAE 1992	Hilton & Duddy (2009)	NREL (2009)	Suraz-Bertoa et al. (2015)	Karavalakis (2012)	Storey	E10			E20		
								CO	NMHC/THC	NOx	CO	NMHC/THC	NOx
1984									-17.4	14.0		-22.7	19.5
1985									-8.1			-23.0	
1986													
1987								-13.4	-5.4	5.1			
1988													
1989													
1990													
1991													
1992													
1993											13.2		24.6
1994													
1995								*	*		*	*	
1996											-32.8		
1997													
1998													
1999													
2000													
2001											-23.2	-13.7	-2.4
2002													
2003								-14.98	-12.0		-12.3	-15.1	
2004										0.0			0.0
2005													
2006													
2007								3.0	-20.0	-42.0	-14.0		-71.0
2008													
2009													
2010													
2011													
2012								13.0	-67.0	-24.0			
2013													

*Assessed by city based on fuel samples

Figure 7: Ethanol Emissions Literature Summary by Vehicle Fleet Age

We have set up a linear and a non-linear adjustment option. In addition to the studies above we added the emissions factors developed from the EPA Complex Model for each city in the regression model. This way we ensured a city-specific contribution to the overall emissions assessment while taking into

account the underlying vehicle fleet. Note that the current linear adjustment in iBEAM reverts back to the average of all studies for the individual pollutants (with additional weight on the complex model results). The non-linear adjustments allows for a more conservative estimate of emissions reductions from ethanol relative to gasoline. We further concluded that effects from ethanol on NOx emissions across all studies is not statistically significant and therefore a true zero.

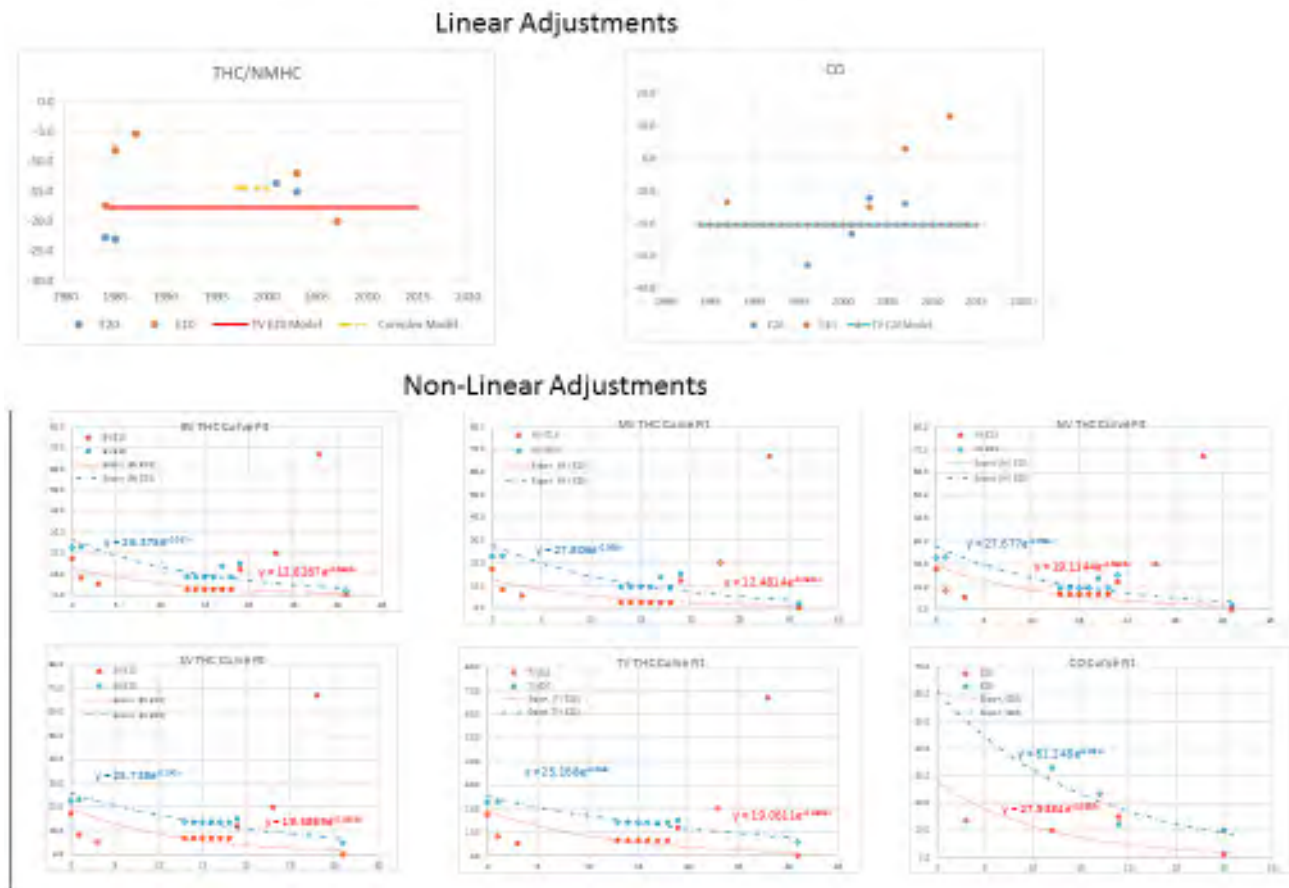


Figure 8: Emissions Factor Adjustment Equations by Vehicle Age

The figure below further illustrates the integration of the Complex Model emissions factors with iBEAM

Complex Model	iBEAM
<ul style="list-style-type: none"> • Assessed Pollutants <ul style="list-style-type: none"> ○ THC ○ NOx ○ Polycyclics ○ Toxins • Allowed us to populate the model with Country Specific Gasoline Blends and Ethanol Blends following that countries current Fuel Properties <ul style="list-style-type: none"> ○ Derived emissions factors for ethanol and gasoline • Model is actually used by US Refiners and can be reproduced • Drawback: Emissions factors are based on the underlying Complex Model Car Fleet from the 1990s 	<ul style="list-style-type: none"> • Assessed Pollutants <ul style="list-style-type: none"> ○ THC ○ NOx ○ PM ○ CO • Uses Country Specific Emission Standards for Gasoline Emissions and Literature Values for Emissions Adjustments from Ethanol • We sorted and applied all the literature-based emissions factors by its vehicle fleet age and included the Complex Model Results based on its underlying Vehicle Fleet Age

Figure 9: Integration of the Complex Model Emissions Factors with iBEAM

7 Emissions Factor Development for Gasoline Exhaust Emissions Based on Standards

In this emissions factor approach we assumed that all gasoline passenger cars follow the permissible limits for the given standard. The table below lists the major sources and citations for the current and predicted standards. Appendix A lists the employed values for each city. When there is an offset of one month or less in the implementation date of a new standard in a year, the standard has been rounded off to be followed through for the whole year.

Table 21: Sources of Gasoline Emissions Factors based on Standards

<u>City</u>	<u>Citation</u>	<u>Notes</u>
Beijing	<ul style="list-style-type: none"> • "Beijing: Light-Duty: Emissions," icct and DieselNet, [Online]. Available: http://transportpolicy.net/index.php?title=Beijing: Light-Duty: Emissions. • K. Derla, "China Capital Beijing To Implement World's Strictest Vehicle Emission Standards By 2017," 26 May 2016. [Online]. Available: http://www.techtimes.com/articles/161103/20160526/china-capital-beijing-to-implement-worlds-strictest-vehicle-emission-standards-by-2017.htm. 	<p>The first citation gives the standards for Beijing. The second citation gives the implementation date for Beijing 6. To show consistency between the studies, Euro 1-3 has been adopted for NOx and HC emissions.</p>
Mexico City	<ul style="list-style-type: none"> • https://www.dieselnet.com/standards/mx/ld.php 	<p>The data has been obtained from the citation. Citation also gives phase in schedules, which is ignored due to the incremental set up done in the model- the implementation dates have still been considered. THC values have been taken for LDV and LDT. Mexico City has not defined future standards, the present standards have been used going forward in the study.</p>

New Delhi	<ul style="list-style-type: none"> • "India Light duty vehicles emissions," [Online]. Available: http://transportpolicy.net/index.php?title=India: Light-duty: Emissions . [Accessed 22 June 2017] 	Data has been obtained from the citation. The implementation dates are obtained from the same citation too. New Delhi will be changing from BS IV to BS VI in 2020, rapid advances to keep the standards in line with global standards.
Seoul	<ul style="list-style-type: none"> • "South Korea: Light-duty: Emissions," ICCT and DieselNet, [Online]. Available: http://transportpolicy.net/index.php?title=South Korea: Light-duty: Emissions . [Accessed 27 June 2017] • https://www.delphi.com/docs/default-source/worldwide-emissions-standards/delphi-worldwide-emissions-standards-passenger-cars-light-duty-2016-7.pdf 	Citations give the limits for the years starting from 2009. Seoul has not defined any prospective standard going forward. The standards are more stringent compared to Euro 6, so going forward from 2020, limits have been kept in par with Euro 6, at least. A taper has been assumed for NMOG emissions, which has been accessed from the second citation.
Tokyo	<ul style="list-style-type: none"> • Transport Policy, "Japan: Light-duty: Emissions," 11 September 2013. [Online]. Available: http://transportpolicy.net/index.php?title=Japan: Light-duty: Emissions . [Accessed 26 July 2017]. • https://www.env.go.jp/en/air/aq/mv/table_290628.pdf 	The first citation gives the present standards for Tokyo. The second citation is the English translated future standards prescribed for Tokyo. Tokyo has changed its testing method from JC08 to WLTC, thus there is a discrepancy in the limits from 2017 to 2018.

In order to facilitate a consistent comparison of our derived emissions standards we graphed the combined [hydrocarbon (HC) plus NO_x] emissions standards for each city below. All cities show dramatic reductions in permissible emissions with Mexico City and New Delhi lagging behind in the earlier years.

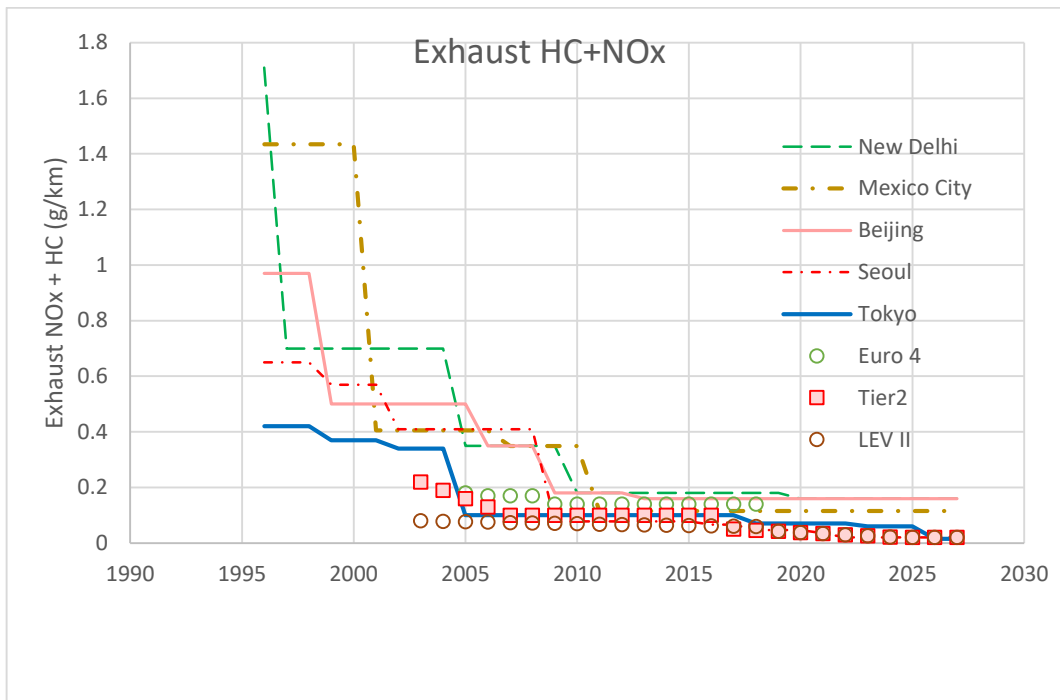


Figure 10: Summary of Exhaust HC+NOx Emissions Standards by City

Regulating particulate matter for gasoline engines in the future is currently a subject of debate and technical evaluation especially in light of the higher PM emissions associated with gasoline direct injection engines. In the absence of emissions standards and an effort to evaluate PM emissions consistently for all the cities we have used the PM emissions factors from the EPA MOVES2014 study [39], which has been derived from the 2004/05 Kansas City study [40]. The table below lists the emissions factors for PM used for all cities

Table 22: PM Emissions Factors MOVES

Year range	PM Factor (mg/km)
2000-2016	1.56
2016-2020	1.25
2021-2027	0.93

8 THC Evaporative Emissions for Gasoline and Ethanol

This section discusses evaporative HC emissions in addition to tailpipe emissions. These emissions include venting and leaks from the evaporative emissions, emissions during vehicle fueling, and permeation of fuel through the fuel system components. The figure below shows the total evaporative emission sources from a vehicle.

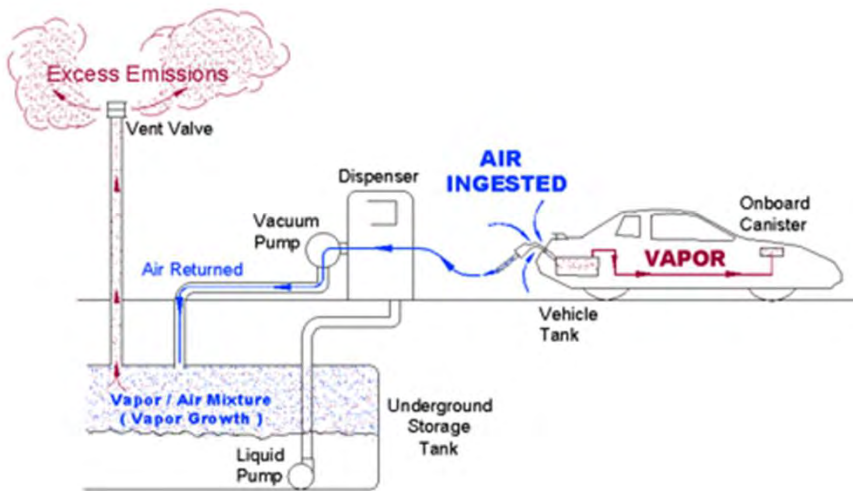


Figure 11: Evaporative Emissions Components (Source: California Air Resources Board)

Venting emissions include diurnal breathing and running losses. The venting emissions are represented by evaporative emission standards with tests that correspond to a sealed housing for evaporative determination (SHED). The evaporative emission standards are regulated in each country. The roll-in of emission standards over time is estimated based on published standards [41] [42]. The figure below shows the employed evaporative emissions factors for each city. The values are listed in Appendix A.

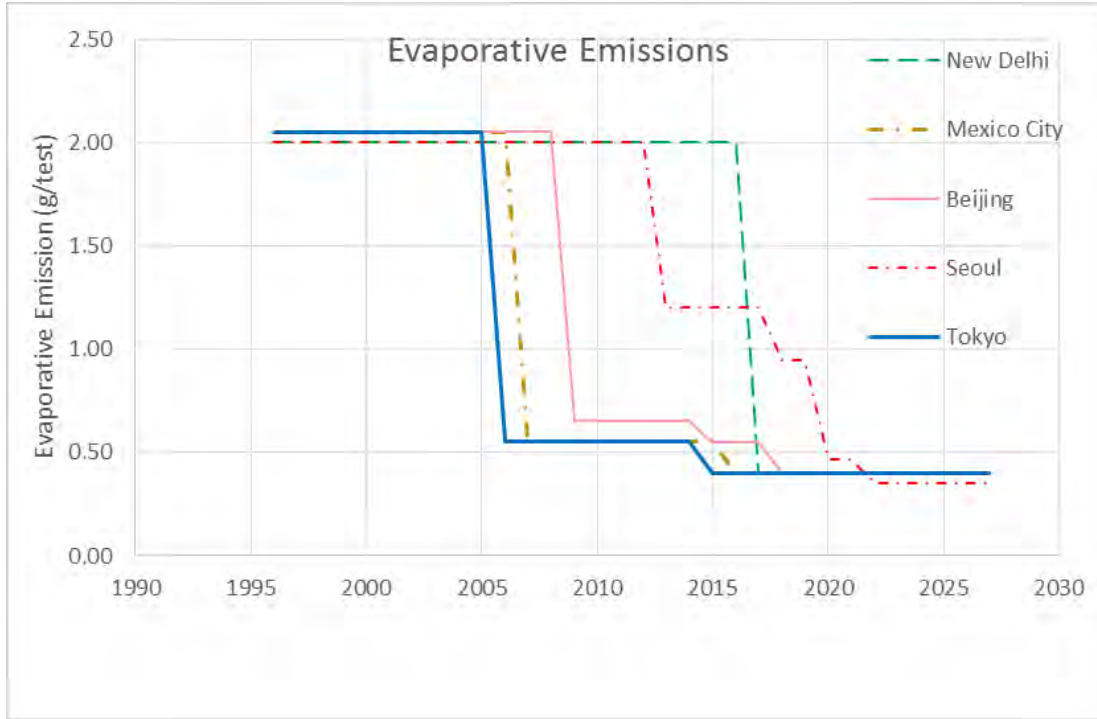


Figure 12: Summary of Evaporative Emissions Standards by City

Vehicle fuel systems also include leaks. The ratio of leaks to venting from MOVES model runs provides the basis for estimating leaks. The table below shows an example of the evaporative emissions in grams per day for selected years.

Evaporative Emission Factors

Year	(g/day)	(g/km)		(g/L)		
	Vent + Leaks	Fueling + Spill	Permeation	Fueling	Spillage	Permeation
1996	3.172	0.123	0.078	1.300	0.0479	0.855
1997	2.465	0.123	0.078	1.300	0.0479	0.855
1998	2.463	0.123	0.078	1.300	0.0479	0.855
1999	2.461	0.123	0.078	1.300	0.0479	0.855
2000	2.459	0.123	0.021	1.300	0.0479	0.230
2001	2.457	0.123	0.012	1.300	0.0479	0.133
2002	2.177	0.123	0.008	1.300	0.0479	0.093
2003	2.175	0.123	0.007	1.300	0.0479	0.072
2004	2.174	0.123	0.005	1.300	0.0479	0.059

Figure 13: Example of Evaporative Emissions Components in iBEAM

In addition to venting and leaks, emissions occur from permeation through the fuel system material such as hoses and gaskets. Permeation emissions are estimated as a function of model year from MOVES model results. Permeation emissions have improved significantly over the past 20 years and the introduction of low permeation materials is a model input for each city (see figure below). Ethanol blends have affected permeation emissions with generally higher emissions from ethanol blend. The

emissions from ethanol vehicles are estimated from the ratio of E10 to gasoline/MTBE blends from the MOVES model.

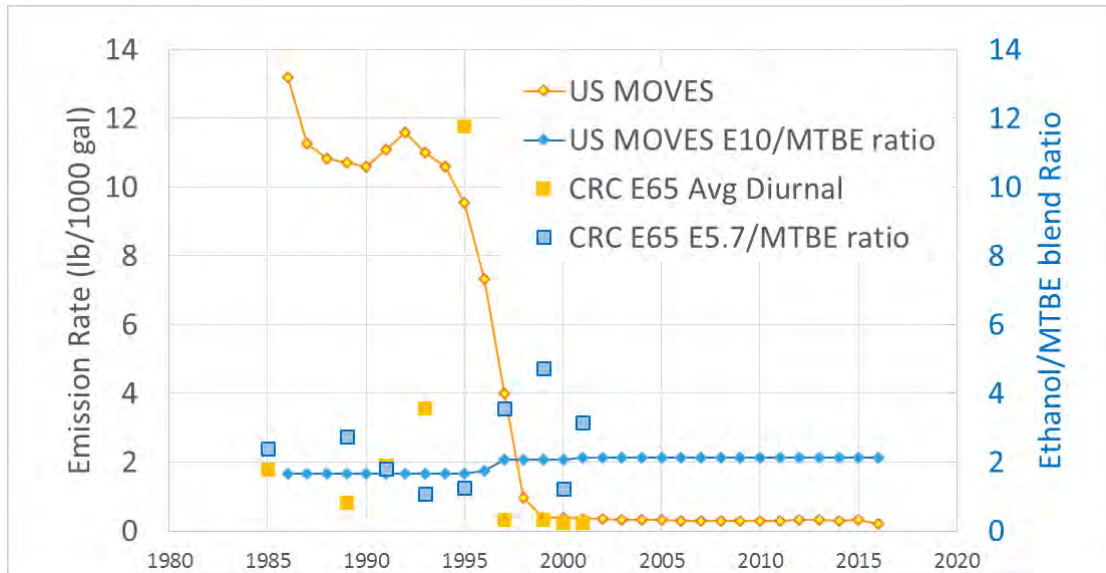


Figure 14: Improvements in Permeation Emissions over Time

Refueling emissions include vapor displacement from the vehicle fuel tank. Fuel displaces vapors in the fuel tank. These vapors are either released into the atmosphere, captured with Stage 2 vapor recovery at the fuel station, or captured with on-board refueling vapor recovery (ORVR). The effectiveness of Stage 2 vapor recovery and ORVR are model represented by the fraction of vapors that are released. The utilization and effectiveness of Stage 2 vapor recovery and ORVR is an input for each city. Emissions of refueling emissions are calculated from the total vehicle fuel consumed based on fuel economy projections and the evaporative emissions per liter of fuel.

The density of fuel vapors in the vehicle fuel tank depends upon the vapor pressure of the fuel at fuel tank conditions combined with altitude (see figure below). The vapor density was calculated from the parameters in the table below. The true vapor pressure (TVP) is a function of Reid Vapor Pressure, molecular weight, and fuel tank temperature based on correlations from the California ARB. Molecular weight of the vapors is also dependent on the fuel RVP with slightly lower molecular weights corresponding to higher RVP fuels. The vapor density in the tank depends on altitude, the fuel's TVP, and molecular weight. The vapor density corresponds to the TVP of the fuel/air pressure at altitude, which is calculated for the elevation of each city.

Vapor Density Calculation Based on Elevation and RVP							
	SV		BV	MV	NV	SV	TV
	Active Case	Baseline	Beijing	Mexico City	New Delhi	Seoul	Tokyo
Altitude (m)	21	0	44	2250	216	21	10
Air Pressure (psi)	14.66	14.70	14.62	11.29	14.34	14.66	14.68
T, C for Air P.	20	22	20	18	26	20	20
T (K)	293.2	295.2	293.2	291.2	299.2	293.2	293.2
RVP	8.7	7.8	9.4	7.8	8.7	8.7	8.7
MW (g/mol)	66.8	66.2	67.4	66.2	66.8	66.8	66.8
Tank Temp ©	22	22	22	20	28	22	22
TVP (psi)	6.19	5.55	6.71	5.21	7.23	6.19	6.19
Vapor in Tank	42.2%	37.7%	45.9%	46.2%	50.5%	42.2%	42.2%
Vapor Density (lb/1000 gal)							
At Sea Level	9.70	8.62	10.60	8.09	11.33	9.70	9.70
In urban area	10.85	8.62	12.89	9.89	15.14	10.85	10.84

Figure 15: City Specific Parameters for Refueling Emissions Calculations

9 Emissions Deterioration Factors

Vehicle emissions deteriorate over the lifetime of a vehicle. A recent report by TNO Netherlands in cooperation with International Institute for Applied Systems Analysis (IIASA) in Austria estimates deterioration factors for EURO 1 and EURO 2 vehicles from data collected over several years from 166 vehicles (96 different models) [43]. The report concludes that the deterioration factors are almost double from their previous work. We have adopted their published values (listed in Table 1 of that publication). The TNO factors seem to be consistent with factors published in another recent paper by Borken-Klefeld and Chen which are assessed as a function of mileage driven (see Table 2 of that publication) [44].

10 Emissions Results

In this section we summarize the emissions adjustments in tonnes and percent by city and by ethanol blend (see figure below). Furthermore, we show the main model inputs and outputs. The model inputs shown for each city below include the projected number of gasoline vehicles and their EV share, the project fuel use and fuel economy as well as the vehicle distance travelled. The model outputs list the key pollutants emitted in tonnes by year (and totals over the time frame) and the percent reductions in air toxins and polycyclic.

On a total tonnage and percentage basis through the year 2027 the results show hydrocarbon (THC, VOC) reductions across all cities from E10 and E20 blends which should result in reduced risk for ozone formation in these cities. Furthermore, the study finds significant polycyclics and weighted toxins reductions (often correlated with cancer) and reduced CO emissions which reduces heart disease and other health effects. The study also shows that NOx emissions remain unaffected by ethanol blends.

The results are also particularly relevant in light of the current debate on electric vehicle deployment. Since iBEAM enables a selection of different EV adoption scenarios we can compare the emissions savings from ethanol blends to the emissions savings expected with EVs. Note that these are tailpipe emissions only and do not include any upstream emissions from electricity production which, in many of the studied countries, may come from coal fired power plants. The comparison between ethanol and EV (dashed red line in graph below) shows that EV vehicles through 2027 will just about save the same amount of THC/VOC emissions as a fleet change to E10 and E20 would produce and that EV vehicles will provide significantly less savings for carbon monoxides and weighted toxins through 2027.

Table 23: Summary of Emissions in Tons by City and Ethanol Blend

	Beijing		Mexico City		New Delhi		Seoul		Tokyo	
	E10	E20	E10	E20	E10	E20	E10	E20	E10	E20
CO	-69,613	-462,832	-94,806	-630,332	-21,844	-145,236	-15,004	-99,754	-21,480	-142,811
THC	-29,238	-24,866	-25,953	-21,593	-9,842	-8,353	-3,562	-2,968	-5,137	-4,581
PM	-10	-58	-11	-69	-6	-35	-1	-8	-4	-23
NOx	0	0	0	0	0	0	0	0	0	0

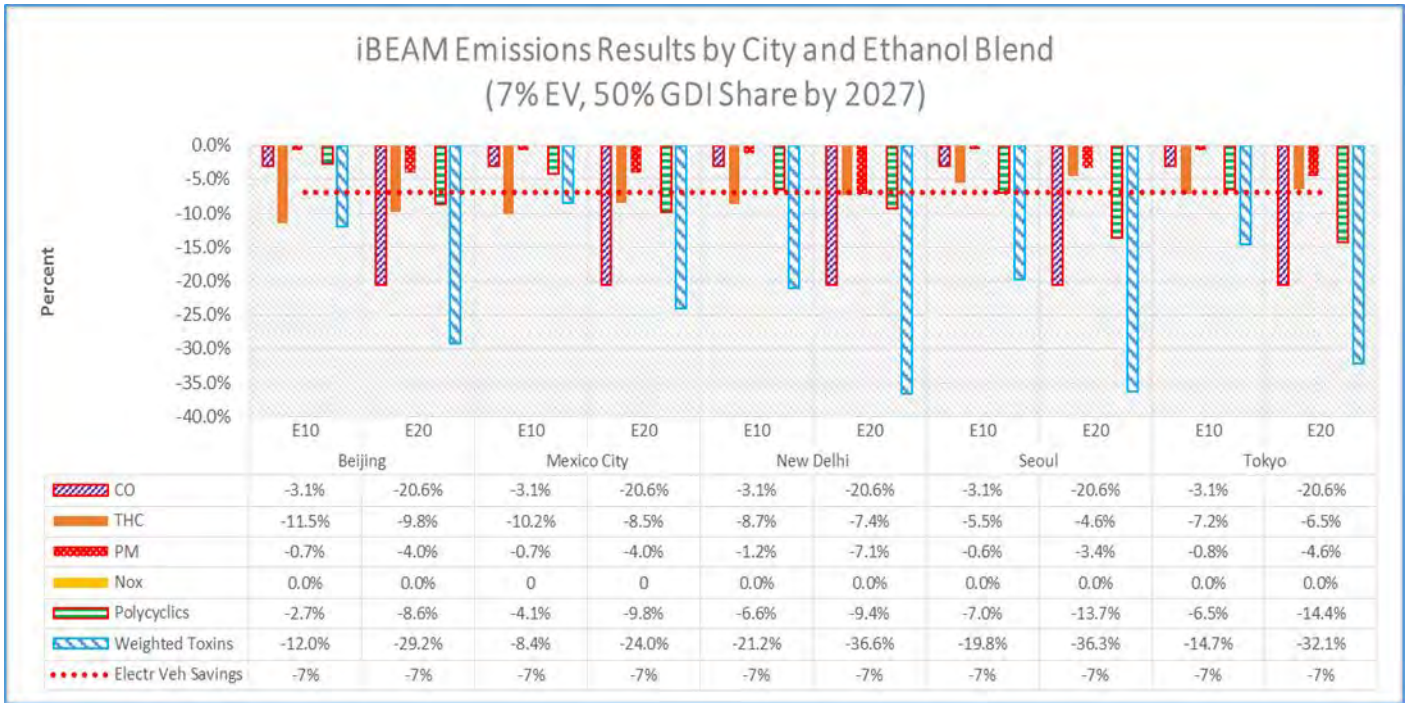
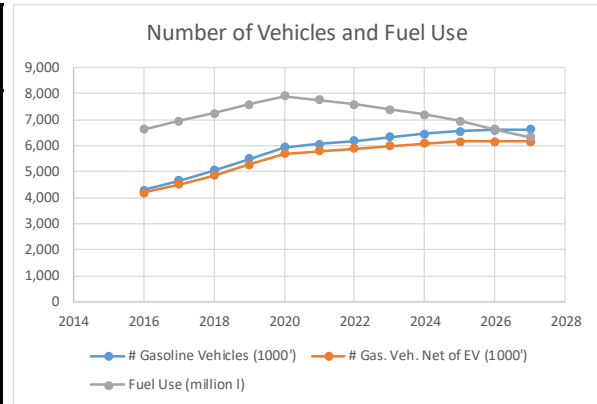


Figure 16: Summary of Emissions in Percent by City and Ethanol Blend

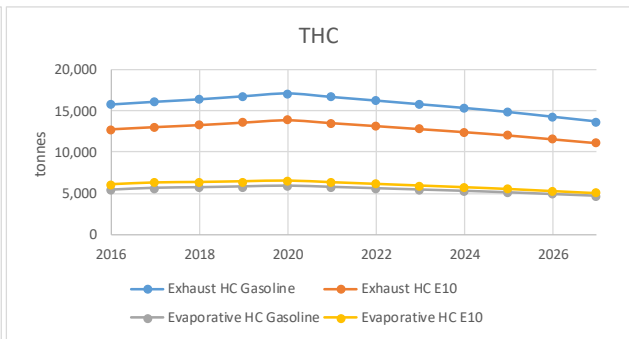
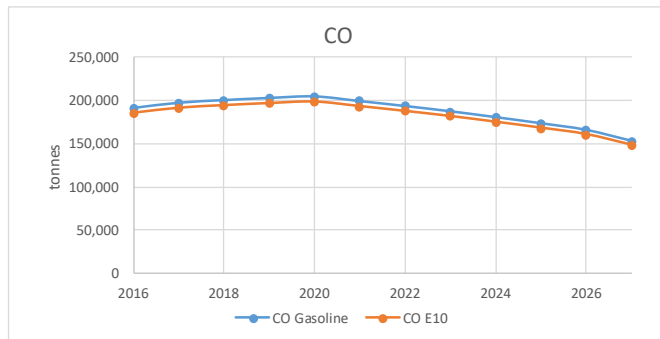
iBEAM Output Beijing E10

GDI Rate: 50% EV Rate: 7%

Year	# Gasoline Vehicles (1000')	# Gas. Veh. Net of EV (1000')	Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
	2016	4,294	4,177	6,623	9.44
2017	4,659	4,514	6,941	9.26	74,936
2018	5,040	4,864	7,248	9.09	79,762
2019	5,483	5,270	7,593	8.89	85,370
2020	5,933	5,679	7,911	8.71	90,869
2021	6,062	5,779	7,751	8.61	89,986
2022	6,193	5,880	7,577	8.51	89,035
2023	6,326	5,982	7,389	8.40	88,015
2024	6,462	6,085	7,186	8.27	86,923
2025	6,560	6,152	6,940	8.14	85,242
2026	6,592	6,157	6,635	8.03	82,675
2027	6,625	6,161	6,330	7.90	80,096



Year	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10
2016	191,235	185,317	15,779	12,790	5,409	6,082	16,630	16,630	110	109
2017	197,253	191,148	16,112	13,060	5,623	6,280	16,792	16,792	115	115
2018	200,359	194,158	16,412	13,303	5,691	6,331	16,892	16,892	120	120
2019	202,844	196,566	16,785	13,606	5,783	6,410	16,995	16,995	126	126
2020	204,661	198,326	17,133	13,888	5,870	6,485	17,043	17,043	133	132
2021	199,229	193,063	16,700	13,536	5,725	6,305	16,495	16,495	129	129
2022	193,473	187,485	16,262	13,182	5,575	6,121	15,938	15,938	126	125
2023	187,355	181,556	15,807	12,813	5,423	5,937	15,373	15,373	123	122
2024	180,544	174,956	15,356	12,447	5,273	5,756	14,814	14,814	119	118
2025	173,428	168,061	14,858	12,044	5,104	5,557	14,232	14,232	115	114
2026	165,765	160,634	14,283	11,578	4,905	5,325	13,606	13,606	111	110
2027	153,071	148,333	13,706	11,110	4,711	5,101	12,982	12,982	106	105
Total:	2,249,216	2,179,603	189,192	153,356	65,091	71,690	187,794	187,794	1,434	1,424
Savings		-69,613		-35,837		6,599		0		-10



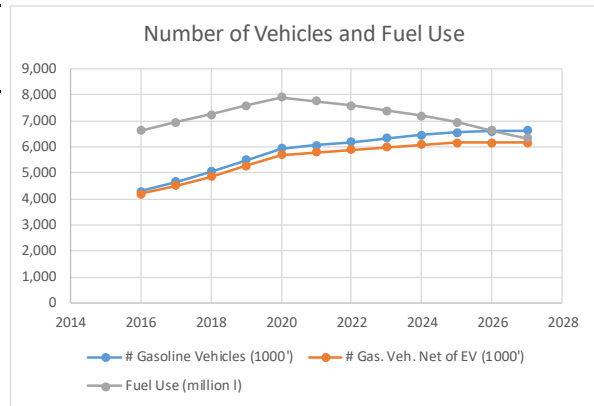
	Relative to EO (%)	Relative to EO (Total Tonnes)
CO	-3.1%	-69,613
THC	-11.5%	-29,238
PM	-0.7%	-10
NOx	0	0
Polycyclics	-2.7%	
Weighted Toxins	-12.0%	

From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-14.6%
acetaldehyde	0.02	163.8%
formaldehyde	0.04	-3.9%
1,3 butadiene	1.00	-12.0%
Polycyclics	0.00	-2.7%
Total Weighted:		-12.0%

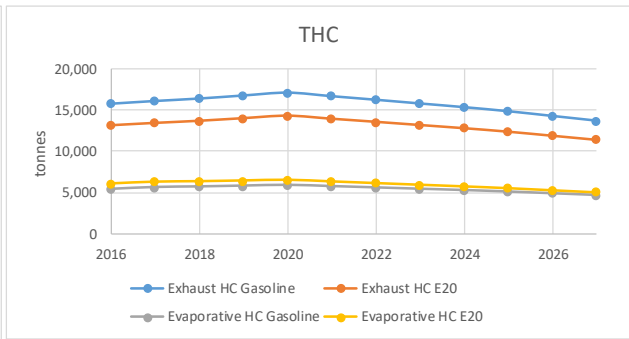
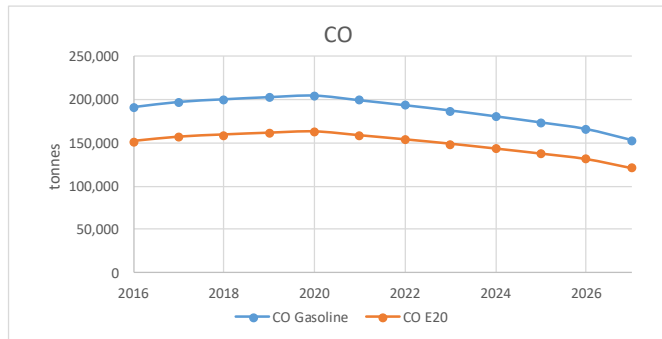
iBEAM Output Beijing E20

GDI Rate: 50% EV Rate: 7%

Year	# Gasoline Vehicles (1000')	# Gas. Veh. Net of EV (1000')	Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
2016	4,294	4,177	6,623	9.44	70,174
2017	4,659	4,514	6,941	9.26	74,936
2018	5,040	4,864	7,248	9.09	79,762
2019	5,483	5,270	7,593	8.89	85,370
2020	5,933	5,679	7,911	8.71	90,869
2021	6,062	5,779	7,751	8.61	89,986
2022	6,193	5,880	7,577	8.51	89,035
2023	6,326	5,982	7,389	8.40	88,015
2024	6,462	6,085	7,186	8.27	86,923
2025	6,560	6,152	6,940	8.14	85,242
2026	6,592	6,157	6,635	8.03	82,675
2027	6,625	6,161	6,330	7.90	80,096



Year	tonnes									
	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20
2016	191,235	151,884	15,779	13,154	5,409	6,082	16,630	16,630	110	108
2017	197,253	156,663	16,112	13,432	5,623	6,280	16,792	16,792	115	113
2018	200,359	159,130	16,412	13,682	5,691	6,331	16,892	16,892	120	117
2019	202,844	161,104	16,785	13,993	5,783	6,410	16,995	16,995	126	122
2020	204,661	162,547	17,133	14,284	5,870	6,485	17,043	17,043	133	128
2021	199,229	158,233	16,700	13,922	5,725	6,305	16,495	16,495	129	124
2022	193,473	153,661	16,262	13,558	5,575	6,121	15,938	15,938	126	121
2023	187,355	148,802	15,807	13,178	5,423	5,937	15,373	15,373	123	117
2024	180,544	143,392	15,356	12,802	5,273	5,756	14,814	14,814	119	113
2025	173,428	137,741	14,858	12,387	5,104	5,557	14,232	14,232	115	109
2026	165,765	131,655	14,283	11,908	4,905	5,325	13,606	13,606	111	104
2027	153,071	121,572	13,706	11,426	4,711	5,101	12,982	12,982	106	99
Total:	2,249,216	1,786,383	189,192	157,728	65,091	71,690	187,794	187,794	1,434	1,376
Savings		-462,832		-31,464		6,599		0		-58



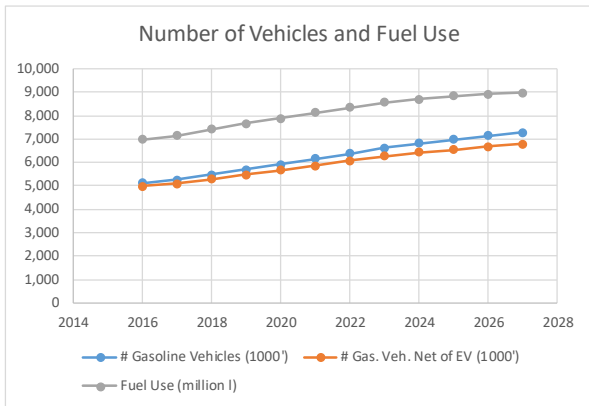
	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-20.6%	-462,832
THC	-9.8%	-24,866
PM	-4.0%	-58
NOx	0	0
Polycyclics	-8.6%	
Weighted Toxins	-29.2%	

From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-32.6%
acetaldehyde	0.02	544.8%
formaldehyde	0.04	-3.9%
1,3 butadiene	1.00	-32.1%
Polycyclics	0.00	-8.6%
Total Weighted:		-29.2%

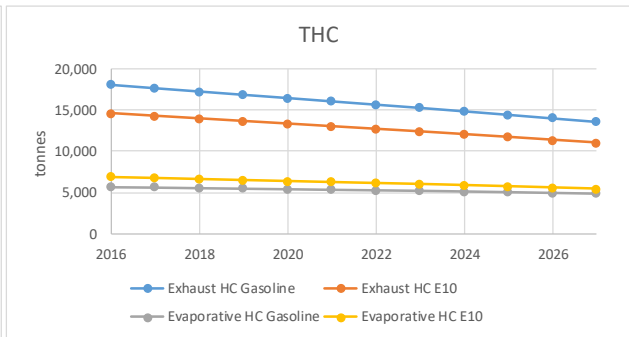
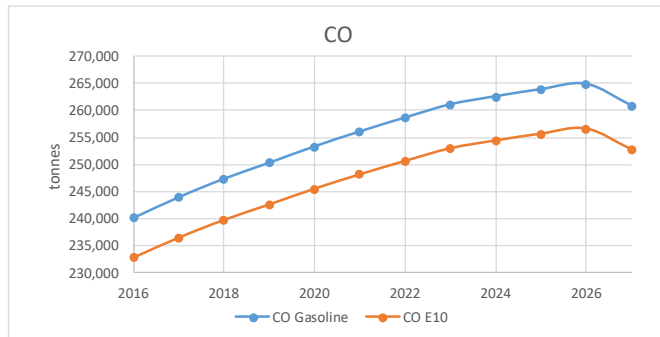
iBEAM Output Mexico (E10)

GDI Rate: 50% EV Rate: 7%

Year	# Gasoline Vehicles (1000')		Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
	# Gas. Veh.	Net of EV (1000')			
2016	5,114	4,975	6,964	8.58	81,131
2017	5,268	5,104	7,153	8.51	84,014
2018	5,481	5,289	7,404	8.43	87,876
2019	5,698	5,477	7,650	8.33	91,840
2020	5,920	5,667	7,889	8.23	95,906
2021	6,151	5,864	8,123	8.11	100,142
2022	6,387	6,064	8,348	7.99	104,488
2023	6,628	6,267	8,561	7.86	108,948
2024	6,817	6,419	8,708	7.73	112,586
2025	6,988	6,553	8,824	7.61	115,934
2026	7,136	6,664	8,905	7.49	118,927
2027	7,288	6,777	8,974	7.36	121,993



Year	tonnes									
	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10
2016	240,214	232,779	18,071	14,610	5,699	6,932	52,726	52,726	127	126
2017	244,013	236,461	17,668	14,284	5,650	6,813	51,181	51,181	130	129
2018	247,398	239,741	17,276	13,967	5,579	6,675	49,515	49,515	134	134
2019	250,342	242,594	16,881	13,648	5,510	6,541	47,804	47,804	139	138
2020	253,349	245,508	16,494	13,335	5,442	6,409	46,096	46,096	143	142
2021	256,081	248,155	16,096	13,013	5,371	6,276	44,320	44,320	146	145
2022	258,641	250,637	15,702	12,695	5,304	6,149	42,578	42,578	148	147
2023	261,063	252,983	15,315	12,382	5,241	6,026	40,818	40,818	151	150
2024	262,551	254,425	14,903	12,049	5,158	5,882	39,030	39,030	153	151
2025	263,841	255,675	14,485	11,711	5,070	5,733	37,241	37,241	154	153
2026	264,842	256,646	14,058	11,365	4,974	5,573	35,452	35,452	155	154
2027	260,876	252,802	13,640	11,028	4,879	5,416	33,774	33,774	156	155
Total:	3,063,212	2,968,406	190,588	154,087	63,877	74,425	520,535	520,535	1,736	1,725
Savings		-94,806		-36,501		10,548	0	0	-11	-11



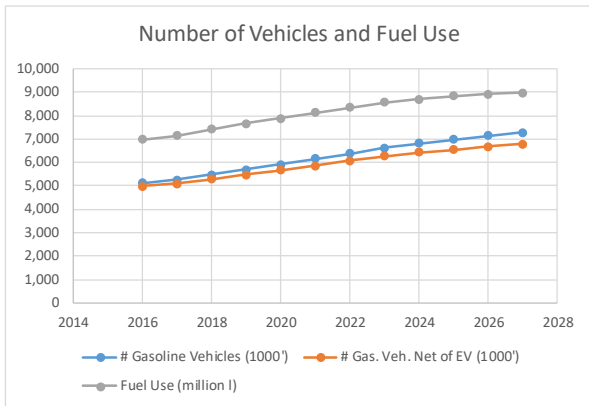
	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-3.1%	-94,806
THC	-10.2%	-25,953
PM	-0.7%	-11
NOx	0	0
Polycyclics	-4.1%	
Weighted Toxins	-8.4%	

From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-6.7%
acetaldehyde	0.02	154.7%
formaldehyde	0.04	-11.5%
1,3 butadiene	1.00	-10.4%
Polycyclics	0.00	-4.1%
Total Weighted:		-8.4%

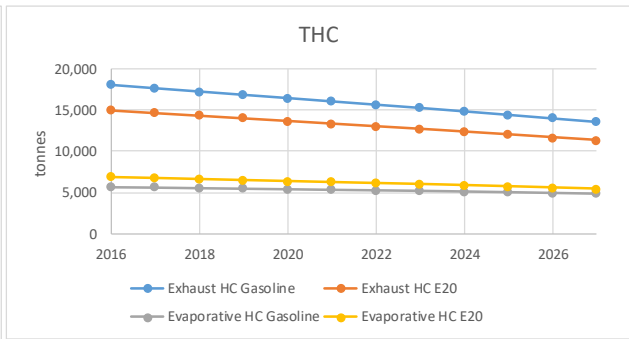
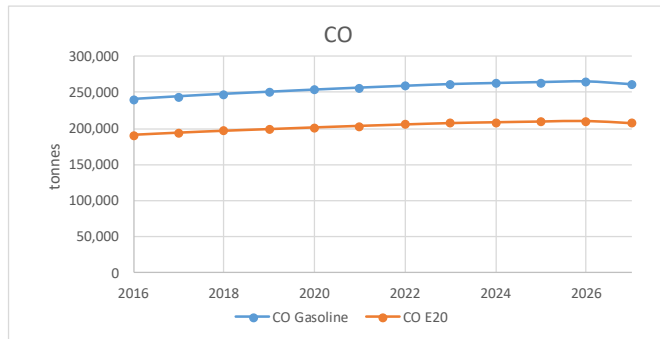
iBEAM Output Mexico (E20)

GDI Rate: 50% EV Rate: 7%

Year	# Gasoline # Gas. Veh.		Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
	Vehicles (1000')	Net of EV (1000')			
2016	5,114	4,975	6,964	8.58	81,131
2017	5,268	5,104	7,153	8.51	84,014
2018	5,481	5,289	7,404	8.43	87,876
2019	5,698	5,477	7,650	8.33	91,840
2020	5,920	5,667	7,889	8.23	95,906
2021	6,151	5,864	8,123	8.11	100,142
2022	6,387	6,064	8,348	7.99	104,488
2023	6,628	6,267	8,561	7.86	108,948
2024	6,817	6,419	8,708	7.73	112,586
2025	6,988	6,553	8,824	7.61	115,934
2026	7,136	6,664	8,905	7.49	118,927
2027	7,288	6,777	8,974	7.36	121,993



Year	tonnes									
	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20
2016	240,214	190,784	18,071	15,024	5,699	6,932	52,726	52,726	127	125
2017	244,013	193,802	17,668	14,688	5,650	6,813	51,181	51,181	130	128
2018	247,398	196,490	17,276	14,362	5,579	6,675	49,515	49,515	134	131
2019	250,342	198,828	16,881	14,034	5,510	6,541	47,804	47,804	139	135
2020	253,349	201,216	16,494	13,712	5,442	6,409	46,096	46,096	143	139
2021	256,081	203,386	16,096	13,381	5,371	6,276	44,320	44,320	146	141
2022	258,641	205,420	15,702	13,054	5,304	6,149	42,578	42,578	148	142
2023	261,063	207,343	15,315	12,732	5,241	6,026	40,818	40,818	151	144
2024	262,551	208,525	14,903	12,390	5,158	5,882	39,030	39,030	153	145
2025	263,841	209,549	14,485	12,043	5,070	5,733	37,241	37,241	154	146
2026	264,842	210,344	14,058	11,687	4,974	5,573	35,452	35,452	155	146
2027	260,876	207,194	13,640	11,340	4,879	5,416	33,774	33,774	156	146
Total:	3,063,212	2,432,880	190,588	158,447	63,877	74,425	520,535	520,535	1,736	1,667
Savings		-630,332		-32,141		10,548		0		-69



	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-20.6%	-630,332
THC	-8.5%	-21,593
PM	-4.0%	-69
NOx	0	0
Polycyclics	-9.8%	
Weighted Toxins	-24.0%	

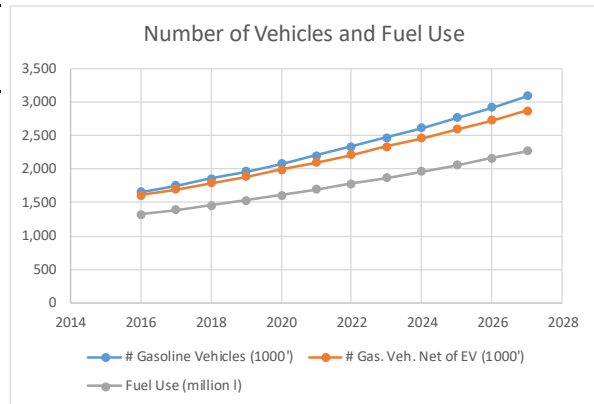
From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-26.2%
acetaldehyde	0.02	522.2%
formaldehyde	0.04	-10.9%
1,3 butadiene	1.00	-27.8%
Polycyclics	0.00	-9.8%
Total Weighted:		-24.0%

iBEAM Output New Del E10

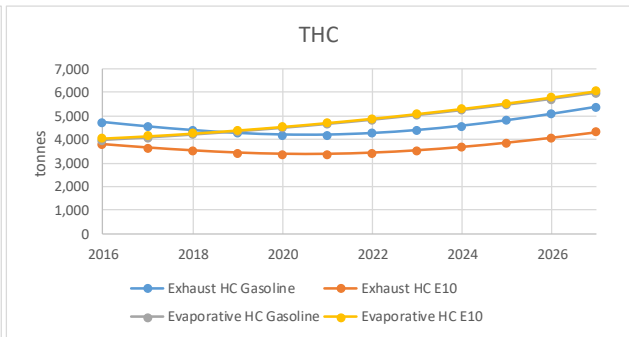
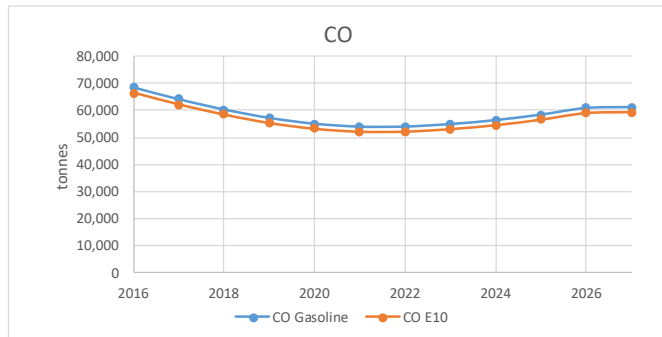
GDI Rate: 50%

EV Rate: 7%

Year	# Gasoline Vehicles (1000')	# Gas. Veh. Net of EV (1000')	Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
2016	1,655	1,610	1,319	6.15	21,454
2017	1,753	1,699	1,388	6.07	22,848
2018	1,857	1,792	1,459	6.00	24,325
2019	1,967	1,890	1,533	5.92	25,891
2020	2,083	1,994	1,611	5.85	27,549
2021	2,205	2,102	1,692	5.77	29,304
2022	2,333	2,215	1,778	5.71	31,162
2023	2,469	2,335	1,869	5.64	33,127
2024	2,612	2,460	1,964	5.58	35,205
2025	2,763	2,591	2,063	5.52	37,401
2026	2,921	2,728	2,166	5.45	39,721
2027	3,088	2,872	2,273	5.39	42,171



Year	tonnes									
	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10
2016	68,694	66,568	4,726	3,804	3,980	4,068	4,997	4,997	34	33
2017	64,272	62,283	4,540	3,655	4,086	4,161	4,682	4,682	35	35
2018	60,427	58,557	4,385	3,529	4,208	4,276	4,417	4,417	36	36
2019	57,258	55,486	4,264	3,433	4,344	4,409	4,212	4,212	38	38
2020	55,067	53,362	4,197	3,379	4,494	4,558	4,028	4,028	40	39
2021	53,969	52,298	4,195	3,377	4,659	4,723	3,928	3,928	40	40
2022	53,997	52,325	4,261	3,430	4,839	4,904	3,908	3,908	41	41
2023	54,935	53,235	4,389	3,533	5,036	5,102	3,951	3,951	42	42
2024	56,414	54,668	4,574	3,682	5,249	5,318	4,044	4,044	43	43
2025	58,479	56,669	4,807	3,869	5,479	5,550	4,172	4,172	44	44
2026	60,962	59,075	5,078	4,088	5,726	5,800	4,322	4,322	46	45
2027	61,324	59,426	5,378	4,329	5,991	6,068	4,482	4,482	47	46
Total:	705,798	683,953	54,795	44,108	58,092	58,937	51,142	51,142	486	480
Savings		-21,844		-10,687		845		0		-6



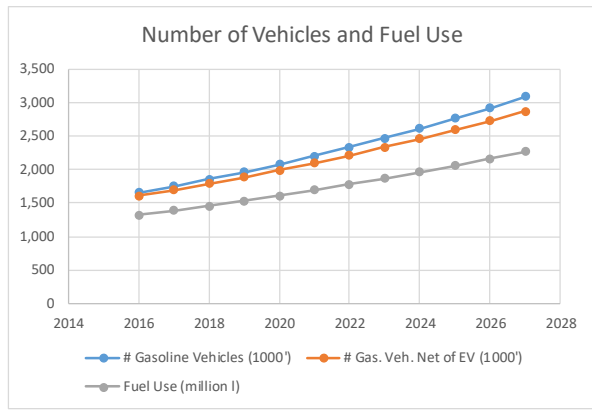
	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-3.1%	-21,844
THC	-8.7%	-9,842
PM	-1.2%	-6
NOx	0	0
Polycyclics	-6.6%	
Weighted Toxins	-21.2%	

From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-21.6%
acetaldehyde	0.02	153.0%
formaldehyde	0.04	-1.5%
1,3 butadiene	1.00	-22.5%
Polycyclics	0.00	-6.6%
Total Weighted:		-21.2%

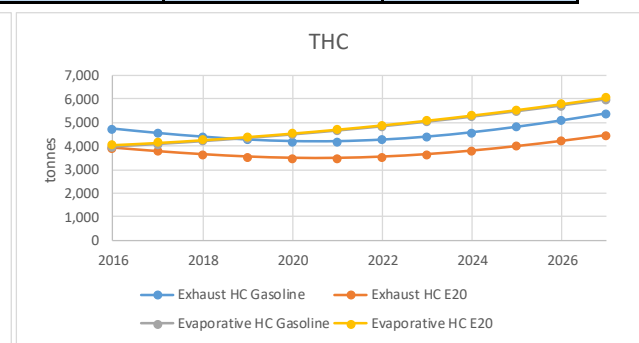
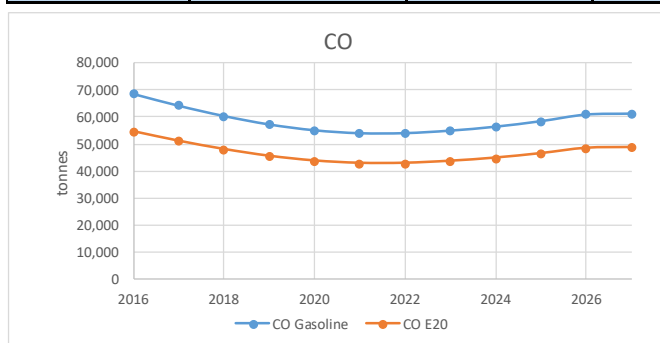
iBEAM Output New Del E20

GDI Rate: 50% EV Rate: 7%

Year	# Gasoline Vehicles (1000')	# Gas. Veh. Net of EV (1000')	Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
2016	1,655	1,610	1,319	6.15	21,454
2017	1,753	1,699	1,388	6.07	22,848
2018	1,857	1,792	1,459	6.00	24,325
2019	1,967	1,890	1,533	5.92	25,891
2020	2,083	1,994	1,611	5.85	27,549
2021	2,205	2,102	1,692	5.77	29,304
2022	2,333	2,215	1,778	5.71	31,162
2023	2,469	2,335	1,869	5.64	33,127
2024	2,612	2,460	1,964	5.58	35,205
2025	2,763	2,591	2,063	5.52	37,401
2026	2,921	2,728	2,166	5.45	39,721
2027	3,088	2,872	2,273	5.39	42,171



Year	tonnes									
	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20
2016	68,694	54,559	4,726	3,933	3,980	4,068	4,997	4,997	34	33
2017	64,272	51,047	4,540	3,778	4,086	4,161	4,682	4,682	35	34
2018	60,427	47,993	4,385	3,649	4,208	4,276	4,417	4,417	36	35
2019	57,258	45,476	4,264	3,549	4,344	4,409	4,212	4,212	38	36
2020	55,067	43,735	4,197	3,493	4,494	4,558	4,028	4,028	40	37
2021	53,969	42,863	4,195	3,491	4,659	4,723	3,928	3,928	40	38
2022	53,997	42,885	4,261	3,546	4,839	4,904	3,908	3,908	41	38
2023	54,935	43,631	4,389	3,653	5,036	5,102	3,951	3,951	42	39
2024	56,414	44,805	4,574	3,806	5,249	5,318	4,044	4,044	43	39
2025	58,479	46,446	4,807	4,000	5,479	5,550	4,172	4,172	44	40
2026	60,962	48,418	5,078	4,226	5,726	5,800	4,322	4,322	46	41
2027	61,324	48,705	5,378	4,475	5,991	6,068	4,482	4,482	47	41
Total:	705,798	560,562	54,795	45,597	58,092	58,937	51,142	51,142	486	451
Savings		-145,236		-9,198		845		0		-35



	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-20.6%	-145,236
THC	-7.4%	-8,353
PM	-7.1%	-35
NOx	0	0
Polycyclics	-9.4%	
Weighted Toxins	-36.6%	

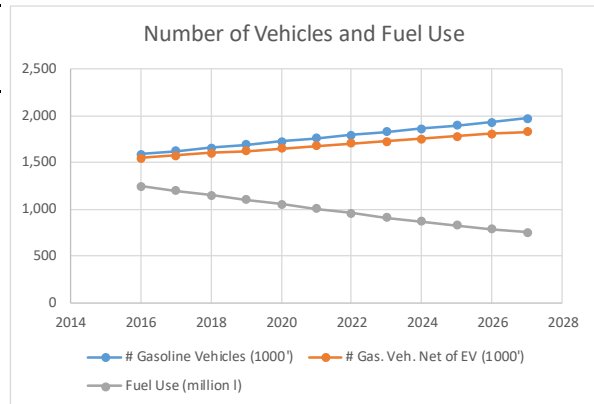
From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-40.7%
acetaldehyde	0.02	549.3%
formaldehyde	0.04	2.5%
1,3 butadiene	1.00	-38.7%
Polycyclics	0.00	-9.4%
Total Weighted:		-36.6%

iBEAM Output Seoul E10

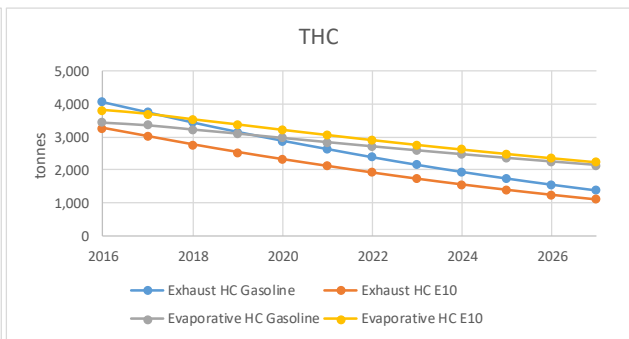
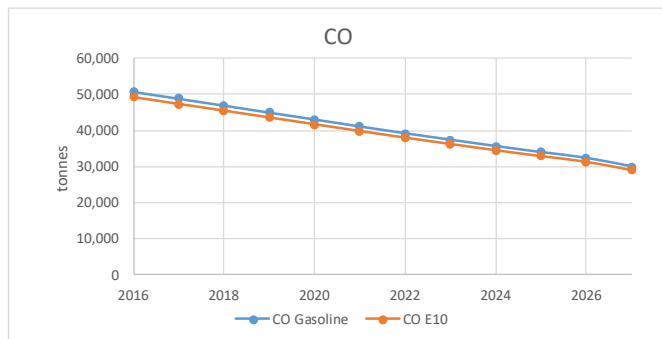
GDI Rate: 50%

EV Rate: 7%

Year	# Gasoline Vehicles (1000')	# Gas. Veh. Net of EV (1000')	Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
2016	1,590	1,546	1,248	7.82	15,967
2017	1,622	1,572	1,200	7.66	15,664
2018	1,655	1,597	1,151	7.49	15,367
2019	1,689	1,623	1,102	7.31	15,076
2020	1,722	1,648	1,051	7.11	14,790
2021	1,756	1,674	1,003	6.91	14,509
2022	1,791	1,700	957	6.72	14,233
2023	1,826	1,726	912	6.53	13,962
2024	1,861	1,752	869	6.35	13,696
2025	1,896	1,778	828	6.16	13,435
2026	1,931	1,803	789	5.99	13,178
2027	1,967	1,829	751	5.81	12,927



Year	tonnes									
	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10
2016	50,803	49,231	4,055	3,262	3,448	3,814	4,981	4,981	25	25
2017	48,880	47,367	3,746	3,014	3,367	3,696	4,629	4,629	24	24
2018	46,964	45,510	3,440	2,767	3,236	3,532	4,278	4,278	24	23
2019	45,024	43,631	3,153	2,536	3,112	3,376	3,947	3,947	23	23
2020	43,091	41,758	2,885	2,321	2,977	3,213	3,633	3,633	22	22
2021	41,160	39,886	2,632	2,118	2,848	3,057	3,364	3,364	21	21
2022	39,267	38,052	2,385	1,918	2,719	2,904	3,076	3,076	21	20
2023	37,463	36,304	2,153	1,732	2,595	2,758	2,803	2,803	20	20
2024	35,693	34,589	1,938	1,559	2,476	2,619	2,551	2,551	19	19
2025	34,003	32,951	1,738	1,398	2,361	2,485	2,317	2,317	18	18
2026	32,396	31,393	1,551	1,247	2,251	2,357	2,099	2,099	18	17
2027	30,028	29,098	1,376	1,107	2,144	2,234	1,850	1,850	17	17
Total:	484,773	469,769	31,052	24,979	33,534	36,045	39,529	39,529	251	249
Savings		-15,004		-6,073		2,510		0		-1



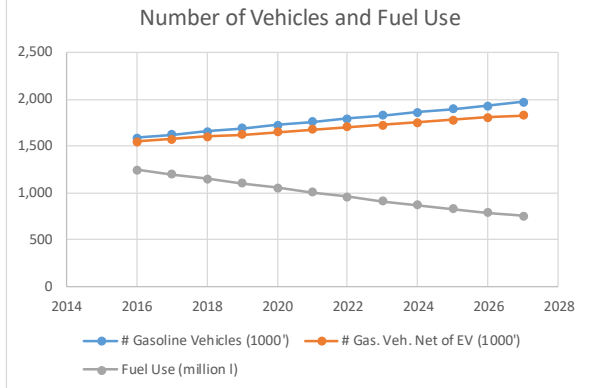
	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-3.1%	-15,004
THC	-5.5%	-3,562
PM	-0.6%	-1
NOx	0	0
Polycyclics	-7.0%	
Weighted Toxins	-19.8%	

From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-21.2%
acetaldehyde	0.02	143.6%
formaldehyde	0.04	3.3%
1,3 butadiene	1.00	-21.1%
Polycyclics	0.00	-7.0%
Total Weighted:		-19.8%

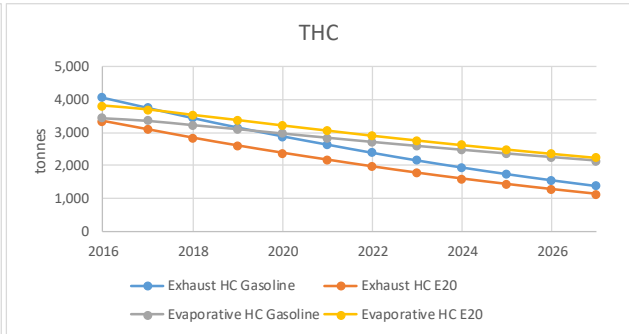
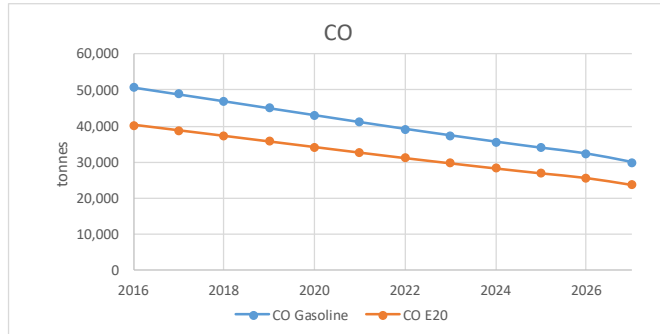
iBEAM Output Seoul E20

GDI Rate: 50% EV Rate: 7%

Year	# Gasoline Vehicles (1000')	# Gas. Veh. Net of EV (1000')	Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
2016	1,590	1,546	1,248	7.82	15,967
2017	1,622	1,572	1,200	7.66	15,664
2018	1,655	1,597	1,151	7.49	15,367
2019	1,689	1,623	1,102	7.31	15,076
2020	1,722	1,648	1,051	7.11	14,790
2021	1,756	1,674	1,003	6.91	14,509
2022	1,791	1,700	957	6.72	14,233
2023	1,826	1,726	912	6.53	13,962
2024	1,861	1,752	869	6.35	13,696
2025	1,896	1,778	828	6.16	13,435
2026	1,931	1,803	789	5.99	13,178
2027	1,967	1,829	751	5.81	12,927



Year	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20
2016	50,803	40,349	4,055	3,339	3,448	3,814	4,981	4,981	25	25
2017	48,880	38,822	3,746	3,085	3,367	3,696	4,629	4,629	24	24
2018	46,964	37,300	3,440	2,833	3,236	3,532	4,278	4,278	24	23
2019	45,024	35,759	3,153	2,597	3,112	3,376	3,947	3,947	23	22
2020	43,091	34,224	2,885	2,376	2,977	3,213	3,633	3,633	22	22
2021	41,160	32,690	2,632	2,168	2,848	3,057	3,364	3,364	21	21
2022	39,267	31,187	2,385	1,964	2,719	2,904	3,076	3,076	21	20
2023	37,463	29,754	2,153	1,773	2,595	2,758	2,803	2,803	20	19
2024	35,693	28,349	1,938	1,596	2,476	2,619	2,551	2,551	19	18
2025	34,003	27,006	1,738	1,431	2,361	2,485	2,317	2,317	18	17
2026	32,396	25,730	1,551	1,277	2,251	2,357	2,099	2,099	18	17
2027	30,028	23,849	1,376	1,133	2,144	2,234	1,850	1,850	17	16
Total:	484,773	385,019	31,052	25,574	33,534	36,045	39,529	39,529	251	242
Savings		-99,754		-5,478		2,510		0		-8



	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-20.6%	-99,754
THC	-4.6%	-2,968
PM	-3.4%	-8
NOx	0	0
Polycyclics	-13.7%	
Weighted Toxins	-36.3%	

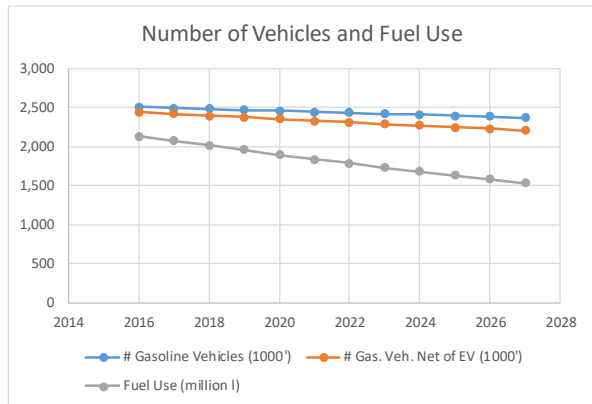
From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-33.6%
acetaldehyde	0.02	465.9%
formaldehyde	0.04	-1.2%
1,3 butadiene	1.00	-41.2%
Polycyclics	0.00	-13.7%
Total Weighted:		-36.3%

iBEAM Output Tokyo E10

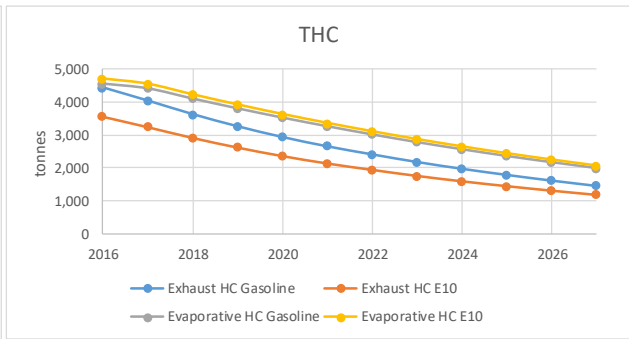
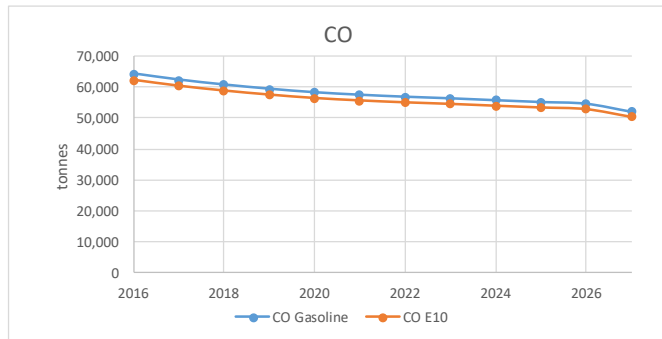
GDI Rate: 50%

EV Rate: 7%

Year	# Gasoline Vehicles (1000')	# Gas. Veh. Net of EV (1000')	Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
2016	2,510	2,442	2,136	6.89	31,013
2017	2,498	2,420	2,078	6.76	30,744
2018	2,485	2,398	2,018	6.62	30,481
2019	2,473	2,377	1,958	6.48	30,224
2020	2,460	2,355	1,897	6.33	29,972
2021	2,448	2,334	1,842	6.18	29,784
2022	2,436	2,313	1,787	6.04	29,599
2023	2,424	2,292	1,735	5.90	29,418
2024	2,412	2,271	1,683	5.75	29,241
2025	2,399	2,250	1,632	5.61	29,068
2026	2,387	2,230	1,583	5.48	28,916
2027	2,376	2,209	1,535	5.34	28,768



Year	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10	Gasoline	E10
2016	64,294	62,305	4,424	3,562	4,552	4,698	5,029	5,029	48	48
2017	62,360	60,430	4,029	3,244	4,407	4,539	4,632	4,632	47	47
2018	60,786	58,904	3,622	2,916	4,097	4,217	4,275	4,275	46	46
2019	59,457	57,617	3,258	2,623	3,801	3,911	3,958	3,958	45	45
2020	58,343	56,537	2,935	2,363	3,520	3,622	3,684	3,684	44	44
2021	57,550	55,769	2,656	2,138	3,258	3,353	3,472	3,472	43	43
2022	56,918	55,156	2,414	1,943	3,010	3,099	3,285	3,285	42	41
2023	56,409	54,663	2,185	1,759	2,777	2,861	3,129	3,129	40	40
2024	55,808	54,081	1,981	1,595	2,561	2,641	3,002	3,002	39	39
2025	55,237	53,527	1,797	1,447	2,357	2,433	2,898	2,898	38	37
2026	54,689	52,996	1,626	1,309	2,169	2,241	2,741	2,741	37	36
2027	52,166	50,551	1,467	1,181	1,992	2,061	2,562	2,562	35	35
Total:	694,017	672,537	32,394	26,078	38,499	39,678	42,668	42,668	506	502
Savings		-21,480		-6,316		1,179		0		-4



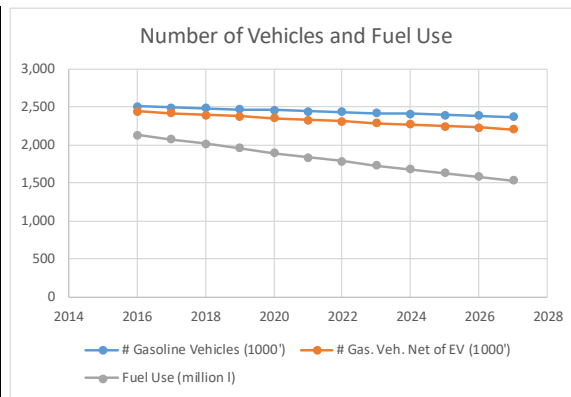
	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-3.1%	-21,480
THC	-7.2%	-5,137
PM	-0.8%	-4
NOx	0	0
Polycyclics	-6.5%	
Weighted Toxins	-14.7%	

From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-14.6%
acetaldehyde	0.02	76.4%
formaldehyde	0.04	0.2%
1,3 butadiene	1.00	-15.8%
Polycyclics	0.00	-6.5%
Total Weighted:		-14.7%

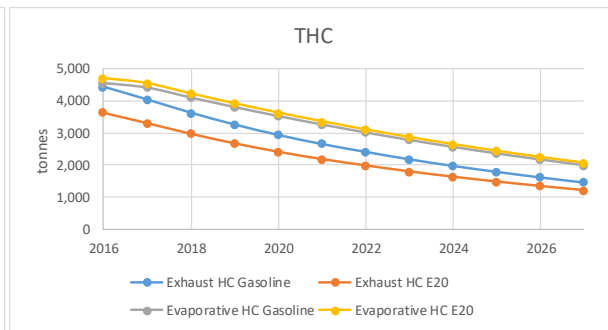
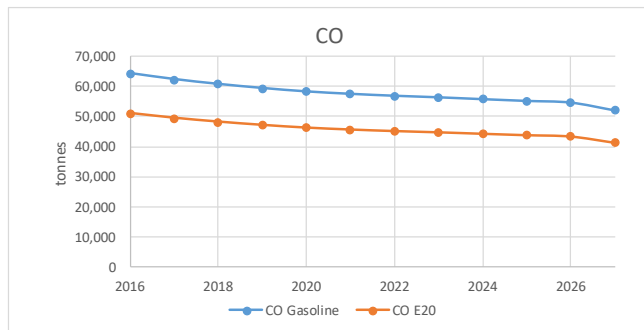
iBEAM Output Tokyo E20

GDI Rate: 50% EV Rate: 7%

Year	# Gasoline Vehicles (1000')	# Gas. Veh. Net of EV (1000')	Fuel Use (million l)	FE (l/100 km)	VDT (million km/year)
2016	2,510	2,442	2,136	6.89	31,013
2017	2,498	2,420	2,078	6.76	30,744
2018	2,485	2,398	2,018	6.62	30,481
2019	2,473	2,377	1,958	6.48	30,224
2020	2,460	2,355	1,897	6.33	29,972
2021	2,448	2,334	1,842	6.18	29,784
2022	2,436	2,313	1,787	6.04	29,599
2023	2,424	2,292	1,735	5.90	29,418
2024	2,412	2,271	1,683	5.75	29,241
2025	2,399	2,250	1,632	5.61	29,068
2026	2,387	2,230	1,583	5.48	28,916
2027	2,376	2,209	1,535	5.34	28,768



Year	CO		Exhaust HC		Evaporative HC		NOx		PM	
	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20
2016	64,294	51,064	4,424	3,637	4,552	4,698	5,029	5,029	48	48
2017	62,360	49,528	4,029	3,313	4,407	4,539	4,632	4,632	47	46
2018	60,786	48,278	3,622	2,978	4,097	4,217	4,275	4,275	46	45
2019	59,457	47,222	3,258	2,679	3,801	3,911	3,958	3,958	45	44
2020	58,343	46,337	2,935	2,413	3,520	3,622	3,684	3,684	44	43
2021	57,550	45,708	2,656	2,183	3,258	3,353	3,472	3,472	43	41
2022	56,918	45,206	2,414	1,984	3,010	3,099	3,285	3,285	42	40
2023	56,409	44,802	2,185	1,796	2,777	2,861	3,129	3,129	40	38
2024	55,808	44,324	1,981	1,629	2,561	2,641	3,002	3,002	39	37
2025	55,237	43,871	1,797	1,478	2,357	2,433	2,898	2,898	38	35
2026	54,689	43,435	1,626	1,337	2,169	2,241	2,741	2,741	37	34
2027	52,166	41,431	1,467	1,206	1,992	2,061	2,562	2,562	35	32
Total:	694,017	551,206	32,394	26,634	38,499	39,678	42,668	42,668	506	483
Savings		-142,811		-5,760		1,179		0		-23



	Relative to E0 (%)	Relative to E0 (Total Tonnes)
CO	-20.6%	-142,811
THC	-6.5%	-4,581
PM	-4.6%	-23
NOx	0	0
Polycyclics	-14.4%	
Weighted Toxins	-32.1%	

From Complex Model Based on Fuel Samples		
Toxic Air Contaminant	Relative Potency	Toxics Mass Change
benzene	0.17	-32.1%
acetaldehyde	0.02	323.3%
formaldehyde	0.04	1.2%
1,3 butadiene	1.00	-35.7%
Polycyclics	0.00	-14.4%
Total Weighted:		-32.1%

Figure 17: Individual Emissions Results By City and Ethanol Blend

11 GHG Life Cycle Emissions Savings from E10 and E20 Blends

In this section we assess the greenhouse gas emissions on a life cycle basis for ethanol produced and shipped from the United States to each of the five studied cities and blended on location into E10 and E20 gasolines. These emissions are then compared to current gasolines produced in the countries.

The GHG spreadsheet in iBEAM calculates the GHG emissions based on data from two life cycle models:

- 1) The GREET model developed by Argonne National Laboratory which is the gold standard for U.S. based life cycle analysis and contains the most up to date information on corn ethanol production. A California version of the GREET model is used for the Low Carbon Fuel Standard. An earlier version was used by the US Environmental Protection Agency for the Renewable Fuel Standard modeling.
- 2) The Biograce Model is a European life cycle model that evaluates European fuel pathways under the Renewable Energy Directive (RED).

The need to assess the GHG Emissions along both the GREET and the Biograce model stems from the fact that the GHG Emissions for gasoline in the Biograce model is based on a study by the European Joint Research Center (JRC) which results in much lower values than those for GREET due to several reasons. The JRC analysis initially relied on a simpler assessment of crude oil production which alone accounted for 4 grams carbon dioxide per megajoule (gCO₂e/MJ) difference from the GREET estimates. Also, the JRC analysis examined the incremental effect of producing gasoline from an oil refinery that is heavily configured for diesel production. Finally, the JRC study looked at incremental gasoline production for a European refinery showing efficiency gains for incremental volumes. In contrast the refinery analysis for the GREET model examined the configurations of US refineries and assigned emissions to the average gallon of gasoline produced.

11.1 GHG Emissions of US Produced Ethanol Shipped to Each City

The iBEAM model displays the energy inputs and emissions from corn ethanol over the life cycle from farming to end use. The carbon in the corn is treated as biogenic carbon neutral and the approach follows the methods for ANL's GREET model. Emissions for the farming step include farming energy, fertilizer inputs, N₂O emission from nitrogen fertilizer and crop residue and corn transport. The ethanol plant produces ethanol and dried distillers grains (DGS). A coproduct credit for DGS is calculated based on its value as animal feed. Ethanol plant emissions include emissions from natural gas, electric power and chemicals and enzymes.

The figure below shows the system boundary diagram for the ethanol pathway. Three analysis approaches are configured into iBEAM.

- 1) The first analysis approach is based on the GREET_2017 model with a substitution credit for the animal feed coproduced at the ethanol plant. In the substitution approach the main product (ethanol) receives a GHG emissions credit based on the life cycle emissions of the products displaced by the animal feed coproduction (DGS). In this case the displaced products are corn, soybean meal, and urea.
- 2) The second analysis approach utilizes GREET data with energy allocation. With the energy allocation approach, the total life cycle emissions are distributed based on an allocation factor.

The allocation is based on the energy content of ethanol vs. the total energy content of all products produced at the ethanol plant (ethanol+DGS).

- 3) The third analysis approach utilizes the BioGrace model with energy allocation. Since the EU certification approach requires energy allocation of emissions this calculation method was incorporated into iBEAM.

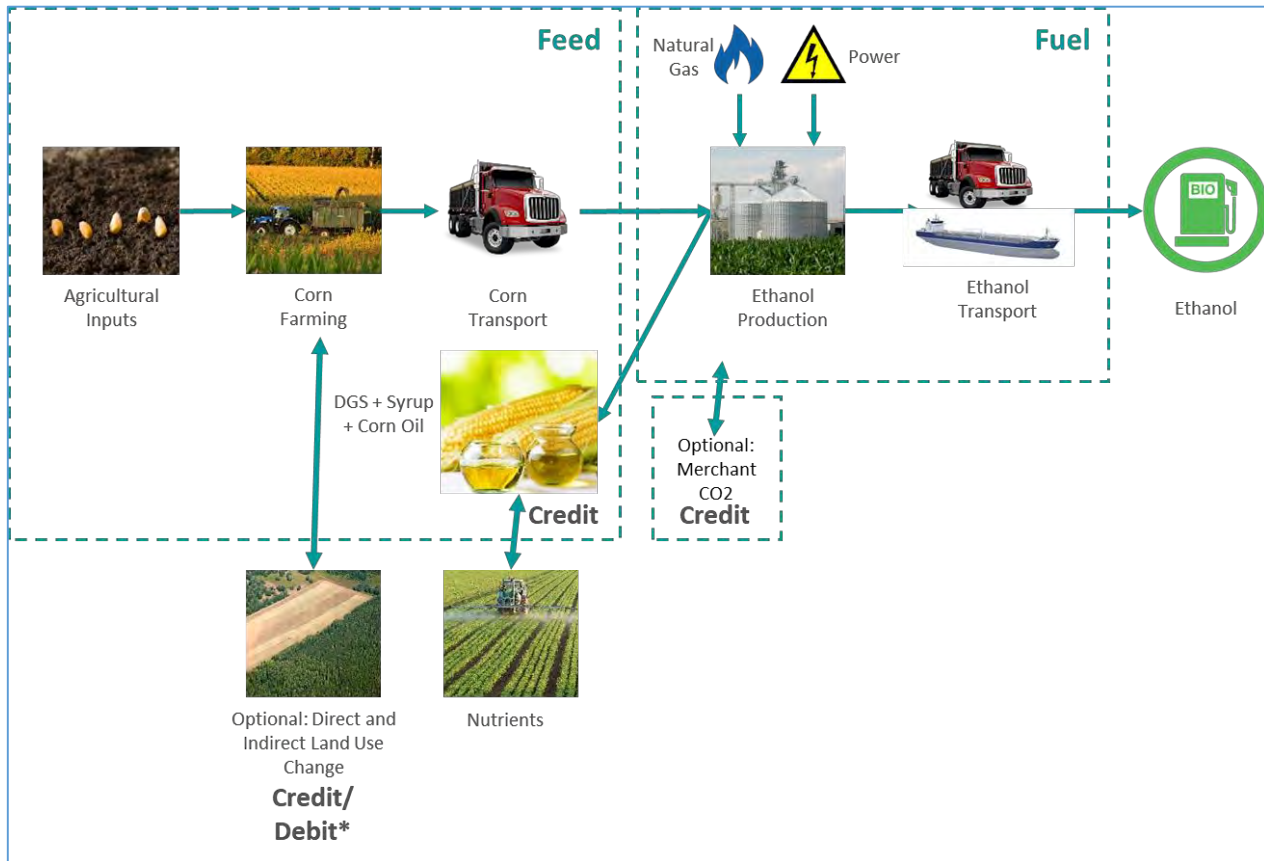


Figure 18: System Boundary Diagram for Corn Ethanol Production

The table below shows the inputs to the iBEAM model.

- The ethanol plant input parameters determine the life cycle GHG emissions for that production step. The DGS displacement ratios produce a GHG emissions credit in the ethanol pathway for the animal food coproduced at ethanol plants.
- Nitrogen emissions from fertilizer application are a large contributor to the ethanol life cycle GHG emissions.
- The energy intensity values for transportation differ between GREET and Biograce and both sets of assumptions are shown.
- Emissions from Indirect Land Use Change (iLUC) are not considered in this analysis which is consistent with the current practice under the EU and Japanese guidelines.
- Emissions credits from Direct Land Use change are considered in the Biograce modeling approach. This is consistent with the RED modeling approach which allows for emissions savings from agriculture based on improved management practices (see Appendix C).

- iBEAM has an option to consider a coproduct GHG credit for ethanol plants that recover CO₂ for sale into the merchant gas markets (beverage CO₂, food processing). Under certain conditions ethanol for certification into the EU markets under the RED can claim a coproduct credit for CO₂ recovery (see Appendix C and Case Study Sweden <http://www.iscc-system.org/en/iscc-system/iscc-trailer/>)
- The transportation distances were changed to reflect the GHG emissions incurred during shipment to the target cities (see table below)

Table 24: Inputs for GHG Emissions Assessments in iBEAM

Ethanol Production inputs

Parameter	Value	Unit
Ethanol Yield	2.82	gal/bu
DGS Yield	5.34	lb/gal
Electricity	0.74	kWh/gal
Natural Gas	20000	Btu/gal
Loss Factor	1.00050	

DGS Displacement ratios

Feed corn	0.781	lb/lb
Soybean meal	0.307	lb/lb
N-urea	0.023	lb/lb

Field Emissions

		REET
Above Ground N	141.6	1.23%
N in Fertilizer	383	1.53%
Total N ₂ O		11.90

Ethanol Transport Distance (mi)

	Beijing	Mexico City	New Delhi	Seoul	Tokyo
Mode	BV	MV	NV	SV	TV
Rail	1,050	1,050	1,050	1,050	1,050
Marine	11,898	655	11,090	11,571	10,663
Truck	100	100	100	100	100

The table below shows the GHG modeling results from the different models (REET, Biograce) and the different coproduct allocation approaches (substitution, energy allocation).

Table 25: GHG Example Calculations for Tokyo

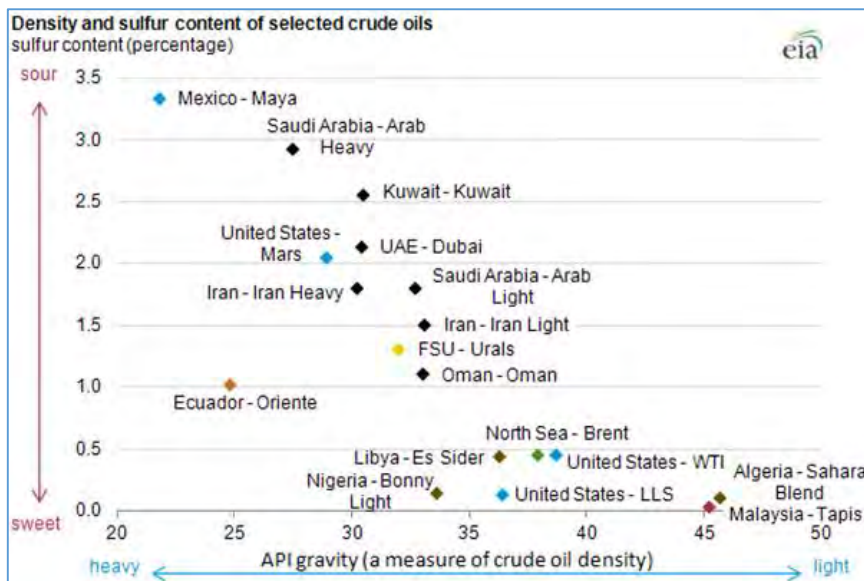
Carbon Intensity Calculations											
EtOH production step			GREET					JRC EU			
			LCI Data		CI (g CO ₂ e/MJ)		kg CO ₂ /bu	CI (g CO ₂ e/MJ)		CI (g CO ₂ e/MJ)	
			Unit	Unit	Substitution	Allocation		LCI Data	Unit	Unallocated	Allocation
Direct Land Use				g CO ₂ e/MJ							
Corn Farming	7.31	MJ/bu	92.1	g CO ₂ e/MJ	2.97	1.93	0.67	-3.8	g CO ₂ e/MJ		-3.77
CO2 emissions from urea	348	g/bu	1.0	g CO ₂ e/g	1.53	1.00	0.35	87.6	g CO ₂ e/MJ	2.82	1.84
Nitrogen Fertilizer	383	g/bu	3.86	g CO ₂ e/g	6.52	4.25	1.48	1	g CO ₂ e/g	1.53	1.00
Field N2O from fertilizer			0.12	g CO ₂ e/g corn	13.90	9.05	3.16	3.86	g CO ₂ e/g	6.52	4.25
P2O5	139	g/bu	1.46	g CO ₂ e/g	0.89	0.58	0.20	0.13	g CO ₂ e/g corn	14.75	9.61
K2O	146	g/bu	0.61	g CO ₂ e/g	0.39	0.25	0.09	1.01	g CO ₂ e/g	0.620	0.40
CaCO3	1290	g/bu	0.01	g CO ₂ e/g	0.06	0.04	0.01	0.58	g CO ₂ e/g	0.372	0.24
Field CO2 from CaCO3	279	g/bu	1	g CO ₂ e/g	1.23	0.80	0.28	0.13	g CO ₂ e/g	0.736	0.48
Herbicide	5.85	g/bu	19.95	g CO ₂ e/g	0.51	0.34	0.12		g CO ₂ e/g	0.283	0.18
Insecticide	0.01	g/bu	22.99	g CO ₂ e/g	0.001	0.00	0.00		g CO ₂ e/g		
Corn Transport	10	MHDDT mi	93.04	g CO ₂ e/MJ	0.47	0.31	0.11		g CO ₂ e/MJ	0.46	0.30
	40	HHDDT mi	94.04	g CO ₂ e/MJ	1.15	0.75	0.26		g CO ₂ e/MJ		
Corn Production					29.62	19.30	6.73			28.10	18.31
Displaced Corn	-4.17		0.26	g CO ₂ e/g corn	-6.22						
Displaced Soybean Meal	-1.64		0.49	g CO ₂ e/g SBM	-4.52						
Displaced Urea	-0.12		1.27	g CO ₂ e/g Urea	-0.8658						
Enteric CH ₄			-2.14	g CO ₂ e/MJ EtOH	-2.14	-1.40				-2.14	-1.40
CO ₂ Bottling	0.00		37.40	g CO ₂ e/MJ	0.00	0.00					
NG Boiler	21.10	MJ/gal	69.54	g CO ₂ e/MJ	18.23	11.88		67.59	g CO ₂ e/MJ	17.72	11.54
Electric Power	2.66	MJ/gal	150.96	g CO ₂ e/MJ	5.00	3.26		150.96	g CO ₂ e/MJ	5.00	3.26
Enzymes & Chemicals			1.96	g CO ₂ e/MJ	1.96	1.28			g CO ₂ e/MJ	1.96	1.28
Ethanol Transport											
	1,050	Rail mi	93.21	g CO ₂ e/MJ	1.16	1.16		127.65	g CO ₂ e/MJ		1.04
	10,663	Marine mi	96.12	g CO ₂ e/MJ	6.40	6.40		87.20	g CO ₂ e/MJ		7.02
	100	Truck mi	93.04	g CO ₂ e/MJ	0.57	0.57		87.64	g CO ₂ e/MJ		0.33
Feed Phase					15.88	17.90					16.91
Fuel Phase					33.31	24.54					24.47
Indirect Land Use					7.84	5.11					
Total Without ILUC					49.19	47.55					41.38
Total With ILUC					57.03	52.66					

Note: no merchant CO₂ credit applied

11.2 GHG Emissions of the Gasoline Baselines in Each City

The GHG emissions from ethanol are compared with the gasoline/oxygenate blends that are available in each of the five cities. The GHG emissions of petroleum gasoline and MTBE is determined in the GREET model. The Japan Research Institute (JRI) estimated the GHG emissions of its current ETBE supply which is incorporated in our modeling effort.

GREET estimates the emissions from crude oil to gasoline based on the complexity of the oil refineries in different regions of the U.S. Among other parameters the GHG emissions from a refinery are directly related to the density of crude oils measured in API gravity. Crude oils that are light (higher degrees of API gravity or lower density) tend to require less intensive processing which results in lower GHG emissions. However, most of the refineries examined in this study, except for New Delhi, have complex cracking and conversion units that are comparable to refineries in the U.S. The figure below shows the API gravity for different crude oils by origin.



Source: <https://www.eia.gov/todayinenergy/detail.php?id=7110>

Figure 19: API Gravity for Major Oil Fields

The API gravity for the crude oil processed in each of our 5 countries of interest was calculated based on the published weighted average mix of crude oil imports from different global fields (<http://www.worldstopexports.com/crude-oil-imports-by-country/>). The table below shows that while the API for major global fields differs significantly the weighted average API values for each of our countries of interest are actually quite similar. We parameterized GREET with the respective weighted average API.

Table 26: API Gravity for Crude Oil Imported into Each of the 5 Countries of Interest

Source	API	China	India	Japan	Mexico (US Mix)*	South Korea
Algeria	45.8				0.9296	0
Ecuador	24.9			0.209	3.6	0
Iran	31.9	9.5	6.7	3.3		5
Kuwait	30.5	4.8	2.7	3.1	3.3	16
Libya	36.4					0
Malaysia	45.2		1.7	0.279		0
Mexico	22.0		1.5	1.3	7.8	0
Nigeria	33.8		6.6		3.8	0
North Sea	38.0	1.7				0
Oman	33.6	11.1		0.642		0
Russia	32.0	16.8		3.3	0.686	4
Saudi Arabia	30.4	15.6	12.1	18	16.6	34
UAE	30.3	3.9	5.6	12.9		12
United States	35.0					0
Average API		31.80	31.60	30.46	28.83	30.58

* Note: Mexico produced crude oil that is exported and imports gasoline and crude oil from the U.S.

11.3 GHG Modeling Results

The table below shows the modeling results by city, life cycle model, and ethanol blend. The energy-weighting of each gasoline blending component is used to determine the GHG value of the currently used baseline gasolines which is a blend of either gasoline and MTBE (for Mexico City, New Delhi, Beijing) or gasoline and ETBE (for Tokyo) or gasoline without MTBE/ETBE. (The GHG emissions for gasoline from New Delhi has additionally been reduced by 1.5gCO₂/MJ to reflect the less complex configuration of the oil refineries). These values are then compared to the GHG emissions of the finished E10 and E20 fuels which are derived by proportionally blending the imported US produced ethanol with each country's baseline gasolines. Note that additional likely GHG reductions from streamlined refinery operations in each country were not considered due to modeling complexity. Finally, we derived the cumulative GHG savings for each ethanol blend through 2027 from the total fuel use in each city.

Table 27: Cumulative GHG Emissions and GHG Values of Gasoline and Ethanol Blends

City	Blend	LCA Model	Current	Ethanol	Ethanol	GHG Savings:	Cumulative
			Gasoline Blend	Ethanol	Blend	Ethanol Blend to	GHG Savings
			gCO ₂ /MJ	gCO ₂ /MJ	gCO ₂ /MJ	%	Metric Tonnes
Beijing	E10	REET Substitution	96.0	49.9	92.1	4.0%	-10,615,326
Beijing	E20	REET Substitution	96.0	49.9	88.9	7.4%	-19,499,582
Beijing	E10	REET Allocation	96.0	48.3	92.0	4.1%	-10,915,333
Beijing	E20	REET Allocation	96.0	48.3	88.7	7.6%	-20,121,184
Beijing	E10	JRC EU	85.3	42.2	81.0	5.0%	-11,731,099
Beijing	E20	JRC EU	85.3	42.2	78.1	8.5%	-19,904,712
Mexico City	E10	REET Substitution	96.5	43.2	91.7	5.0%	-14,893,452
Mexico City	E20	REET Substitution	96.5	43.2	88.0	8.8%	-26,366,559
Mexico City	E10	REET Allocation	96.5	41.5	91.6	5.1%	-15,230,325
Mexico City	E20	REET Allocation	96.5	41.5	87.8	9.1%	-27,064,546
Mexico City	E10	JRC EU	86.2	34.8	80.5	6.6%	-17,496,494
Mexico City	E20	JRC EU	86.2	34.8	77.0	10.6%	-28,308,137
New Delhi	E10	REET Substitution	93.9	49.4	90.7	3.4%	-2,181,807
New Delhi	E20	REET Substitution	93.9	49.4	87.6	6.8%	-4,332,611
New Delhi	E10	REET Allocation	93.9	47.8	90.6	3.5%	-2,256,084
New Delhi	E20	REET Allocation	93.9	47.8	87.3	7.0%	-4,486,510
New Delhi	E10	JRC EU	84.2	41.7	81.0	3.8%	-2,193,193
New Delhi	E20	JRC EU	84.2	41.7	78.0	7.4%	-4,242,740
Seoul	E10	REET Substitution	96.1	49.7	92.2	4.0%	-1,468,176
Seoul	E20	REET Substitution	96.1	49.7	88.9	7.4%	-2,699,014
Seoul	E10	REET Allocation	96.1	48.1	92.1	4.2%	-1,509,496
Seoul	E20	REET Allocation	96.1	48.1	88.7	7.7%	-2,784,626
Seoul	E10	JRC EU	85.3	42.0	81.0	5.0%	-1,622,789
Seoul	E20	JRC EU	85.3	42.0	78.0	8.5%	-2,754,358
Tokyo	E10	REET Substitution	93.7	49.2	92.2	1.7%	-1,107,776
Tokyo	E20	REET Substitution	93.7	49.2	88.9	5.2%	-3,412,877
Tokyo	E10	REET Allocation	93.7	47.5	92.0	1.8%	-1,184,231
Tokyo	E20	REET Allocation	93.7	47.5	88.6	5.4%	-3,571,289
Tokyo	E10	JRC EU	83.2	41.4	81.3	2.4%	-1,374,099
Tokyo	E20	JRC EU	83.2	41.4	78.2	6.0%	-3,513,337

The total cumulative GHG savings are also graphically represented in the figure below. The GHG savings are remarkably similar regardless of the employed modeling methodology. Cities with high fuel demand and current MTBE use can realize large GHG savings due to the high GHG intensity of the MTBE production pathway.

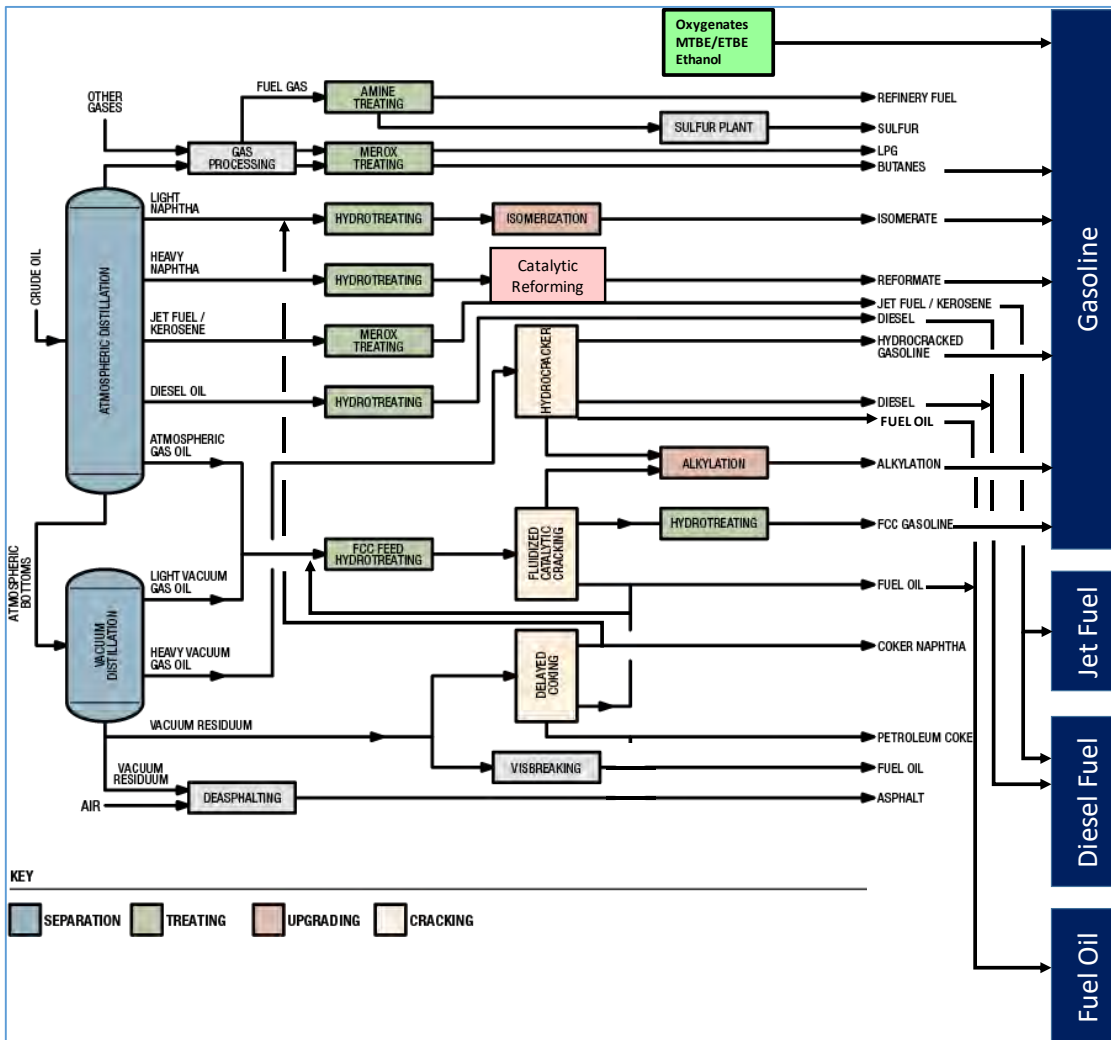


Figure 20: Cumulative GHG Savings by City, Blend, and Model

12 Refining Impact of E10 and E20 Deployment in Each Country

12.1 Petroleum Refining Overview

The processing steps in petroleum refining are designed to convert crude oil primarily into transportation fuels. The first step in refining is fractionation of the petroleum crude oil feed into major components: naphtha, distillate, gas oil, and residual oil (resid or residuum). Subsequent steps convert these streams into lighter components or treat them to improve their quality, for example, by removing sulfur and nitrogen, improving octane or cetane, or making other changes to enable maximum production of the most valuable products. A schematic of a typical refinery is shown in the figure below.



Source: from <https://www.mogas.com/en-us/industries/refining> with additions
Figure 21: Refinery Schematic

A brief description of the process units follows:

- Atmospheric Distillation Unit also called Crude Distillation Unit or CDU—The crude distillation unit fractionates the crude oil feed into straight run naphtha, kerosene, distillate and heavy atmospheric resid. The CDU is a single column with a one or two-stage preflash and a desalter. Fuel gas, C3s and C4s are sent to the gas plant. Naphtha is sent to the naphtha hydrotreating unit (NHT). Kerosene and atmospheric gas oil go to the DHT (Distillate Hydrotreating Unit). The CDU atmospheric residue bottoms (AR) is sent to the vacuum distillation unit (VDU) for further gas oil recovery.
- Vacuum Distillation Unit or VDU—The vacuum distillation unit (VDU) produces vacuum resid, which is sent to a delayed coking unit, and light and heavy vacuum gas oils (VGOs) are sent to the Gas Oil Hydrotreating Unit (GOHT). The CDU and VDU are heat integrated.
- Delayed Coking Unit—The coking unit converts vacuum resid from the VDU into lighter components, fuel gas, C3 and C4 paraffins and olefins, naphtha, distillate, gas oils and solid petroleum coke product. The delayed coker consists of several coke drums that feed a common fractionator. Fuel gas, C3s and C4s go to the Gas Plant. Naphtha from the coker is routed to the naphtha hydrotreating unit (NHT). The light coker gas oil (LCGO) from the coker is low in cetane number and high in sulfur and requires processing in the distillate hydrotreating unit (DHT). The heavy coker gas oil (HCGO) is further processed in the gas oil hydrotreating unit (GOHT) to achieve the sulfur target. Coke from the delayed coker is routed to sales. The solid coke from this unit can be used as a fuel substitute in power production or cement manufacture or in some cases it is used to make anodes for aluminum production.
- Visbreaking Unit—The Visbreaking unit is an alternative processing route to reduce the amount of vacuum residue that must go to fuel oil if there is no delayed coking unit or other bottoms upgrading unit.
- Gas Oil Hydrotreating Unit or GOHT—The gas oil hydrotreating unit (GOHT) desulfurizes heavy gas oil from the CDU, VDU, and coking units. The level of desulfurization can be set so that the feed to the fluidized catalytic cracking (FCC) unit contains less than 1,000 weight parts per million (ppm) sulfur, which is often sufficient to avoid needing an FCC naphtha hydrotreating unit. The GOHT is a significant user of hydrogen.
- Hydrocracking—The hydrocracking unit is a high pressure unit that cracks gas oil and vacuum gas oil to lighter products in the gasoline and diesel range. Distillate range products are often of high enough quality that they can be blended to products with little or no additional processing. Gasoline range material generally needs further processing – heavy naphtha in a catalytic reforming unit and light naphtha in an isomerization unit. Unconverted product from the hydrocracking unit is an excellent low sulfur feed to the fluidized catalytic cracking unit (FCC) or can be blended to fuel oil.
- Fluidized Catalytic Cracking Unit or FCC—The FCC unit converts heavy gas oils, vacuum gas oils, and heavy hydrotreated gas oils to lighter products. Light cycle oil (LCO) from the FCC unit is sent to the distillate hydrotreating (DHT) unit. FCC naphtha is sent to gasoline blending if it is low enough in sulfur or it can be treated in an FCC naphtha desulfurization unit. Unconverted oil from the FCC unit (called slurry oil) can be blended to fuel oil or recycled to the coking unit to avoid producing fuel oil. The FCC unit consists of a reactor / regenerator, a main fractionator, and a wet gas compressor. Flue gas treating with a third stage separator is generally necessary to meet emission specifications.

- FCC Naphtha Desulfurization Unit—The FCC naphtha desulfurization unit removes sulfur from FCC naphtha to meet low sulfur specifications in most modern gasolines. As a result of olefin saturation during desulfurization, there can be significant octane loss.
- Alkylation—The alkylation unit reacts C3 and C4 olefins with isobutane to produce alkylate for gasoline blending. Purchased isobutane often supplements that produced in the refinery.
- Oligomerization—The oligomerization unit combines mainly C3 olefins but in some cases also C4 olefins into larger, gasoline range molecules. Product octane is lower than alkylate, the product is olefinic, and there is lower yield than from alkylation because this process reacts two olefins together rather than one olefin with one isobutane molecule. Alkylation and oligomerization units convert LPG range material to gasoline.
- Naphtha Hydrotreating Unit or NHT—Naphtha from the CDU, coker, DHT, hydrocracking and GOHT units are hydrotreated in the NHT. The resulting product can be fractionated to send the C6/C7+ components to the catalytic reforming unit and the C5/C6 components to the isomerization unit. The cut-point between light and heavy naphtha can be set to minimize benzene and its precursors in the feed to the catalytic reforming unit. Depending on the feed and degree of desulfurization, the NHT is a low to moderate user of hydrogen.
- Catalytic Reforming Unit or Reformer—The catalytic reforming unit processes heavy naphtha from the naphtha splitter that follows the naphtha hydrotreating unit. The catalytic reforming unit or reformer is the major producer of high octane for gasoline blending. The severity (Research Octane or RON) of the unit is adjusted to meet overall gasoline octane specifications for finished gasoline resulting from blending all gasoline range components. Most of the octane in reformate from the catalytic reforming unit comes from aromatics produced in this process, which results in volume loss due to hydrogen removal in making aromatics. There is also volume loss in catalytic reforming as some naphtha is cracked to gas. The extent of volume loss and gas production depends on the severity that the catalytic reforming unit is operated at: higher severity (RON) results in more octane, hydrogen, and aromatics, but less volume. The catalytic reforming unit is an important source of hydrogen in the refinery.

To meet the benzene limits imposed by gasoline regulations in most countries, the naphtha feed to the catalytic reforming unit can be fractionated in a naphtha splitter to concentrate benzene precursors in light naphtha that can be blended directly to gasoline or processed in a light naphtha isomerization unit. Alternatively to meet benzene specifications, the reformate product from the catalytic reforming unit can be fractionated to produce light and heavy reformate. Light reformate containing most of the benzene is processed together with the light naphtha from the naphtha splitter in the C5/C6 isomerization unit.

When oxygenates are added in gasoline blending, there is less need for octane from the catalytic reforming unit and more hydrotreated naphtha feed to the catalytic reforming unit can be bypassed around this unit and blended directly to gasoline and/or the severity (RON) of the catalytic reforming unit can be reduced. The result is more gasoline production as a result of adding oxygenates and less processing in the catalytic reforming unit. However, as a result of operating at lower severity and processing less feed, there is less hydrogen produced from this unit. Oxygenate addition to gasoline, especially ethanol, can increase gasoline vapor pressure (Reid vapor pressure or RVP) and it may be necessary to remove light components such as butane and sometimes pentanes from the gasoline mix, which results in less gasoline volume. Typical properties of oxygenates are shown in the table below.

Table 28: Oxygenate Properties

	MTBE	ETBE	Ethanol
Blending Octane			
Research Octane (RON)	117	115	*
Motor Octane (MON)	98	98	*
RVP (100 °F), psi	7.8	4.0	*
Oxygen Content, wt%	18.2	15.7	34.8
Specific Gravity	0.746	0.761	0.793

Octane and RVP from ethanol blending depend on the properties of neat gasoline and the amount of ethanol blended.

For most gasoline blends with 10 volume percent (vol%) ethanol

- RVP increases by ~ 1 psi over the RVP of the neat gasoline
- RON increases by ~ 6 RON over the RON of neat gasoline
- MON increases by ~ 3 MON over the MON of the neat gasoline

For most gasoline blends with 20 vol% ethanol

- RVP increases by ~ 1 psi over the RVP of the neat gasoline
- RON increases by ~ 11 RON over the RON of neat gasoline
- MON increases by ~ 5 MON over the MON of the neat gasoline

MTBE and ETBE have RVPs close to typical finished gasoline RVP and thus their addition results in little or no need for butane or pentane removal to meet gasoline RVP specifications. Ethanol has a much bigger impact on RVP and it is generally necessary to remove butane and sometimes even pentanes to enable ethanol blending especially in low RVP gasoline. At 10 vol% in gasoline, ethanol adds around 1 psi to the RVP of the neat gasoline without ethanol.

Ethanol adds more octane than MTBE or ETBE on an equivalent volume basis. In some gasoline blends with ethanol – especially if the gasoline octane specification is low – there is no need for octane from the catalytic reforming unit and there is therefore no hydrogen production from this unit. A refinery producing gasoline with high concentrations of ethanol will need to replace the hydrogen lost from the catalytic reforming, which is usually done by converting natural gas or refinery fuel gas to hydrogen in a steam methane reforming unit (SMR).

- Isomerization Unit or C5/C6 Isom—The isomerization unit is a once-through unit that processes light naphtha and light reformat to increase their research octane from the mid-70s to the low-80s and eliminate benzene. If the feed to the isomerization unit exceeds 5 vol% benzene, a separate benzene saturation reactor is used ahead of the isomerization reactor. The isomerization unit uses a small amount of hydrogen to isomerize the C5/C6 paraffins. Isomerization increases the RVP in the product relative to the feed. Three moles of hydrogen per mole of benzene are used to convert benzene to cyclohexane. A depentanizer can be used ahead of the Isom unit to minimize the RVP impact of isomerization.
- Benzene Saturation—An alternative to eliminating benzene in an isomerization unit is to simply saturate it in a benzene saturation unit. Because there is no isomerization of C5/C6 paraffins that helps offset the octane loss from benzene saturation, it is necessary to operate the catalytic reforming unit at slightly higher severity than when an isomerization unit is used to

eliminate benzene. The net effect is less overall gasoline yield but more hydrogen from the catalytic reforming unit as a result of operating at higher severity.

- Distillate Hydrotreating Unit or DHT—The Distillate Hydrotreating Unit (DHT) reduces sulfur in the distillate range material (kerosene and distillate) from the CDU, coker, GOHT units and sometimes from the hydrocracking unit. In addition, the DHT processes light cycle oil (LCO) from the FCC unit to meet ultra-low sulfur diesel (ULSD) specifications. The DHT unit is a significant user of hydrogen.
- Hydrogen—Hydrogen is produced in the catalytic reforming unit and in the hydrogen plant, by converting natural gas and/or refinery fuel gas to hydrogen via steam methane reforming. Process heat to the hydrogen plant is supplied by fuel gas supplemented by natural gas as needed. The hydrogen plant includes a pressure swing adsorption unit (PSA) to achieve 99%+ purity hydrogen.
- Merox Treating—Merox treating units are relatively low cost units that convert or remove mercaptans from LPG, FCC naphtha, and jet fuel. As refined product sulfur levels are reduced to meet clean fuel specifications, Merox treating is not sufficient and it becomes necessary to hydrotreat FCC naphtha and jet fuel.
- Gas Plants—Gas plants are designed to achieve high recoveries of C3s and C4s. Process units include a Primary Absorber, Stripper, Debutanizer, and Amine Treating.
- Sulfur Plant—Sulfur is recovered in the sulfur plant from H₂S that is produced during the refining steps. The sulfur plant consists of a Claus unit, Tail Gas Treating Plant, Amine Regeneration, and Sour Water stripper.

The major products from petroleum refining are transportation fuels – gasoline, jet fuel, and diesel fuel. Fuel oil for stationary use and for ships (bunker fuel) is produced from heavy material that the refinery cannot process or upgrade. Fuel oil is a declining market. New regulations on bunker fuel sulfur go into effect in 2020, which will affect bunker fuel demand. Growing international trade in liquefied natural gas (LNG) and the drop in its price puts further pressure on fuel oil demand.

Petroleum refineries also produce products for the petrochemical industry. These can be propylene, other olefins and diolefins, naphthas, and aromatics. In addition, petroleum refineries produce asphalt for roads and a host of other specialty products.

Transportation fuels from petroleum are increasingly augmented with fuels from other sources. Gasoline is often blended with oxygenates, which can be MTBE, ETBE, or ethanol. Diesel can be blended with biodiesel, a fatty acid methyl ester with methanol (FAME) produced from bio-derived fats and oils. Or diesel can be blended with renewable diesel, a paraffin made from hydrotreating bio-derived fats and oils. Jet fuel can be augmented with renewable jet fuel, which is similar to renewable diesel.

12.2 Refining Industry Profile

The refining industries supplying fuels to the five cities analyzed in this study are very different as are the fuel specifications, fuel demand, and fuel demand growth. A brief description of the major characterizations of the petroleum refining industries and demand for products from petroleum in each country follows.

12.2.1 China

China is a rapidly growing economy with high demand for refined products. The following description of major trends in China is from the latest country report by the U.S. Energy Information Administration (EIA).

Annual growth in oil consumption in China has come down from 11% in 2010, reflecting the effects of the most recent global financial and economic downturn as well as policies in China to reduce excessive investment and capacity overbuilding. Despite slower growth, China still accounted for more than one-third of global oil demand growth in 2014, according to estimates by the EIA.

The EIA forecasts that China's oil consumption will exceed that of the United States by 2034. China's demand growth for oil products has decelerated following a growth spike in 2010. Diesel (gasoil) is a key driver of China's oil products demand and accounted for an estimated 34% of total oil products demand in 2014. Diesel demand declined on an absolute level in 2014 for the first time in two decades, as a result of several factors—slower economic growth, decreased production from the coal and mining sectors that transport products via rail and trucks, greater efficiency in heavy-duty vehicles, and increased use of natural gas fired vehicles in recent years.

Gasoline, the second-largest consumed petroleum fuel in China with an estimated 23% share in 2014, is still experiencing robust demand growth as a result of high light-duty car sales. China's middle class has expanded in the past decade, giving rise to high car sales. Future gasoline consumption will depend on the pace of economic development and income growth, fuel efficiency rates, and government regulations on passenger vehicle use in certain congested urban areas. Liquefied petroleum gas continues to experience some growth from the petrochemical industry, while fuel oil demand has weakened considerably.

China has steadily expanded its oil refining capacity to meet its strong demand growth and to process a wider range of crude oil types. The country now ranks behind only the United States and the European Union in the amount of refining capacity. China's installed crude refining capacity reached nearly 14.2 million barrels per day (BPD) by 2015, about 680,000 BPD higher than in 2013.

Some of the new refineries are designed to accept all grades of crude oil, making Chinese refineries a strong regional competitor. The country intends to meet its domestic demand, which has grown rapidly in the past several years, but also to export petroleum products within the region. Refinery utilization rates have declined to less than 75% in the past year as Chinese companies continued to build refining capacity against a backdrop of slower oil demand growth in China and around the world.

The National Development and Reform Commission (NDRC) claims that incremental refining capacity is expected to be 3.4 million BPD between 2016 and 2020. However, industry analysts anticipate China would add only 1.5 million BPD of net capacity between 2015 and 2020, as a result of several project delays and overcapacity during the past two years.

Recent heavy pollution in certain areas of China prompted the NDRC to adopt stricter petroleum product specifications that are intended to lower sulfur emissions from gasoline and diesel use. The agency requires refineries to implement the equivalent of Euro IV standards for transportation fuels

nationwide in 2015 and Euro V standards by January 2017, a year ahead of the prior schedule. Shanghai and Beijing are already supplying only fuels that meet Euro V standards. Sinopec and CNPC are investing in refinery upgrades to meet these emissions standards, but the small independent refineries are facing economic challenges of additional cost.

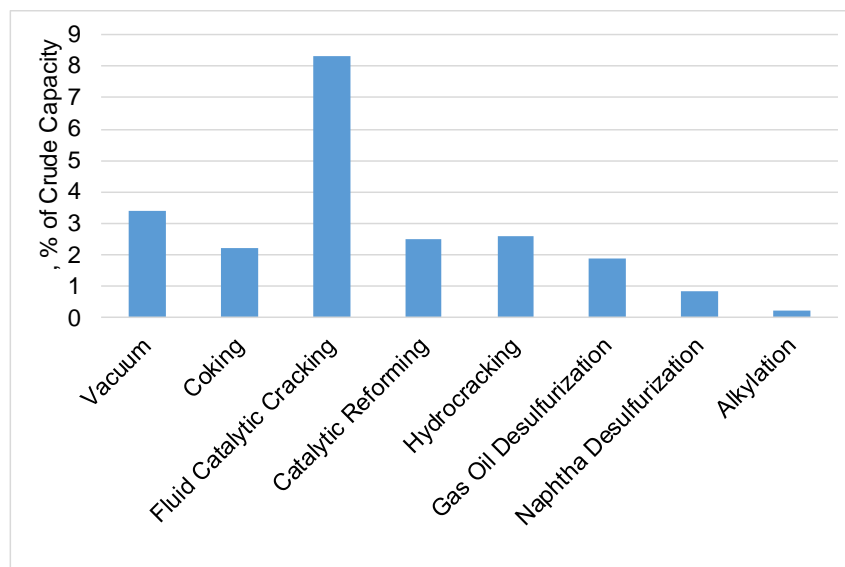
The two primary oil companies in China: are China National Petroleum Corporation (CNPC) and Sinopec. In addition, two other companies also operate in China, West Pacific Petrochemical Corp and Yanan. Crude Oil Distillation capacity in 2014 was broken down as follows:

Table 29: Crude Oil Distillation Capacity -China

	Crude Distillation Capacity, BPD
China National Petroleum Corp	2,875,000
Sinopec	3,971,000
West Pacific Petrochemical Corp.	160,000
Yanan Refinery	60,000

Source: Pennwell Worldwide Refining Survey, 2014

The breakdown of Chinese refining capacity by major processing units as percent of crude oil distillation capacity is shown below.



Source: Pennwell Worldwide Refining Survey, 2014

Figure 22: Refining Capacity - China

12.2.2 Mexico

Mexico is a developing country with slow growth in demand for refined products. Despite being one of the leading oil producers in the world, as a result of under-investment in its oil sector by its state owned oil monopoly, PEMEX, Mexico is highly dependent on imports of refined products to meet

domestic demand. The following description of major trends in Mexico is from the latest country report by the U.S. Energy Information Administration (EIA).

Mexico is one of the largest producers of petroleum and other liquids in the world. Mexico is also the fourth-largest producer in the Americas after the United States, Canada, and Brazil, and an important partner in U.S. energy trade. Despite its status as a large crude oil exporter, Mexico is a net importer of refined petroleum products. According to PEMEX, Mexico imported 740,000 BPD of refined petroleum products in 2015, of which 58% was gasoline, and most of the remainder was diesel and liquefied petroleum gases (LPG). Mexico was the destination for 50% of U.S. exports of motor gasoline in 2015.

In 2015, Mexico exported 195,000 BPD of refined petroleum products. The United States imported 70,000 BPD of that export total, most of which was residual fuel oil, naphtha, and pentanes plus. As with crude oil, U.S. imports of refined petroleum products from Mexico have declined in recent years, from a high of 132,000 BPD in 2010.

PEMEX operates an extensive petroleum pipeline network in Mexico that connects major production centers with domestic refineries and export terminals. According to PEMEX, this network consists of pipelines spanning more than 3,000 miles, with the largest concentration occurring in southern Mexico.

Mexico's total oil consumption remained relatively steady over the past decade, averaging about 1.7 million BPD in 2015. According to Mexican government data, gasoline accounted for roughly 46% of the country's petroleum product sales in 2015, and diesel accounted for another 23%.

Mexico's six refineries, all operated by PEMEX, had a total refining capacity of 1.54 million BPD as of the end of 2015. According to PEMEX, refinery output was 1.27 million BPD in 2015, a 9% decline from 2014. PEMEX also controls 50% of the 334,000 BPD Deer Park refinery in Texas.

Mexico hopes to reduce its imports of refined products by improving domestic refining capacity and the output quality. In February 2012, PEMEX awarded a contract for the design of a new refinery at Tula, but in December 2014 the company opted for a \$4.6 billion expansion of the existing facility. Gasoline and diesel production will increase from 140,000 BPD to 300,000 BPD at Tula when it is completed in 2018. Despite this and other expansions, analysts contend that Mexico does not have a natural competitive advantage in refining, given the country's close proximity to a sophisticated U.S. refining center. Some analysts feel that it would be more productive to apply PEMEX's limited capital to the upstream sector.

Source: <https://www.eia.gov/beta/international/analysis.cfm?iso=MEX>

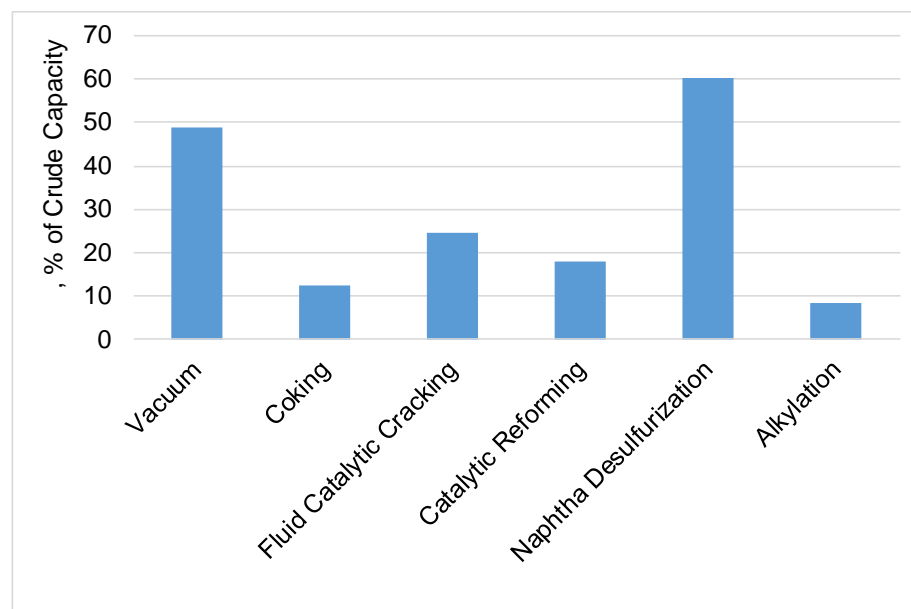
The breakdown of crude oil distillation capacity in Mexico is shown in below.

Table 30: Crude Oil Distillation Capacity – Mexico

	Crude Distillation Capacity, BPD
Pemex	1,540,000

Source: Pennwell Worldwide Refining Survey, 2014

The breakdown of Mexican refining capacity by major processing units as percent of crude oil distillation capacity is shown below.



Source: Pennwell Worldwide Refining Survey, 2014

Figure 23: Refining Capacity - Mexico

12.2.3 India

India is a rapidly growing economy with high demand for refined products. The following description of major trends in India is from the latest country report by the U.S. Energy Information Administration (EIA).

India was the fourth-largest consumer of crude oil and petroleum products after the United States, China, and Japan in 2015, and it was also the fourth-largest net importer of crude oil and petroleum products. The gap between India's oil demand and supply is widening, as demand in 2015 reached nearly 4.1 million BPD, compared to around 1 million BPD of total domestic liquids production. The EIA expects demand to accelerate in the 2016 through 2017 timeframe as India's transportation and industrial sectors continue to expand under economic development.

The refining industry is an important part of India's economy. The state-owned company, Oil India Limited (IOCL), holds most of the refining activity in India. Private Indian companies like Reliance Industries (RIL) and Essar Oil have become major refiners. The private sector owns about 37% of total capacity. In early 2016, India had 4.6 million BPD of nameplate refining capacity, making it the second-largest refiner in Asia after China.

The two largest refineries by crude capacity, located in the Jamnagar complex in Gujarat, are world-class export facilities and are owned by Reliance Industries. The Jamnagar refineries account for 26% of India's current capacity. These refineries are on the country's western coast close to crude oil-

producing regions in the Middle East, which allows them to take advantage of lower transportation costs.

India projects an increase of the country's refining capacity to 6.3 million BPD by 2017 based on its current five-year plan to meet rising domestic demand and supply export markets, although several refinery projects have faced delays in the past few years as a result of financial issues, bad weather, and regulatory hurdles. Also, there is now greater competition in Asia from countries such as China that have built large refineries able to process more complex crude oil types.

After several years of delays, India's new Paradip refinery in Odisha began commercial operations in 2016 and added about 300,000 BPD of capacity. This refinery is one of India's most complex facilities with the ability to process more sulfurous sour crude oil grades and maximize production of high-valued oil products such as diesel and gasoline.

India's government started encouraging energy companies to invest in refineries at the end of the 1990s, and the investment helped the country become a net exporter of petroleum products in 2001. In particular, the government eliminated customs duties on crude imports, lowering the cost of fuel supply for refiners. These reforms made domestic production of petroleum products more economic for Indian companies. In its 11th Five Year Plan (2007-12), India's government set the goal of making India a global exporting hub of refined products. Between 2005 and 2013, India's oil product exports, mostly from gasoil and gasoline, almost tripled to more than 1.3 million BPD before falling back to less than 1.2 million BPD in 2015 as domestic demand for products escalated at a faster pace. Some export-oriented refineries began reorienting oil production for domestic use in 2009 to help ease shortages of motor gasoline, gasoil, kerosene, and liquefied petroleum gas (LPG).

Diesel remains the most-consumed oil product, accounting for 41% of petroleum product consumption in 2015 and is used primarily for commercial transportation and, to a lesser degree, in the industrial, electric power, and agricultural sectors. Following the government's lifting of diesel subsidies during 2013 and 2014 and attendant higher retail prices that ensued, diesel demand growth flattened during this period before rising again in 2015. Gasoline use has increased at a fast pace over the past decade, and in the past few years, this fuel has replaced some diesel in the transportation sector.

Indian companies have plans to upgrade several existing refineries to produce higher-quality auto fuels to comply with more stringent specifications for vehicle fuel standards. India plans to adopt the equivalent of Euro IV fuel efficiency standards on a nationwide basis by April 2017 and both Euro V and Euro VI standards on transportation fuels by 2020. Indian companies have proposed several expansions to existing facilities and new refineries by 2020, although the timeline of these projects depends on the success of project investments and fuel sales in both domestic and export markets.

Source: <https://www.eia.gov/beta/international/analysis.cfm?iso=IND>

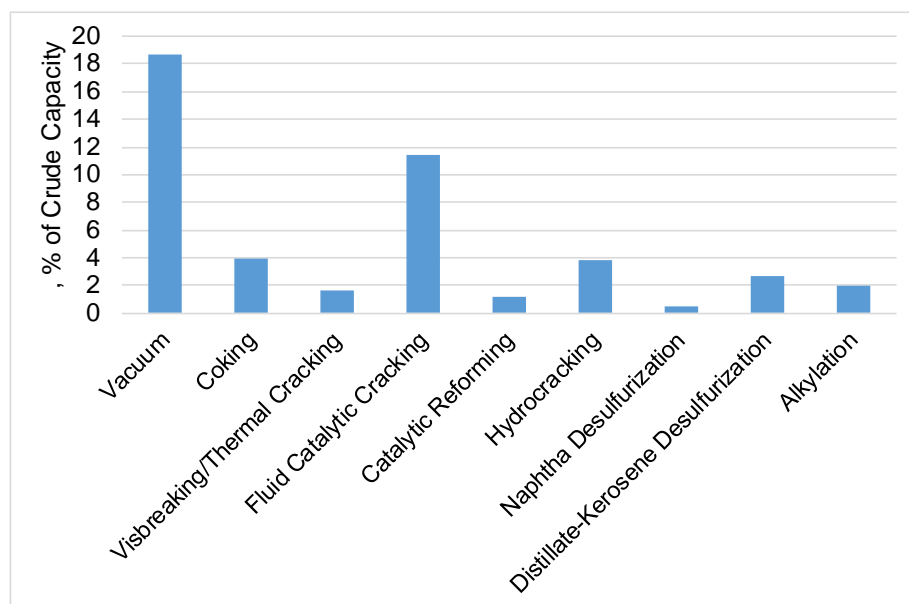
The breakdown of crude oil refining capacity in India by company is shown below.

Table 31: Crude Oil Distillation Capacity – India

	Crude Distillation Capacity, BPD
Reliance	1,240,000
Indian Oil Corp	1,146,796
Bharat Petroleum Corp	465,344
Essar Refinery	405,000
Hindustan Petroleum Corp	298,000
Chennai Petroleum Corp. Ltd.	227,261
Mangalore Refinery & Petrochemicals Ltd.	194,000
HCPL-Mittal Energy Ltd.	180,000
Bharat Oman Refineries Ltd.	120,000
Numaligarh Refinery Ltd.	64,932
Oil & Natural Gas Corp. Ltd.	1,428

Source: Pennwell Worldwide Refining Survey, 2014

The breakdown of Indian refining capacity by major processing units as percent of crude oil distillation capacity is shown below.



Source: Pennwell Worldwide Refining Survey, 2014

Figure 24: Refining Capacity - India

12.2.4 South Korea

South Korea is a developed country and has a flat to declining demand for refined products. The following description of major trends in South Korea is from the latest country report by the U.S. Energy Information Administration (EIA).

Despite its lack of domestic energy resources, South Korea is home to some of the largest and most advanced oil refineries in the world. Although petroleum and other liquids, including biofuels, accounted for the largest portion (41%) of South Korea's primary energy consumption in 2015, liquid fuel's share has been declining since the mid-1990s, when it reached a peak of 66%. This trend is attributed to the steady increase in natural gas, coal, and nuclear energy consumption, which has reduced oil use in the power sector and the industrial sector. Higher vehicle efficiencies have also reduced oil consumption.

According to the Oil & Gas Journal (OGJ), 3 of the 10 largest crude oil refineries in the world are located in South Korea, making it one of Asia's largest petroleum product exporters. According to Facts Global Energy (FGE), South Korea exported about 1.3 million BPD of refined oil products in 2015, mostly in the form of middle distillates such as gasoil, gasoline, and jet fuel. Oil product imports, about 0.9 million BPD in 2015, were primarily naphtha and LPG. Because of increased demand in Asia during the past decade, South Korea's exports of refined products have grown rapidly. The future growth rate of oil product exports will depend on demand from regional trading partners, which has been weak over the past few years, and on rising competition from new Asian and Middle Eastern refineries.

Korea's downstream sector includes several large international oil companies including SK Energy, the nation's largest international oil company (IOC). SK Energy is the largest marketer of petroleum products, followed by GS Caltex, S-Oil, and Hyundai Oilbank. These companies have historically focused on refining, but some have put increasing emphasis on crude oil extraction projects in other countries. SK Energy also owns the largest stake in the Daehan Oil Pipeline Corporation (DOPCO), which exclusively owns and manages South Korea's oil pipelines, although most of the country's oil is distributed by tankers or trucks.

According to OGJ, South Korea had about 3 million BPD of crude oil distillation refining capacity at the end of 2016 and ranked sixth largest for refining capacity in the world. The country's three largest refineries are owned by SK Energy, GS Caltex, and S-Oil Corporation (partially owned by Saudi Aramco).

Korean refineries are increasingly producing light, clean oil products as a result of refinery upgrades in recent years. The high degree of sophistication of South Korean refineries results in high capacity utilization. As a result, South Korea is expected to remain a leading refiner in Asia, with significant exports to other Asian countries. Recently, South Korean refiners have faced the headwinds of slower demand in export markets in recent years, although lower oil prices boosted refining margins in 2015.

In response to South Korea's diversification of its energy portfolio over the past few decades, oil companies not only upgraded refining facilities and increased upstream investment, but they also began investing in oil storage and alternative energy projects.

Source: <https://www.eia.gov/beta/international/analysis.cfm?iso=KOR>

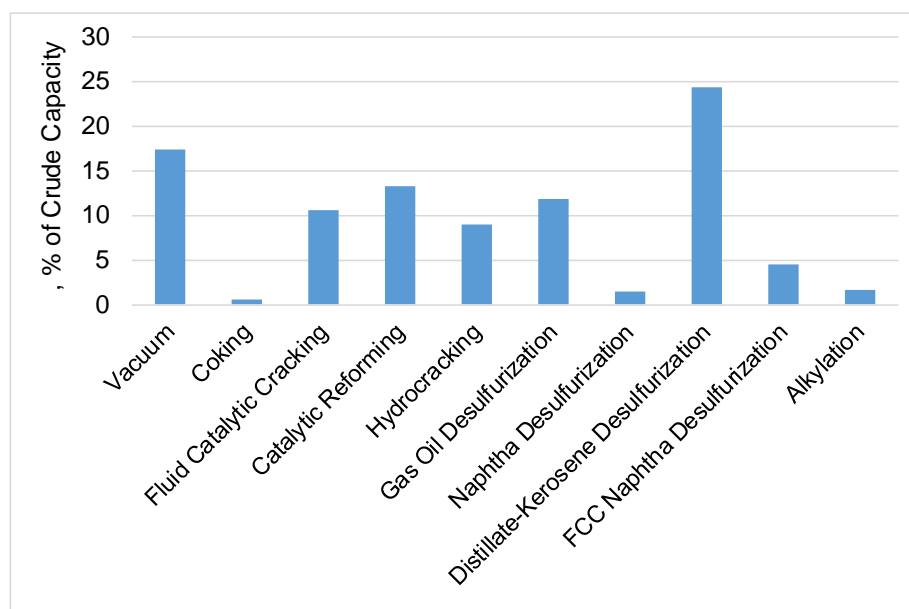
The breakdown of crude oil distillation capacity in South Korea is shown in below.

Table 32: Crude Oil Distillation Capacity – South Korea

	Crude Distillation Capacity, BPD
SK Innovation	1,115,000
GS Caltex Corp.	775,000
S-Oil Corp.	669,000
Hyundai Oilbank Corp.	390,000
Hyundai Lube Oil	9,500

Source: Pennwell Worldwide Refining Survey, 2014

The breakdown of South Korean refining capacity by major processing units as percent of crude oil distillation capacity is shown in Figure x-5.



Source: Pennwell Worldwide Refining Survey, 2014

Figure 25: Refining Capacity – South Korea

12.2.5 Japan

Japan is a developed country and has a flat to declining demand for refined products. The following description of major trends in Japan is from the latest country report by the U.S. Energy Information Administration (EIA).

Japan consumed an estimated 4 million BPD in 2016, making it the fourth-largest petroleum consumer in the world, behind the United States, China, and India. However, oil demand in Japan has declined by 23% overall since 2006. This decline results from structural factors, such as fuel substitution, a declining and an aging population, and energy efficiency measures.

Japan consumes most of its oil in the transportation and industrial/chemical sectors (about 43% and 30% of petroleum products, respectively, in 2013). In addition to being highly dependent on petroleum imports it is also highly dependent on naphtha and liquefied petroleum gases (LPG) imports.

Private Japanese firms dominate the country's large and competitive downstream sector, as foreign companies have historically faced regulatory restrictions. But over the past several years, these regulations have been eased, which has led to increased competition in the petroleum-refining sector. Chevron, BP, Shell, and BHP Billiton are among the foreign energy companies involved in providing products and services to the Japanese market as well as joint venture (JV) partnerships in many of Japan's overseas projects.

According to the Petroleum Association of Japan (PAJ), Japan had 3.8 million BPD of crude oil refining capacity at 22 facilities as of October 2016. Japan has the fourth-largest refining capacity globally, behind the United States, China, and India. JX Holdings is the largest of eight oil refinery companies in Japan, and other key operators include Idemitsu Kosan, Cosmo Oil, TonenGeneral Sekiyu, and Showa Shell Group. In recent years, the refining sector in Japan has encountered excess capacity because domestic petroleum product consumption has declined. This decline is a result of the contraction of industrial output, the mandatory blending of ethanol (often as ETBE) into transportation fuels, more fuel-efficient vehicles, and shifting demographics leading to less driving each year. In addition to declining domestic demand for oil products, Japanese refiners now must compete with new, sophisticated refineries in emerging Asian markets.

The Japanese government seeks to promote operational efficiency in the refining sector, including increasing refinery competitiveness, which may lead to further refinery closures in the future. As a result, Japan has scaled back refining capacity from about 4.7 million BPD less than a decade ago. In 2010, METI announced an ordinance that would raise refiners' mandatory cracking-to-crude distillation capacity ratio from 10% to 13% or higher by March 2014. To adhere to METI's directive, some refiners reduced capacity by nearly 20% between April 2010 and April 2014 by closing plants entirely or by consolidating facilities. METI initiated a second phase of refinery restructuring, which involved improving the overall processing capacity to 50% from a current overall processing capacity of 45% and affected a broader range of processing units. The government calls for this phase to be implemented by March 2017, with a goal that an estimated 400,000 BPD of capacity will be curtailed through further reductions in refining operations and facility closures.

There has been discussion that METI could issue a third phase to further consolidate the number of refiners and the total capacity, although no details about this phase are available. These capacity reductions come at a time when the country's oil demand continues to decline as a result of an aging population, energy conservation measures, expectations of nuclear facilities returning to serve the power sector, and financial burdens of companies having to upgrade and maintain Japan's old refining plants.

In 2015, two large mergers of refining corporations were proposed, one between JX Holdings and TonenGeneral and the other between Idemitsu Kosan and Showa Shell Group. JX Holdings and TonenGeneral plan to reduce their combined refinery capacity in the Chiba area, to share infrastructure, and to gain a majority share of the country's gasoline retail market. Final approval and completion of this merger is expected by April 2017. The Idemitsu/Showa Shell merger has been held

up by recent resistance from the Idemitsu founding family, who claims that the two companies have different corporate cultures. This potential merger block could delay further refining capacity reduction in Japan. Source: <https://www.eia.gov/beta/international/analysis.cfm?iso=JPN>

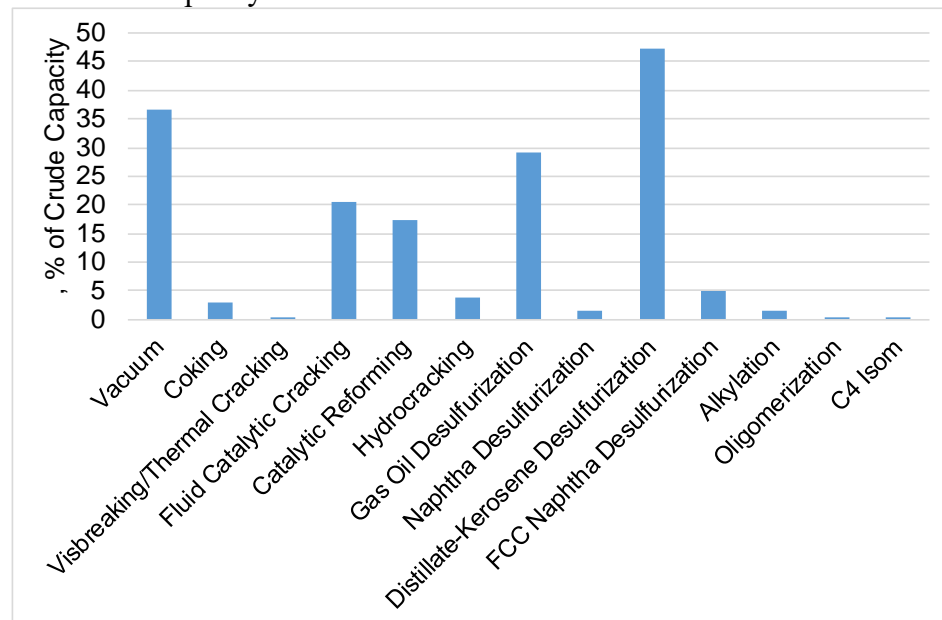
The breakdown of crude oil distillation capacity in Japan by company is shown in below.

Table 33: Crude Oil Distillation Capacity – Japan

	Crude Distillation Capacity, BPD
JX Nippon Oil & Energy	1,423,200
Idemitsu Kosan	608,000
Tonen/General Sekiyu Seisei KK	595,500
Cosmo Oil Co. Ltd.	451,250
Japan Energy Corp.	194,940
Fuji Oil Co. Ltd.	192,000
Kashima Oil Co. Ltd.	180,500
Toa Oil Co	175,000
Kyokuto Petroleum Industries Ltd.	171,500
Taiyo Oil Co. Ltd.	120,000
Seibu Oil Co. Ltd.	111,000
Nansei Sekiyu KK	100,000
Okinawa Sekiyu Seisei	100,000

Source: Pennwell Worldwide Refining Survey, 2014

The breakdown of Japanese refining capacity by major processing units as percent of crude oil distillation capacity is shown below.



Source: Pennwell Worldwide Refining Survey, 2014

Figure 26: Refining Capacity – Japan

13 Impact on Refining Profits

The table below shows the net revenue impact from changes in hydrogen and gasoline production relative to the Base Case for each city. The assumed prices were as follows:

- Gasoline price: average spot price per gallon for NY Harbor for conventional gasoline from July 2016 to July 2017 - from the EIA.
- Natural gas: city gate price for natural gas from July 2016 to June 2017 - from the EIA.

The cost of hydrogen was calculated from the cost of natural gas using yields from a steam methane reforming unit hydrogen plant model operating on natural gas and steam. An estimate of additional operating costs for the hydrogen plant is included. As shown in the tables the incremental hydrogen and incremental gasoline were determined for each case vs. the Base Case for each city. The results are shown on the basis of barrels of gasoline in the Base Case for each city. As can be seen in the individual tables and the summary graph below all ethanol blended fuels return equal or increased revenue for refiners.

Table 34: Beijing Refining Cost

		Beijing		
		MTBE	E10	E20
CHANGE FROM BASE		Base		
Change in Production				
Hydrogen Production	MM SCFD	10.41	5.43	2.17
Gasoline Volume	BPD	10,176	10,590	12,132
Delta Hydrogen	MM SCFD	0.00	-4.98	-8.24
Delta from Base Gasoline	BPD	0	414	1,955
Prices - Avg July 2016 to June 2017				
Natural Gas Price - City Gate	\$/1000 SCF	4.25	4.25	4.25
Hydrogen Price	\$/1000 SCF	2.68	2.68	2.68
Gasoline Price	\$/gal	1.50	1.50	1.50
Incremental Revenue				
Revenue from Hydrogen	\$/Day	0	-13,351	-22,115
Revenue from Gasoline	\$/Day	0	26,133	123,478
Net Revenue	\$/Day	0	12,781	101,362
Net Revenue per barrel Base Gasoline	\$/Bbl Base Gasoline	\$0	\$1	\$10

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Table 35: Mexico City Refining Cost

		Mexico City		
		MTBE	E10	E20
CHANGE FROM BASE		Base		
Change in Production				
Hydrogen Production	MM SCFD	51.81	43.01	28.38
Gasoline Volume	BPD	46,464	46,587	52,176
Delta Hydrogen	MM SCFD	0.00	-8.80	-23.43
Delta from Base Gasoline	BPD	0	123	5,712
Prices - Avg July 2016 to June 2017				
Natural Gas Price - City Gate	\$/1000 SCF	4.25	4.25	4.25
Hydrogen Price	\$/1000 SCF	2.68	2.68	2.68
Gasoline Price	\$/gal	1.50	1.50	1.50
Incremental Revenue				
Revenue from Hydrogen	\$/Day	0	-23,571	-62,740
Revenue from Gasoline	\$/Day	0	7,761	360,725
Net Revenue	\$/Day	0	-15,810	297,985
Net Revenue per barrel Base Gasoline	\$/Bbl Base Gasoline	\$0	\$0	\$6

Table 36: New Delhi Refining Cost

		New Delhi		
		MTBE	E10	E20
CHANGE FROM BASE		Base		
Change in Production				
Hydrogen Production	MM SCFD	5.37	0.00	0.00
Gasoline Volume	BPD	11,717	14,171	16,888
Delta Hydrogen	MM SCFD	0.00	-5.37	-5.37
Delta from Base Gasoline	BPD	0	2,454	5,171
Prices - Avg July 2016 to June 2017				
Natural Gas Price - City Gate	\$/1000 SCF	4.25	4.25	4.25
Hydrogen Price	\$/1000 SCF	2.68	2.68	2.68
Gasoline Price	\$/gal	1.50	1.50	1.50
Incremental Revenue				
Revenue from Hydrogen	\$/Day	0	-14,395	-14,395
Revenue from Gasoline	\$/Day	0	154,952	326,541
Net Revenue	\$/Day	0	140,556	312,146
Net Revenue per barrel Base Gasoline	\$/Bbl Base Gasoline	\$0	\$12	\$27

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Table 37: Seoul Refining Cost

		Seoul		
		No Oxygenates	E10	E20
CHANGE FROM BASE		Base		
Change in Production				
Hydrogen Production	MM SCFD	59.30	39.59	23.28
Gasoline Volume	BPD	23,189	26,269	30,589
Delta Hydrogen	MM SCFD	0.00	-19.71	-36.02
Delta from Base Gasoline	BPD	0	3,081	7,400
Prices - Avg July 2016 to June 2017				
Natural Gas Price - City Gate	\$/1000 SCF	4.25	4.25	4.25
Hydrogen Price	\$/1000 SCF	2.68	2.68	2.68
Gasoline Price	\$/gal	1.50	1.50	1.50
Incremental Revenue				
Revenue from Hydrogen	\$/Day	0	-52,872	-96,636
Revenue from Gasoline	\$/Day	0	194,548	467,358
Net Revenue	\$/Day	0	141,676	370,722
Net Revenue per barrel Base Gasoline	\$/Bbl Base Gasoline	\$0	\$6	\$16

Table 38: Tokyo Refining Cost

		Tokyo		
		ETBE	E10	E20
CHANGE FROM BASE		Base		
Change in Production				
Hydrogen Production	MM SCFD	51.67	36.69	27.48
Gasoline Volume	BPD	35,083	36,592	41,773
Delta Hydrogen	MM SCFD	0.00	-14.98	-24.19
Delta from Base Gasoline	BPD	0	1,510	6,691
Prices - Avg July 2016 to June 2017				
Natural Gas Price - City Gate	\$/1000 SCF	4.25	4.25	4.25
Hydrogen Price	\$/1000 SCF	2.68	2.68	2.68
Gasoline Price	\$/gal	1.50	1.50	1.50
Incremental Revenue				
Revenue from Hydrogen	\$/Day	0	-40,180	-64,892
Revenue from Gasoline	\$/Day	0	95,360	422,546
Net Revenue	\$/Day	0	55,180	357,654
Net Revenue per barrel Base Gasoline	\$/Bbl Base Gasoline	\$0	\$2	\$10

Impact of Higher Ethanol Blends on Vehicle Emissions

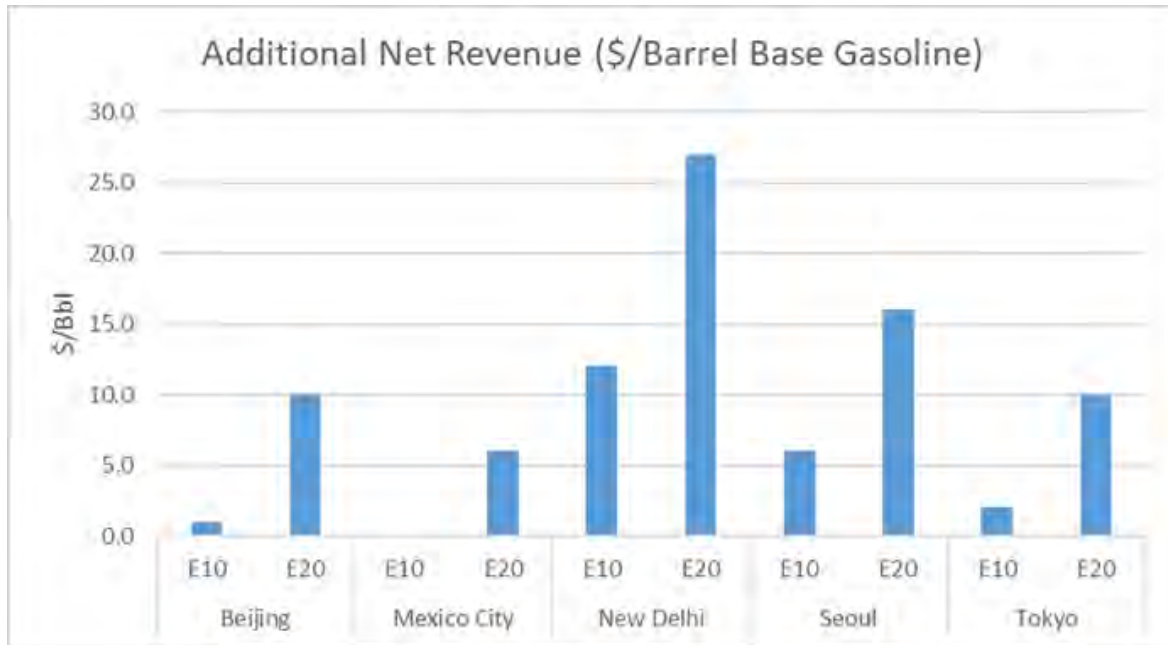


Figure 27: New Revenue Adjustments to Refiners from Adopting Ethanol Blends

14 Health Impacts from Ethanol in Gasoline

This chapter was written in collaboration with Dr. Zigang Dong (Executive Director) and Dr. K. S. Reddy, The Hormel Institute, University of Minnesota. Additional contributions were provided by Dr. Rachel Jones, Associate Professor of Environmental and Occupational Health Sciences, UIC School of Public Health.

This section of the report builds on the results of previous chapters and it completes the integrated approach to assess the pathway of air toxins and other polluting compounds from fuel blending to health impacts.

14.1 Modeling Approach to Assess the Health Impact from Blending Ethanol

The figure below shows the five step process employed in the present study to assess the health impact of ethanol blends across the studied cities. In previous chapters we performed an analysis of the refining impact of adding ethanol and determined the emissions mass reductions in vehicles. Now we convert the mass reductions to concentrations in the atmosphere which then allows us to apply health risk factors and subsequently quantify the impact on cancer cases, health cost, and years of life lost. In the following each step will be detailed.

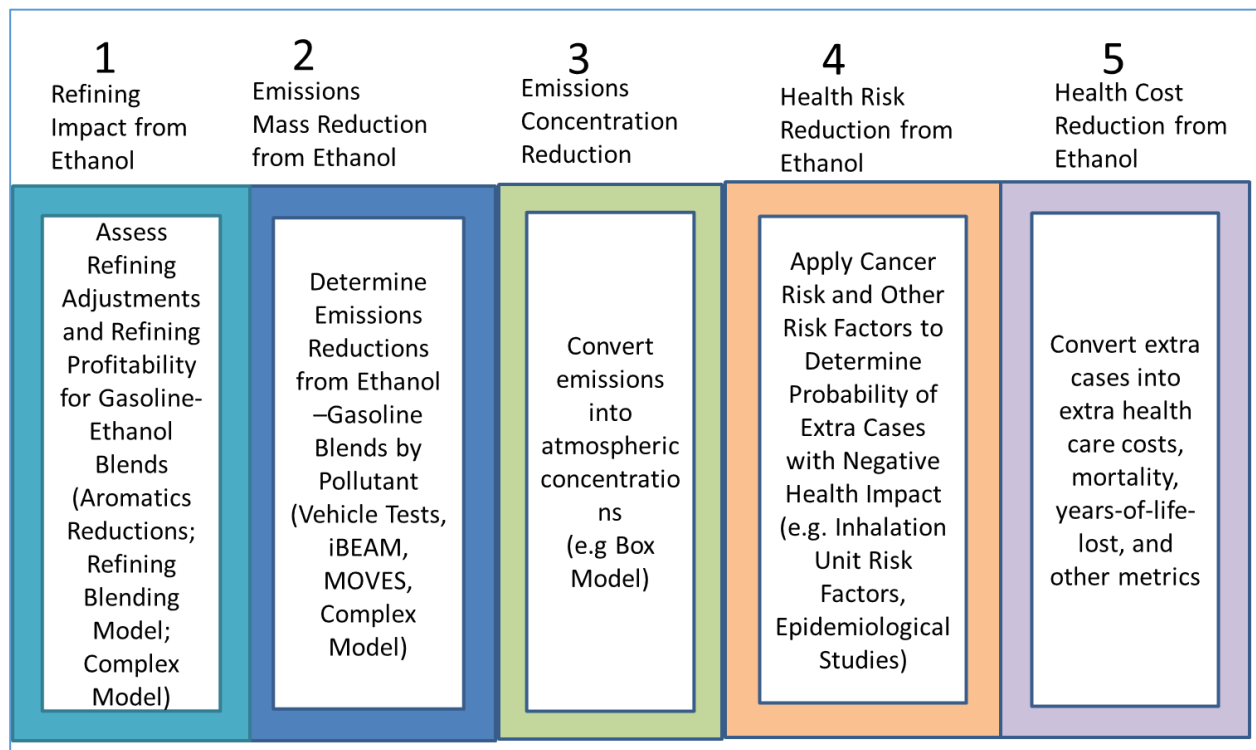


Figure 28: Health Impact Modeling Sequence

Refining Impact from Ethanol

Gasoline contains a large amount of aromatic hydrocarbons that are added to gasoline because they have relatively high octane values and therefore serve as anti-knock agents in vehicle engines. Some aromatics are toxic compounds. Ethanol also has a high octane value and contains no aromatic compounds. It therefore substitutes and dilutes aromatics in gasoline. Moreover, ethanol also alters the distillation curve resulting in an adjustment of the distillation properties of the fuel with, for example a higher volume fraction of the fuel distilled at 200 degrees Fahrenheit. This effect further reduces the formation of toxic emissions in a vehicle.

The catalytic reforming unit within a refinery is the major producer of high octane for gasoline blending. The severity (Research Octane or RON) of the unit is adjusted to meet overall gasoline octane specifications for finished gasoline resulting from blending all gasoline range components. Most of the octane in reformat from the catalytic reforming unit comes from aromatics produced in this process.

With ethanol blended into gasoline the reforming unit severity is adjusted to lower research octane numbers (RON), which generally results in lower benzene and aromatics content (see Figure below). The recent Fuels Trends Report by the US Environmental Protection Agency discloses the connection between ethanol and aromatics in gasoline and states: "Ethanol's high octane value has also allowed refiners to significantly reduce the aromatic content of the gasoline, a trend borne out in the data" [45].

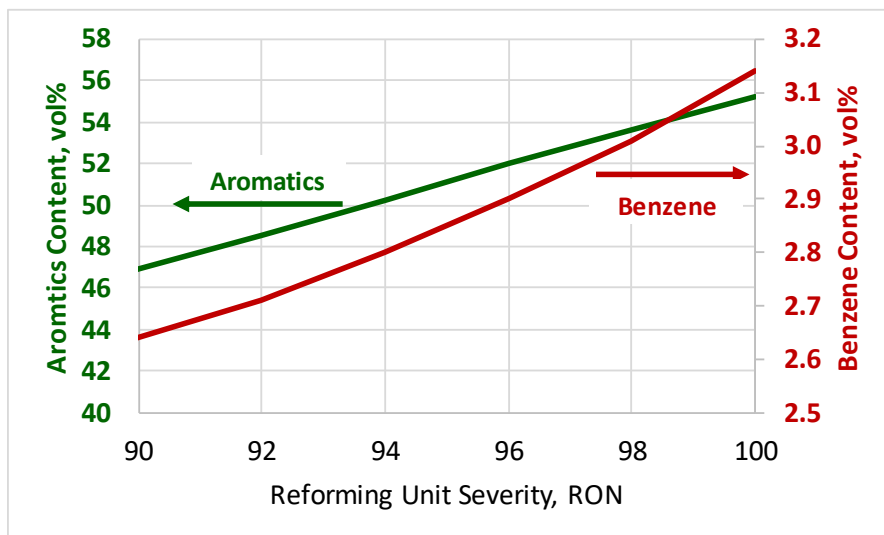


Figure 29: Aromatics Production at Refinery to Meet Octane Requirements

The blending behavior from refiners whereby aromatics are reduced in anticipation of the addition of ethanol was also documented in the present study. The panel of figures below shows the results from a blending model that changes the gasoline recipe based on the addition of ethanol. As can be seen across all cities the aromatics and benzene content drops with the addition of ethanol. Benzene levels may also be separately regulated.

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Blending results for Seoul and Beijing show a reduction in benzene and aromatics as ethanol replaces MTBE. Adding ethanol at 10 vol% reduces the need for octane from the catalytic reforming unit and adds volume for dilution. Going to 20 vol% ethanol further reduces benzene and aromatics in the final gasoline blends. Results for Delhi and Tokyo show similar results as for Seoul and Beijing. For Mexico City E20 follows the blending model pattern observed for all cities. However, for Mexico City E10 the blending model would predict about the same addition of aromatics than for the baseline gasoline but the adjustments in the distillation curve from ethanol still results in a reduction of predicted tailpipe emissions.



Figure 30: Projected Blending Behavior of Refiners

The toxic compounds from the fuel as well as additional compounds formed during the combustion process are either emitted through exhaust, crankcase and evaporative processes. Some of the toxic pollutants affected by ethanol blends are aromatics (e.g. benzene, polycyclic

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aromatic hydrocarbons also known as PAHs), alkanes (such as butadiene) and aldehydes (e.g. formaldehyde, acetaldehyde).

Emissions Mass Reductions from Ethanol

Besides the fuel formulations the emitted quantities depend on vehicle technology, driving patterns, climate, and geography. In emissions inventory models such as the US EPA's MOTO Vehicle Emission Simulator (MOVES) model the emissions of many of the toxic compounds are estimated as fractions of the emissions of volatile organic compounds (including benzene, butadiene, acetaldehyde, formaldehyde) or for toxic species in the particulate phase (including many PAHs such as Benzopyrene) as fractions of total organic carbon < 2.5 μm [46]. The equations for several toxics are in turn a carry-over from the EPA Complex Model which is used to determine whether gasoline complies with reformulated gasoline (RFG) and anti-dumping emissions performance standards. The Complex Model's original emissions equations derives benzene emissions as a function of a fuel batch's benzene, non-benzene aromatics, and sulfur content, as well as distillation fractions at E200 and E300 [47].

In previous chapters we quantified the emissions reductions (in tonnes) that can be achieved from blending E10 and E20. The mass of emissions reductions depends on the vehicle fleet in each city, fuel consumption, vehicle emissions standards and fuel parameters. For example, the table below lists the expected emissions from gasoline vehicles for the city of Beijing as well as the emissions and emissions savings from a 20% ethanol blend for selected pollutants. As can be seen over the next ten years blending E20 would save a cumulative 6,400 tonnes of benzene emissions into the Beijing air shed.

Table 39: Example of Emissions Reductions from E20 - Beijing

Year	Benzene		Acetaldehyde		Polycyclics		CO		PM		Formaldehyde		1,3 Butadiene	
	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20	Gasoline	E20
2016	1,370	924	184	1,188	123	112	191,235	151,884	110	108	448	431	450	305
2017	1,463	986	197	1,268	131	120	197,253	156,663	115	113	479	460	480	326
2018	1,558	1,050	209	1,350	140	128	200,359	159,130	120	117	510	490	511	347
2019	1,667	1,124	224	1,445	150	137	202,844	161,104	126	122	545	524	547	371
2020	1,774	1,196	239	1,538	159	146	204,661	162,547	133	128	581	558	582	395
2021	1,757	1,185	236	1,523	158	144	199,229	158,233	129	124	575	553	577	391
2022	1,739	1,172	234	1,507	156	143	193,473	153,661	126	121	569	547	571	387
2023	1,719	1,159	231	1,490	154	141	187,355	148,802	123	117	562	541	564	383
2024	1,697	1,144	228	1,471	152	139	180,544	143,392	119	113	555	534	557	378
2025	1,665	1,122	224	1,443	149	137	173,428	137,741	115	109	545	524	546	371
2026	1,614	1,088	217	1,399	145	132	165,765	131,655	111	104	528	508	530	360
2027	1,564	1,054	210	1,356	140	128	153,071	121,572	106	99	512	492	513	348
Total:	19,588	13,204	2,633	16,977	1,758	1,607	2,249,216	1,786,383	1,434	1,376	6,409	6,161	6,429	4,364
Savings		-6,384		14,344		-152		-462,832		-58		-249		-2,065

Converting Mass Emissions to Concentrations

In this step the mass emissions were converted into emissions concentrations using a box model. The Box model calculates air changes for each city taking into account the width of the box area drawn over a city, its wind speed and mixing height.

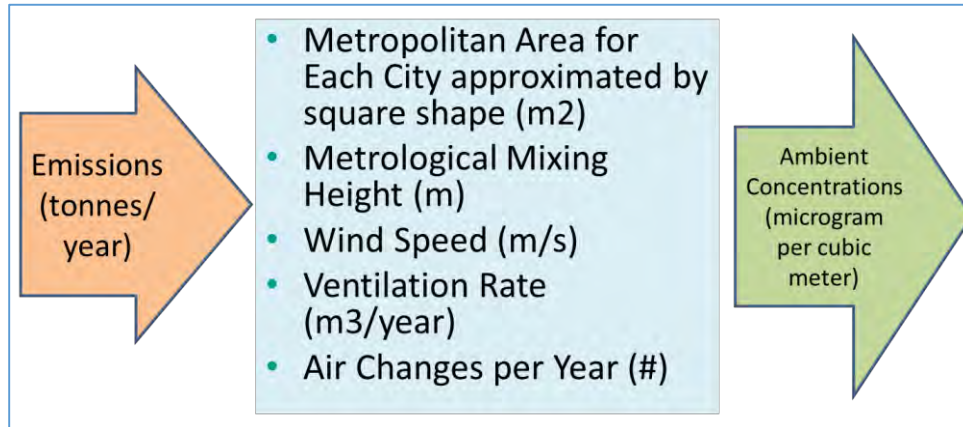


Figure 31: Box Model Flow Diagram

The images below show the box model boundaries.

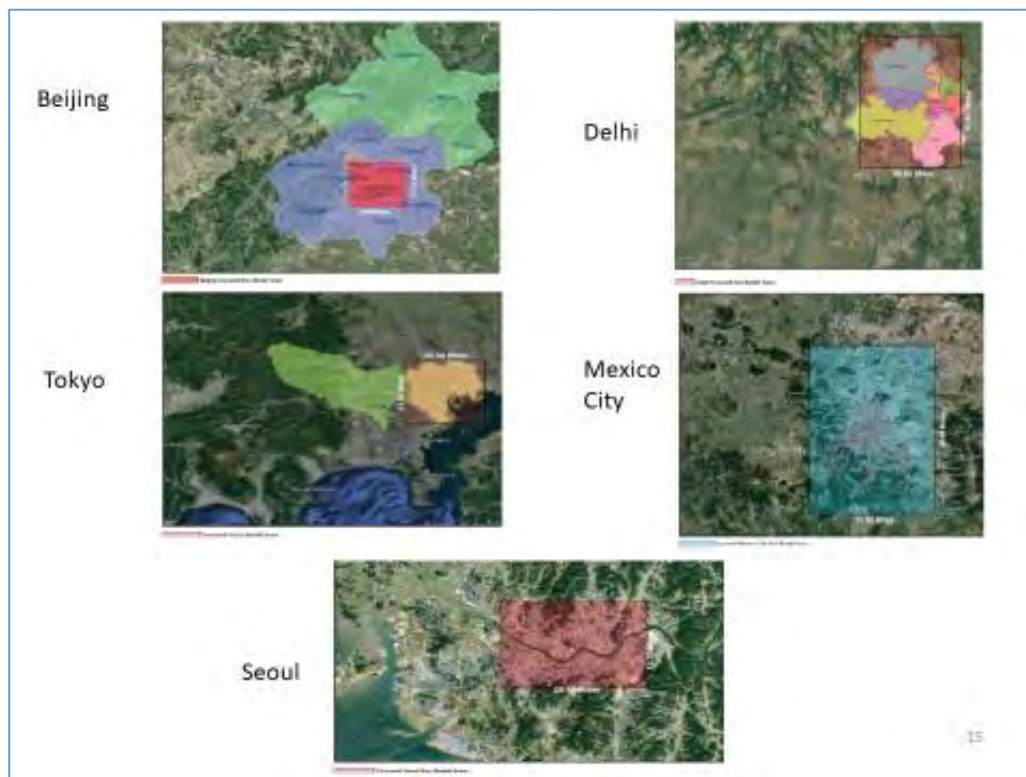


Figure 32: Box Model Boundaries for Each City

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The metrological conditions and the shape of the box can significantly alter the relative emissions concentrations even in simple box models. As can be seen in the figure below Beijing and Mexico City have about the same Benzene emissions per year but the higher air changes in Beijing result in overall lower concentrations in that city.

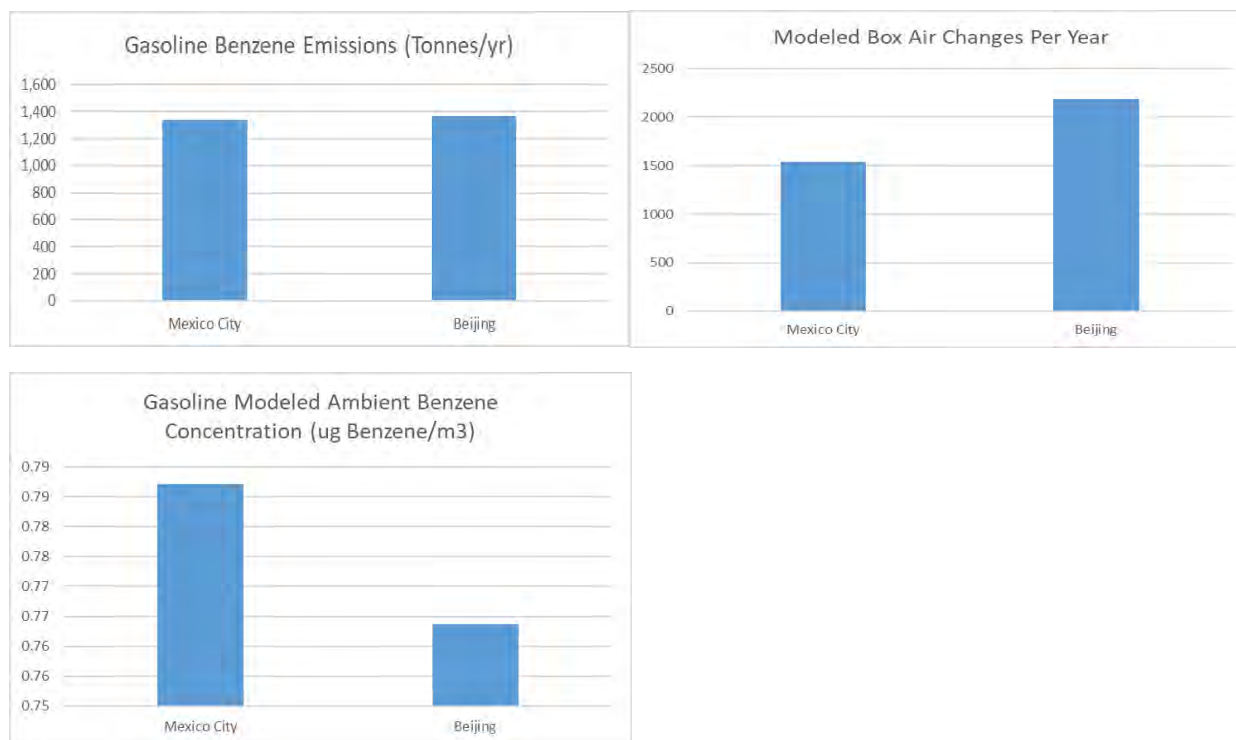


Figure 33: Box Model Relating Mass Emissions to Concentrations – Example Beijing

The box model provides a good approximation of concentrations. It should be noted that the model is limited by its inability to reflect a) hot spots where higher population density areas within a city are exposed to higher emissions concentrations and b) geographic features including mountains etc. that affect air changes. Also, we employed a conservatively adjusted mixing height based on Pendergast 1974 and Schubert 1976 who show that the temperature based assessments of the mixing height may overestimate the true mixing height. The reduction is consistent with the EPA Workbook of Atmospheric Dispersion Estimates (EPA, 1970): when most people in a densely populated urban area are surrounded by sources (streets) with some traffic volume, they are likely exposed to pollutants which haven't mixed to the full atmospheric mixing heights.

On the other hand, we did not take into account population growth within a city which given the growth of the studied cities will most certainly result in an underestimation of the derived health effects or exposure of particular occupational risk groups such as gasoline refueling station workers.

Pollutants Assessed for Health Impacts

Of the emissions affected by ethanol blended gasoline, several of the pollutants are well known to have adverse impacts on public health. In this study, the health impact of inhaling the following pollutants is considered:

Acetaldehyde. Acetaldehyde has been classified as *possibly carcinogenic to humans* (Group 2B) by the International Agency for Research on Cancer. The US EPA classifies acetaldehyde as a probable human carcinogen based on nasal and laryngeal tumors observed in rodents after inhalation exposure [48], [49].

Benzene. Benzene has been classified as *carcinogenic to humans* (Group 1) by the International Agency for Research on Cancer. Benzene causes acute myeloid leukemia (acute non-lymphocytic leukemia), and has been positively associated with acute lymphocytic leukemia, chronic lymphocytic leukemia, multiple myeloma and non-Hodgkin lymphoma [50], [51].

Benzo[a]pyrene (BaP). BaP has been classified as *carcinogenic to humans* (Group 1) by the International Agency for Research on Cancer. The basis for this classification is a clear mechanism of genotoxicity that impacts lung tumors, though epidemiologic studies have observed increased lung and skin cancer risks. Animal studies have observed cancers at many locations after exposure to BaP in mixtures through multiple routes. BaP is one of many polycyclic aromatic hydrocarbons (PAHs) emitted in vehicle exhaust, many of which are thought to be carcinogenic. For this analysis, BaP is used as an indicator of carcinogenic risk from PAHs because it is the most potent of the PAHs, and has been found to dominate the cancer risk posed by PAHs emitted by gasoline vehicles [52],[53],[54],[55].

Butadiene. 1,3-butadiene has been classified as *carcinogenic to humans* (Group 1) by the International Agency for Research on Cancer. 1,3-butadiene has been associated with cancer of the haematolymphatic organs, such as leukemia [56].

Carbon monoxide (CO). CO is an acute toxicant, and can result in unintentional vehicle-associated deaths, such as CO poisoning resulting from failures of the vehicle exhaust system. In general, ambient CO is not present at levels capable of causing CO poisoning, but acute exposures to ambient CO has been associated with increased mortality from cardiovascular disease, coronary heart disease and stroke [57], [58].

Fine Particulate Matter (PM). PM is a complex material, which may contain toxic heavy metals, PAHs, organic carbon, elemental carbon and other chemicals. The composition of PM varies geographically, in part due to fleet composition and fuels. Epidemiologic studies observe differences in the association between PM exposure and mortality, but it is not clear what drives geographical differences (e.g., PM composition, PM sources, topography, or other urban attributes). Inhalation of PM has been associated with a variety of health impacts that depend, in part, upon the duration and magnitude of exposures and the age of the population exposed. Herein we focus on mortality associated with chronic exposures, which is the outcome utilized by the US EPA risk assessment for long-term exposures to PM [59], [60].

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Formaldehyde. Formaldehyde has been classified as *carcinogenic to humans* (Group 1) by the International Agency for Research on Cancer. There is scientific consensus that formaldehyde contributes to the development of cancer in the nasal tissues, though the association with lymphohematopoietic cancers is more controversial [61]; [62]; [63].

Many additional pollutants in vehicle exhaust adversely impact health, or are formed from vehicle emissions, but are not specifically quantified in this study.

Cancer Outcomes and Impacts

The approach taken to estimate the impact of ethanol fuels on cancer outcomes is as follows. For each of the five cities, the airborne concentrations of the pollutants were estimated annually 2016-2027 for the three fuel scenarios (standard gasoline, E10 gasoline, and E20 gasoline). In general, the trend in airborne pollutant concentrations varies among years, and was not monotonic.

For each of the fuel scenarios, the average airborne pollutant concentration across the period of study (2016-2027) was calculated. Next, the mean impact of ethanol fuel (E10 and E20) on airborne pollutant concentrations was calculated by taking the difference between the mean concentration for the ethanol fuel scenario and the standard gasoline scenario. This difference was assumed to represent the long-term average change in airborne pollutant concentrations with the shift to ethanol fuel, and the reduction in inhalation exposure among the population. The approximate number of cancers avoided (or increased) by the change to ethanol fuel was then calculated as the product of the difference in the airborne pollutant concentrations between the scenarios, the inhalation unit risk factor, and the population of the city. This calculation includes a number of assumptions that are not fully valid in this context, such as lifetime continuous inhalation exposure at the mean modeled values, but serves to provide an estimate of potential impact of ethanol fuel introduction.

The inhalation unit risk (IUR) factor is a standard metric for estimating excess lifetime cancer risk associated inhalation exposure, and assumes a lifetime of continuous exposure. The IUR factor has units of risk per 1 $\mu\text{g}/\text{m}^3$ inhalation exposure. The IUR factors used in this study are shown in the table below, and were derived by the California Office of Environmental Health Hazard Assessment (OEHHA). The OEHHA values were selected because they tend to be more health-conservative than values derived by the US EPA [64a].

For polycyclic aromatic hydrocarbons additional clarification is required. Vehicle exhaust contains a host of PAHs which are more or less carcinogenic. The carcinogenicity of BaP is well studied and toxic equivalency factors to characterize other PAHs have been developed [64b]. However, the overall cancer risk from PAHs is dominated by BaP for newer and older gasoline cars [64c]. Therefore, we followed the approach described in Bostrom et al [64c]: “in the past, EPA has assessed risks posed by mixtures of PAHs by assuming that all carcinogenic PAHs are as potent as benzo[a]pyrene (B[a]P), one of the most potent PAHs.” We also acknowledge the

Impact of Higher Ethanol Blends on Vehicle Emissions

statement in Bostrom et al that this approach is likely overestimating the risk.

Table 40. Inhalation Unit Risk (IUR) factors for selected carcinogens in vehicle exhaust

Pollutant	IUR Factor (risk per ug/m ³)	Relative Potency
Acetaldehyde	2.7×10^{-6}	0.002
Benzene	2.9×10^{-5}	0.026
Benzo[a]pyrene	1.1×10^{-3}	1.00
1,3-Butadiene	1.7×10^{-4}	0.155
Formaldehyde	6.0×10^{-6}	0.005

The change in the number of cases of cancer estimated to result from the introduction of ethanol fuels relative to the continued use of gasoline is shown in the tables below. The emission for the “possibly known carcinogen in humans” acetaldehyde is estimated to increase with the use of ethanol fuels, resulting in an increase in the estimated number of associated cancers. For example, using E10 in Beijing may increase the lifetime cancer risk from associated increases in acetaldehyde emissions by 5.2 cases.

Table 41: Change in Cancer Cases for Acetaldehyde

Acetaldehyde	Change in Number of Cancer Cases
E10 Fuel	
Beijing	5.2
Delhi	3.9
Mexico City	11
Seoul	2.9
Tokyo	2.7
E20 Fuel	
Beijing	14
Delhi	11
Mexico City	28
Seoul	7.3
Tokyo	7.3

However, the increase from acetaldehyde cases is small relatively to the known carcinogens to humans including benzene, butadiene, benzopyrene/polycyclics, and formaldehyde (see figure below). Particularly noteworthy is the magnitude of the percent change in predicted cancer cases by pollutant. For example, adding ten percent ethanol by volume reduces benzene related cancers from gasoline vehicles in Delhi and Beijing by 27% and 23% respectively. Butadiene related

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cancer cases from gasoline in Delhi and Seoul can be reduced by 20% with the addition of ten percent ethanol and cut in half with the addition of twenty percent ethanol.

Table 42: Change in Number of Cancer Cases from Selected Air Toxins

Change in Number of Cancer Cases by Pollutant					
	Acetaldehyde	Benzene	Polycyclics	1,3-Butadiene	Formaldehyde
<i>E10 Fuel</i>					
Beijing	5.2	-79.0	-30.6	-97.9	-3.3
Delhi	3.9	-95.7	-59.8	-107.8	-2.2
Mexico City	10.5	-123.2	-43.5	-142.8	-9.5
Seoul	2.9	-33.9	-40.3	-83.5	-1.4
Tokyo	2.7	-39.4	-42.5	-76.5	-1.5
<i>E20 Fuel</i>					
Beijing	13.7	-116.3	-99.6	-287.4	-4.6
Delhi	10.7	-136.9	-85.4	-251.7	-2.8
Mexico City	27.5	-192.6	-95.7	-456.7	-12.5
Seoul	7.3	-44.4	-79.2	-207.7	-2.4
Tokyo	7.3	-57.6	-93.4	-288.9	-2.1

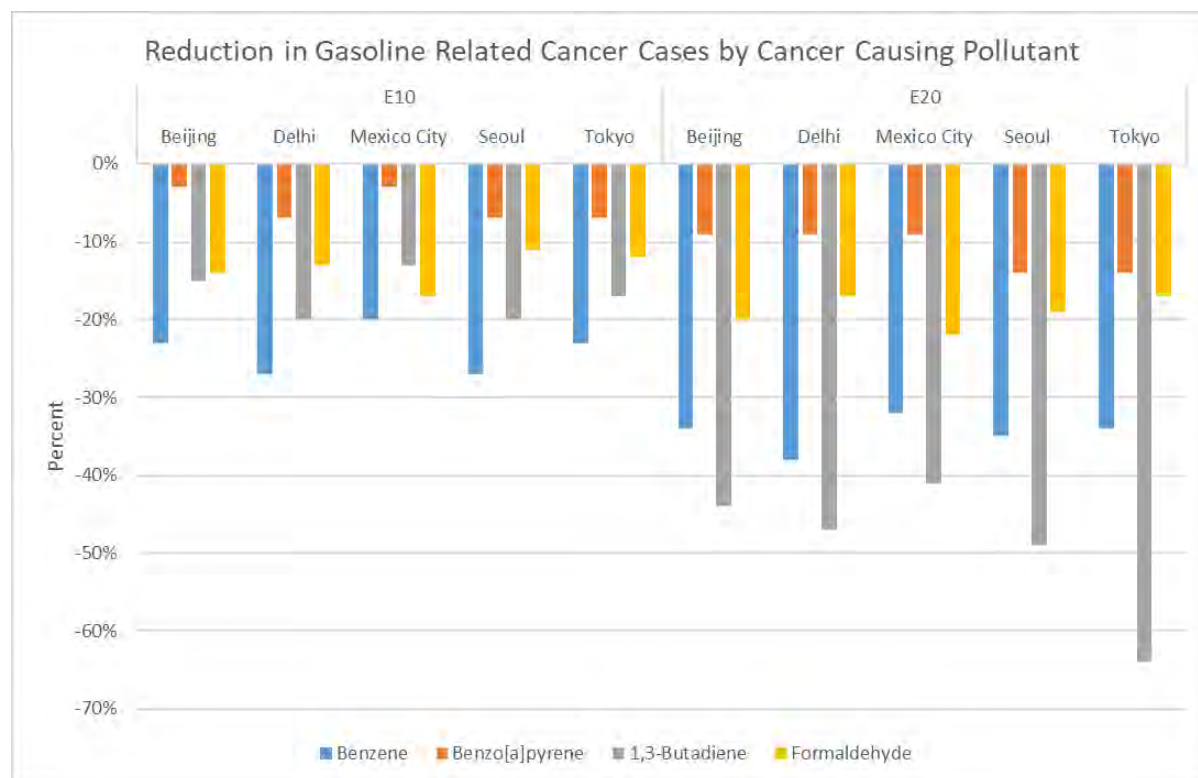


Figure: Reduction in Gasoline Related Cancer Cases by Pollutant

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Cancer is a serious disease, and adversely impacts the quality and length of patient lives. Treatment of cancer incurs substantial healthcare costs, but has additional individual and social costs associated with diminished quality of life, such as lost income. To better characterize the impact to patients and society of the transition to ethanol fuels, we estimate the expected years of life lost and the direct healthcare costs associated with the change in the number of cancer cases. Years of life lost provide a summary measure of premature mortality. Potential years of life lost may be defined as the years of potential life lost due to premature deaths.

The carcinogenic pollutants considered in this study each cause a variety of cancers, each of which have different prognoses. The table below summarizes the years of potential life lost for the cancers relevant to the pollutants studied for the US population [65]. For each pollutant, the years of potential life lost owing to different types of cancers were averaged and applied to all cities. This simplification treats each type of cancer as equally likely, and the treatment/prognosis as uniform globally.

Table 43: Years of Potential Life Lost by Pollutant

	Benzene	Acetaldehyde	Formaldehyde	Butadiene	Polycyclics
leukemia	15.6			15.6	
lung and bronchus					15.2
non-Hodgkin lymphoma	14.0			14.0	
melanoma/adenocarcinoma					
Melanoma		17.0	17.0		
Esophagus		16.2	16.2		16.2
Pancreas		15.1	15.1		
Prostate		10.0	10.0		
Myeloma	13.5				
Stomach				16.3	16.3
Hodgkin lymphoma				22.2	
Average	14.4	14.6	14.6	17.0	15.9

Ambient concentrations of acetaldehyde are estimated to increase with the transition to ethanol fuels, thus additional years of potential life will be lost. For all other pollutants, the transition to ethanol fuels is predicted to reduce ambient concentrations and the number of excess cancers, and thus save potential life lost relative to continued use of gasoline. In all cities, the transition to ethanol fuels is estimated to save thousands of years of potential life lost from exposure to these pollutants. In Mexico City, for example, the introduction of E10 will save over 5,000 years of life lost across the studied air toxins. In the US, a person-year of life lost has been valued at \$150,000 which leads our assessment to show several hundred million dollars of savings from ethanol blends [73].

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Table 44. Change in years of potential life lost or gained by pollutant.

	Acetal- dehyde	Benzene	Polycyclics/ Benzo[a]pyrene	Butadiene	Formal- dehyde	Total	Years of Life Value Saved
E10 Fuel							
Beijing	76	-1,135	-487	-1,667	-48	-3,262	-\$489,246,266
Delhi	57	-1,375	-951	-1,835	-32	-4,136	-\$620,409,006
Mexico City	154	-1,770	-692	-2,431	-138	-4,877	-\$731,507,141
Seoul	43	-488	-641	-1,422	-20	-2,529	-\$379,311,492
Tokyo	40	-566	-676	-1,303	-21	-2,527	-\$379,052,100
E20							
Beijing	200	-1,671	-1,583	-4,894	-67	-8,015	-\$1,202,226,527
Delhi	156	-1,967	-1,357	-4,286	-40	-7,494	-\$1,124,045,017
Mexico City	401	-2,767	-1,521	-7,775	-182	-11,843	-\$1,776,517,781
Seoul	106	-638	-1,259	-3,537	-35	-5,363	-\$804,397,713
Tokyo	106	-828	-1,486	-4,918	-30	-7,155	-\$1,073,306,075

Note: Negative values indicate that the change to ethanol fuel will increase the years of potential life lost.

Cancer treatment incurs substantial costs of the healthcare system, but these costs are only part of the total costs of cancer. A recent study shows that among national cost in the United States female breast was the cancer site with the highest cost in 2010 (\$16.50 billion) followed by colorectal (\$14.14 billion), lymphoma (\$12.14 billion), lung (\$12.12 billion), and prostate (\$11.85 billion). Of particular interest in our study are lymphocytic and lung cancers [66].

We were not able to identify standardized global data about the individual costs of treatment for cancers, though it is clear that treatment costs vary widely among cancers and countries. Consider leukemia, which has one of the most expensive cancer treatment costs. In New Zealand, total treatment costs for leukemia and non-Hodgkin lymphoma are approximately \$95,000 and \$72,000, respectively [67]. In the United Kingdom, treatment costs for leukemia are approximately \$70,000 (£43,109) [68].

Treatment costs are typically higher in the US, where treatment costs for the last year of life alone are approximately \$195,000 [69]. Data from the National Cancer Institute shows Last Year of Life treatment costs alone for leukemia total \$195,196 (year 2010 basis). Treatment for acute myeloid leukemia involving stem cell transplant and chemotherapy costs more than \$540,000, on average [70]. Treatment cost for lung cancers also vary widely and can approximate those of leukemia especially during the initial treatment phase after diagnosis (often assessed separately relative to continuing care and last year of life phase of care) [71]. Given that the pollutants considered in this study predominantly cause lymphohematopoietic and lung cancers, and that treatment costs in developing countries are likely low relative to costs in the US, we assumed that each cancer case required \$70,000 in treatment costs.

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Ambient concentrations of acetaldehyde are estimated to increase with the transition to ethanol fuels, thus additional cancers and additional treatment costs are expected (see table below). For all other pollutants, the transition to ethanol fuels is predicted to reduce ambient concentrations and the number of excess cancers, and thus save treatment costs relative to continued use of gasoline. In all cities, the transition to ethanol fuels is estimated to save millions of dollars in cancer treatment costs to the healthcare system. For example, using E10 in Mexico City will likely decrease health care cost by \$23 million across the studied air toxins.

Table 45. Change in cancer treatment costs (thousands of dollars) to the healthcare system by pollutant.

		Acetaldehyde	Benzene	Polycyclics/ Benzo[a]pyrene	1,3- Butadiene	Formaldehyde
	E10 Fuel					
	Beijing	\$367,056	-\$5,532,297	-\$2,145,093	-\$6,854,602	-\$231,735
	Delhi	\$272,476	-\$6,701,673	-\$4,185,756	-\$7,544,755	-\$151,757
	Mexico City	\$738,203	-\$8,622,903	-\$3,047,558	-\$9,993,893	-\$661,731
	Seoul	\$204,229	-\$2,375,488	-\$2,821,579	-\$5,848,254	-\$98,195
	Tokyo	\$192,256	-\$2,759,586	-\$2,976,347	-\$5,358,432	-\$102,630
		E20				
	Beijing	\$959,188	-\$8,140,585	-\$6,971,273	-\$20,120,556	-\$320,442
	Delhi	\$749,673	-\$9,582,473	-\$5,974,581	-\$17,621,264	-\$193,124
	Mexico City	\$1,927,411	-\$13,481,065	-\$6,696,530	-\$31,968,450	-\$872,589
	Seoul	\$510,147	-\$3,107,325	-\$5,543,671	-\$14,541,445	-\$169,236
	Tokyo	\$510,728	-\$4,033,351	-\$6,540,055	-\$20,221,907	-\$144,726

Note: Negative values indicate a savings in healthcare costs.

Non-Cancer Outcomes

Components of vehicle exhaust contribute to a variety of non-cancer health outcomes. We considered two agents, PM and CO, as emissions of these were part of our mass emissions assessment.

The PM concentrations estimated in this analysis are specific to gasoline vehicles, and thus represent only one of many sources of PM in urban areas. Furthermore, emissions savings from ethanol blends in this study are only associated with the increasing share of gasoline direct injection engines as outlined in previous chapters. During the last 3 years of the study horizon when GDI engines are the dominant power train we show that the introduction of E20 fuels in particular could yield savings in heart failure cases and percent reductions in heart failure from gasoline related PM emissions.

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Table 46: Particulate Matter Change in Heart Failure Cases

	Change in Number of Heart Failure Cases (% Change) for PM
Beijing	-8.8 (-11%)
Delhi	-11.2 (-6.1%)
Mexico City	-2.8 (-4.9%)
Seoul	-4.5 (-7.7%)
Tokyo	-7.5 (-6)

Ambient PM concentrations change from day-to-day, and these acute exposures have also been associated with a variety of adverse health outcomes, such a heart failure, but these exposure-response relationships have not been considered in this analysis because the models predict annual average exposures, rather than daily exposures [58].

Exposure CO causes acute intoxication, which can result in death. From 1968 to 1998 the crude death rate from unintentional motor vehicle-related CO poisoning decreased from 3.86 per 1 million person-years to 0.88 per 1 million person years, with the reduction attributed, in part, to reduction in CO emissions from motor vehicles [72]. From these data, we determined that 1.8 deaths per year are associated with the emission of 1 g CO per mile. In this study, we estimated CO emission reduced by 0.1-0.2 g/mile with the use E10 fuel and 0.4-0.9 g/mile with the use of E20 fuel relative to continued use of gasoline. These reductions would be associated with preventing 0-2 deaths annually, in each city.

14.2 Summary of the Health Impact Assessment

This chapter of the 5 Cities Study assessed the health impact of ethanol blended gasoline. The introduction of ethanol fuels was estimated to yield a net reduction of approximately 200-300 cancers per city, associated with several of the key pollutants in vehicle exhaust relative to continued use in gasoline, and varying among cities and between ethanol fuel blends. Avoiding these cancers will save several thousand years of potential life lost in each city and an additional tens of millions of dollars of direct healthcare costs for cancer treatment.

The impact of cancer, however, is much greater than these metrics, as cancer adversely impacts the quality of life, can lead to loss of income, and devastates families. For example, in the US, a person-year of life lost has been valued at \$150,000 which leads our assessment to show several hundred million dollars of savings from ethanol blends [73].

For context, other regulatory actions have been taken to prevent numbers of cancers that seem modest relative to the total burden of disease. For example, in the reduction of the Permissible Exposure Limit for 1,3-butadiene in the United States to 1 ppm was estimated by the Occupational Safety and Health Administration to avoid 59 cancers among approximately 9000 exposed workers over a working lifetime of 45 years, or 1.3 cancers per year [74]. Costs to employers to comply with the new 1,3-butadiene standard was estimated to be \$2.9 million in 1996 dollars annually, or approximately \$2.3 million per cancer avoided per year. Similarly, the reduction in the Permissible Exposure Limit for benzene from 10 ppm to 1 ppm was estimated

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by the Occupational Safety and Health Administration to avoid 326 deaths from leukemia and other lymphohematopoietic cancers over 45 years, or 7.2 cancers per year; a reduction of similar magnitude to the presented ethanol blended gasoline efforts. [75]. Costs to employers to comply with the new benzene standard was estimated to be \$24 million in 1986 dollars annually, or \$3.3 million per cancer avoided per year.

The health benefit of transitioning to ethanol fuels in these five cities is quantifiable and significant relative to the total burden of disease within the context that gasoline vehicle exhaust is one of many contributors to air pollution. The results of the study suggest that transition to ethanol fuels will benefit public health.

15 Update: Korea Gasoline Resampling

Our original fuel samples for Seoul did not show any MTBE content in the fuel. We learned that only a relatively small supply that may not be representative of fuels sold into the Seoul market may in fact not contain MTBE. Therefore, we resampled three gasoline stations and the resampled stations showed MTBE content in their fuel ranging from 5.4 vol % to 11.6 vol % with a mean of 10 vol%. Directionally, the higher MTBE content in the sampled fuel will reduce the tailpipe emissions savings expected from ethanol blends but increase the GHG emissions savings. This is due to the fact that ethanol will mostly substitute for MTBE in the finished fuel.

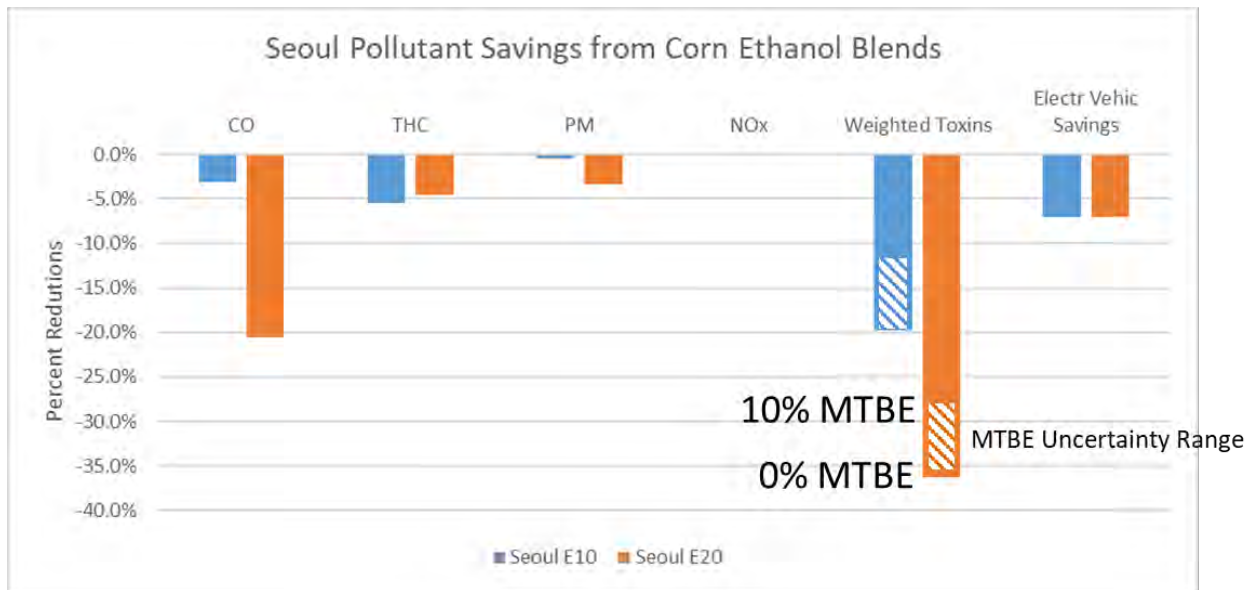


Figure 34: Tailpipe Emissions Adjustments for Seoul

The updated GHG emissions savings reflecting 10% MTBE are show below.

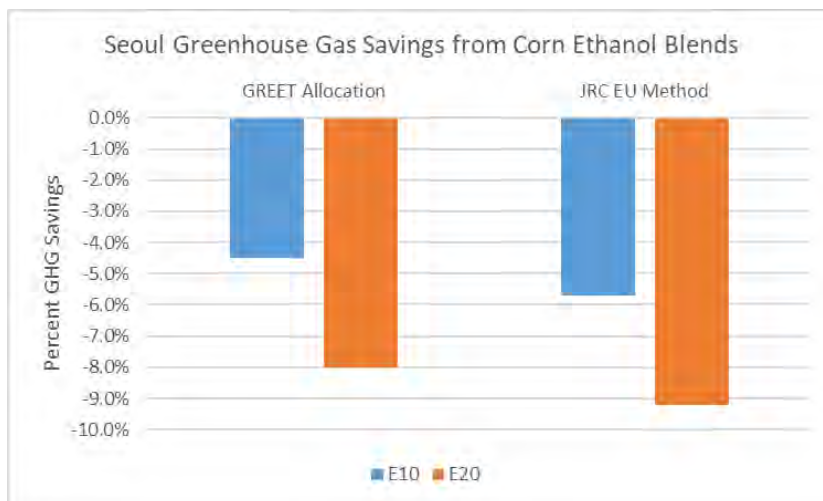


Figure 35: GHG Emissions Adjustments with 10% MTBE for Seoul

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Appendix A: Emissions Standards by City

Table 47: Emissions Standards Beijing

	Beijing				
	Exhaust Emission Factors (g/km)				
Year	CO	THC	NOx	PM	HC Evap
1996	2.3	0.6	0.37	0.001563	2.05
1997	2.3	0.6	0.37	0.001563	2.05
1998	2.3	0.4	0.57	0.001563	2.05
1999	2.3	0.25	0.25	0.001563	2.05
2000	2.3	0.25	0.25	0.001563	2.05
2001	2.3	0.25	0.25	0.001563	2.05
2002	2.3	0.25	0.25	0.001563	2.05
2003	2.3	0.25	0.25	0.001563	2.05
2004	2.3	0.25	0.25	0.001563	2.05
2005	2.3	0.25	0.25	0.001563	2.05
2006	2.3	0.2	0.15	0.001563	2.05
2007	2.3	0.2	0.15	0.001563	2.05
2008	2.3	0.2	0.15	0.001563	2.05
2009	2.3	0.1	0.08	0.001563	0.65
2010	1	0.1	0.08	0.001563	0.65
2011	1	0.1	0.08	0.001563	0.65
2012	1	0.1	0.08	0.001563	0.65
2013	1	0.1	0.06	0.001563	0.65
2014	1	0.1	0.06	0.001563	0.65
2015	1	0.1	0.06	0.001563	0.55
2016	1	0.1	0.06	0.001563	0.55
2017	1	0.1	0.06	0.00125	0.55
2018	0.7	0.1	0.06	0.00125	0.40
2019	0.7	0.1	0.06	0.00125	0.40
2020	0.7	0.1	0.06	0.00125	0.40
2021	0.7	0.1	0.06	0.000938	0.40
2022	0.7	0.1	0.06	0.000938	0.40
2023	0.7	0.1	0.06	0.000938	0.40
2024	0.7	0.1	0.06	0.000938	0.40
2025	0.7	0.1	0.06	0.000938	0.40
2026	0.7	0.1	0.06	0.000938	0.40
2027	0.7	0.1	0.06	0.000938	0.40

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Table 48: Emissions Standards Mexico City

	Mexico				
	Exhaust Emission Factors (g/km)				
Year	CO	THC	NOx	PM	HC Evap
1996	2.11	0.41	1.025	0.001563	2.05
1997	2.11	0.41	1.025	0.001563	2.05
1998	2.11	0.41	1.025	0.001563	2.05
1999	2.11	0.41	1.025	0.001563	2.05
2000	2.11	0.41	1.025	0.001563	2.05
2001	2.11	0.156	0.25	0.001563	2.05
2002	2.11	0.156	0.25	0.001563	2.05
2003	2.11	0.156	0.25	0.001563	2.05
2004	2.11	0.156	0.25	0.001563	2.05
2005	2.11	0.156	0.25	0.001563	2.05
2006	2.11	0.156	0.25	0.001563	2.05
2007	2.11	0.099	0.25	0.001563	0.55
2008	2.11	0.099	0.25	0.001563	0.55
2009	2.11	0.099	0.25	0.001563	0.55
2010	2.11	0.099	0.25	0.001563	0.55
2011	1	0.047	0.068	0.001563	0.55
2012	1	0.047	0.068	0.001563	0.55
2013	1	0.047	0.068	0.001563	0.55
2014	1	0.047	0.068	0.001563	0.55
2015	1	0.047	0.068	0.001563	0.55
2016	1	0.047	0.068	0.001563	0.40
2017	1	0.047	0.068	0.00125	0.40
2018	1	0.047	0.068	0.00125	0.40
2019	1	0.047	0.068	0.00125	0.40
2020	1	0.047	0.068	0.00125	0.40
2021	1	0.047	0.068	0.000938	0.40
2022	1	0.047	0.068	0.000938	0.40
2023	1	0.047	0.068	0.000938	0.40
2024	1	0.047	0.068	0.000938	0.40
2025	1	0.047	0.068	0.000938	0.40
2026	1	0.047	0.068	0.000938	0.40
2027	1	0.047	0.068	0.000938	0.40

Impact of Higher Ethanol Blends on Vehicle Emissions

Table 49: Emissions Standards New Delhi

New Delhi				
Exhaust Emission Factors (g/km)				
CO	THC	NOx	PM	HC Evap
5	1.36	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
5	0.35	0.35	0.001563	2.00
2.3	0.2	0.15	0.001563	2.00
2.3	0.2	0.15	0.001563	2.00
2.3	0.2	0.15	0.001563	2.00
2.3	0.2	0.15	0.001563	2.00
2.3	0.2	0.15	0.001563	2.00
1	0.1	0.08	0.001563	2.00
1	0.1	0.08	0.001563	2.00
1	0.1	0.08	0.001563	2.00
1	0.1	0.08	0.001563	2.00
1	0.1	0.08	0.001563	2.00
1	0.1	0.08	0.001563	2.00
1	0.1	0.08	0.001563	2.00
1	0.1	0.08	0.00125	0.40
1	0.1	0.08	0.00125	0.40
1	0.1	0.08	0.00125	0.40
1	0.1	0.06	0.00125	0.40
1	0.1	0.06	0.000938	0.40
1	0.1	0.06	0.000938	0.40
1	0.1	0.06	0.000938	0.40
1	0.1	0.06	0.000938	0.40
1	0.1	0.06	0.000938	0.40
1	0.1	0.06	0.000938	0.40
1	0.1	0.06	0.000938	0.40
1	0.1	0.06	0.000938	0.40

Impact of Higher Ethanol Blends on Vehicle Emissions

Table 50: Emissions Standards Seoul

	Seoul				
	Exhaust Emission Factors (g/km)				
Year	CO	THC	NOx	PM	HC Evap
1996	2.11	0.4	0.25	0.001563	2.00
1997	2.11	0.4	0.25	0.001563	2.00
1998	2.11	0.4	0.25	0.001563	2.00
1999	2.11	0.32	0.25	0.001563	2.00
2000	2.11	0.32	0.25	0.001563	2.00
2001	2.11	0.32	0.25	0.001563	2.00
2002	2.11	0.16	0.25	0.001563	2.00
2003	2.11	0.16	0.25	0.001563	2.00
2004	2.11	0.16	0.25	0.001563	2.00
2005	2.11	0.16	0.25	0.001563	2.00
2006	2.11	0.16	0.25	0.001563	2.00
2007	2.11	0.16	0.25	0.001563	2.00
2008	2.11	0.16	0.25	0.001563	2.00
2009	2.11	0.047	0.031	0.001563	2.00
2010	2.11	0.047	0.031	0.001563	2.00
2011	2.11	0.047	0.031	0.001563	2.00
2012	2.11	0.047	0.031	0.001563	2.00
2013	1	0.047	0.031	0.001563	1.20
2014	1	0.047	0.031	0.001563	1.20
2015	1	0.047	0.031	0.001563	1.20
2016	1	0.047	0.02	0.001563	1.20
2017	1	0.047	0.02	0.00125	1.20
2018	1	0.027	0.02	0.00125	0.95
2019	1	0.027	0.02	0.00125	0.95
2020	1	0.027	0.02	0.00125	0.47
2021	1	0.025	0.01	0.000938	0.47
2022	1	0.01	0.01	0.000938	0.35
2023	1	0.01	0.01	0.000938	0.35
2024	1	0.01	0.01	0.000938	0.35
2025	1	0.01	0.01	0.000938	0.35
2026	1	0.01	0.01	0.000938	0.35
2027	1	0.01	0.01	0.000938	0.35

Impact of Higher Ethanol Blends on Vehicle Emissions

Table 51: Emissions Standards Japan

	Tokyo				
	Exhaust Emission Factors (g/km)				https://ww
Year	CO	THC	NOx	PM	HC Evap
1996	2.1	0.25	0.17	0.001563	2.05
1997	2.1	0.25	0.17	0.001563	2.05
1998	2.1	0.25	0.17	0.001563	2.05
1999	2.1	0.2	0.17	0.001563	2.05
2000	2.1	0.2	0.17	0.001563	2.05
2001	2.1	0.2	0.17	0.001563	2.05
2002	0.63	0.17	0.17	0.001563	2.05
2003	0.63	0.17	0.17	0.001563	2.05
2004	0.63	0.17	0.17	0.001563	2.05
2005	1.15	0.05	0.05	0.001563	2.05
2006	1.15	0.05	0.05	0.001563	0.55
2007	1.15	0.05	0.05	0.001563	0.55
2008	1.15	0.05	0.05	0.001563	0.55
2009	1.15	0.05	0.05	0.001563	0.55
2010	1.15	0.05	0.05	0.001563	0.55
2011	1.15	0.05	0.05	0.001563	0.55
2012	1.15	0.05	0.05	0.001563	0.55
2013	1.15	0.05	0.05	0.001563	0.55
2014	1.15	0.05	0.05	0.001563	0.55
2015	1.15	0.05	0.05	0.001563	0.40
2016	1.15	0.05	0.05	0.001563	0.40
2017	1.15	0.05	0.05	0.00125	0.40
2018	1.15	0.02	0.05	0.00125	0.40
2019	1.15	0.02	0.05	0.00125	0.40
2020	1.15	0.02	0.05	0.00125	0.40
2021	1.15	0.02	0.05	0.000938	0.40
2022	1.15	0.02	0.05	0.000938	0.40
2023	1.15	0.01	0.05	0.000938	0.40
2024	1.15	0.01	0.05	0.000938	0.40
2025	1.15	0.01	0.05	0.000938	0.40
2026	1.15	0.0075	0.008	0.000938	0.40
2027	1.15	0.0075	0.008	0.000938	0.40

Appendix B: iBEAM (2017) Module 1 Interface Summary

The International Biofuels Emissions Analysis Model (iBEAM) was developed to calculate emissions from different air emissions pollutants in major global cities. The model structure allows users to choose from different scenarios or add scenarios that are deemed appropriate. The model structure also provides a structure that can be easily expanded to other cities in the future.

Currently, iBEAM is populated with data for five cities including Beijing, Seoul, Tokyo, New Delhi, and Mexico City.

Input+Output Worksheet – Left Section

- When clicking on the rose-colored cells in this tab a drop down menu appears that enables a selection of the options listed in the table right below that cell.
- Inputs 1a and 1b allow to select the city and ethanol blend of interest.
- Inputs 2a and 2b allow the selection of the end point of EV shares and GDI penetration by 2027.
- Input 3 allows to select between “average” and the more conservative “curve fit” emissions adjustments by vehicle age.
- Input 4 enables advanced users to change the efficiency and assumed evaporative emissions control technology adoption by city.
- Input 5 pertains to greenhouse gas modeling and allows the users to change between models and allocation methods as well as consideration of optional CO₂ recovery at the plant level.
- Finally, a table of the relative potency of toxic air contaminants is provided on this sheet.

Input+Output Worksheet – Right Section

The right section of this tab references and displays the summary findings for the scenarios selected in the left section. It displays the number of projected vehicles, their projected fuel use, the respective fuel economy and vehicle distances travelled. Just below the modeled emissions results are displayed for gasoline, E10, and E20 blends.

Individual City Worksheets

A total of 13 worksheets contain the databases and calculations behind the emissions assessments. The worksheet tabs contain the following information:

<u>Description</u>	<u>Sheet</u>	<u>Protected</u>
Enables Selection of City and Biofuels Emissions Scenario	InputOutput	No
Greenhouse Gas Calculations	GHG	Yes
Emission Calculations for all Cities	EmissCacs	Yes
Vehicle Roll-In Calculations based on Population and Vehicle Retirement	VehMatrix	Yes
Evaporative Emissions Data and Calculations	EVAP	Yes
Ethanol Emissions Factors and Fuel Effects	EthanolFact	Yes
Complex Model Factors and City Specific Blending Results	ComplexFact	Yes
Beijing Vehicle and Gasoline Factors	BV	No
Mexico City Vehicle and Gasoline Factors	MV	No
New Delhi Vehicle and Gasoline Factors	NV	No
Seoul Vehicle Data and Gasoline Factors	SV	No
Tokyo Vehicle Data and Gasoline Factors	TV	No
Graphs and Tables for City to City Comparisons	Standards	No

Appendix C: European Union RED Reference

Note: ISCC is one of the most commonly used certification protocols recognized by the EU



ISCC system update 12 May 2015

Further specifications on the calculation of emission savings from carbon capture and replacement (e_{ccr}), carbon capture and geological storage (e_{ccs}), soil carbon accumulation via improved agricultural management (e_{sca}) and the assignment of emission savings from e_{ccr} , e_{ccs} , e_{sca} and excess electricity (e_{ee}):

According to the Renewable Energy Directive (RED) and the Fuel Quality Directive (FQD), the GHG saving thresholds and GHG emission reduction requirements are increasing. In addition, a GHG quota has been implemented in Germany in January 2015. Therefore, there are strong incentives to conduct actual GHG calculations.

In this context, ISCC wants to highlight the rules on how to take e_{ccr} , e_{ccs} and e_{sca} into account and how to deal with the assignment of emission saving.

1. Emission saving from carbon capture and replacement (e_{ccr}) and from carbon capture and geological storage (e_{ccs}):

Annex V Section C No. 15 of the Directive 28/2009/EC defines this emission saving as follows: „Emission saving from carbon capture and replacement (e_{ccr}) shall be limited to emissions avoided through the capture of CO₂ of which the carbon originates from biomass and which is used to replace fossil-derived CO₂ used in commercial products and services.“

and

“Emission saving from carbon capture and geological storage (e_{ccs}), that have not already been accounted for in e_p , shall be limited to emission avoided through the capture and sequestration of emitted CO₂ directly related to the extraction, transport processing and distribution of fuel.”

The following formula shall be used to calculate e_{ccr} (in g CO₂e per MJ):

$$e_{ccr} \left[\frac{g \text{ CO}_2e}{MJ} \right] = \frac{\text{produced CO}_2[kg] - \text{energy consumed}[MWh] \cdot EF \left[\frac{kg \text{ CO}_2e}{MWh} \right] - \text{input materials} [kg] \cdot EF \left[\frac{kg \text{ CO}_2e}{kg} \right]}{\text{produced quantity of biofuel} [t] \cdot \text{lower heating value biofuel} \left[\frac{MJ}{kg} \right]}$$

The following formula shall be used to calculate e_{ccs} (in g CO₂e per MJ):

$$e_{ccs} \left[\frac{g \text{ CO}_2e}{MJ} \right] = \frac{\text{produced CO}_2[kg] - \text{energy consumed}[MWh] \cdot EF \left[\frac{kg \text{ CO}_2e}{MWh} \right] - \text{input materials} [kg] \cdot EF \left[\frac{kg \text{ CO}_2e}{kg} \right]}{\text{produced quantity of biofuel} [t] \cdot \text{lower heating value biofuel} \left[\frac{MJ}{kg} \right]}$$

For the calculation of e_{ccr} and e_{ccs} the following information needs to be provided and verified:

- Produced quantity of biofuel
- Quantity of biogenic CO₂ captured during the biofuel production process
- Quantity of energy consumed for the capturing and the processing of CO₂ (e.g. compression and liquefaction)
- Other input materials consumed in the process of CO₂ capture and processing
- GHG emission factor and its source for all inputs

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e_{ccr} can only be taken into account if it can be proven that the CO₂ replaces fossil-derived CO₂ used in commercial products and services. One option to proof a commercial use of the bio-genic CO₂ is by showing that the CO₂ has been commercially marketed or used directly.

e_{ccs} can only be taken into account if there are valid evidences that CO₂ was effectively captured and safely stored. If the CO₂ is directly stored it should be verified whether the storage is in good condition, leakages are nonexistent and the existing storage guarantees that the leakage does not exceed the current state of technology. If the CO₂ is sold for storage, one option to proof storage is to provide contracts and invoices of a professional recognized storage company.

2. Emission saving from soil carbon accumulation via improved agricultural management (e_{sca}):

Improved agricultural management refers to practices that lead to an increase in soil carbon. According to the Communication from the European Commission (2010/C160/02), this can include practices such as:

- Shifting to reduced or zero-tillage
- Improved crop rotations and/or cover crops, including crop residue management
- Improved fertilizer or manure management
- Use of soil improver (e.g. compost)

Emission savings from such improvements can be taken into account if evidence is provided that the above-mentioned practices have been adopted after January 2008. Furthermore, it must be verified that they are implemented in best practice so that an increase in soil carbon can be expected over the period in which the raw materials concerned were cultivated. Measurement of soil carbon could also serve as additional evidence.

For calculating e_{sca} , the formula as indicated in point 7, Annex V of the RED and as further specified in Annex II of the Communication from the Commission (2010/C160/02) shall be used:

$$e_{sca} \left[\frac{g \text{ CO}_2 e}{kg} \right] = \frac{(CS_R - CS_A) \left[\frac{g \text{ C}}{ha * yr} \right] * 3.664 \left[\frac{g \text{ CO}_2}{g \text{ C}} \right]}{\text{period of cultivation of crops concerned [yrs]} * P \left[\frac{kg}{ha} \right]}$$

Where:

- e_{sca} Annualized GHG emissions from carbon stock changes due to improved agricultural management
- CS_R Carbon stock per unit area associated with the reference land use (January 2008 or 20 years before the raw material was obtained, whichever was the later)
- CS_A Carbon stock per unit area associated with the actual land use (The estimated stock per unit area after 20 years or when the crop reaches maturity, whichever the earlier)
- P Productivity of the crop

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The methodology is based on the IPCC methodology. The further procedure of calculating CS_R and CS_A is explained within the Commission Decision on guidelines for calculating land carbon stocks (Commission Decision of June 2010 on guidelines for the calculation of land carbon stocks for the purpose of Annex V to Directive 2009/28/EC (2010/335/EU). Brussels. 2010).

3. Assignment of emission saving from e_{ccr} , e_{ccs} , e_{sca} , and e_{ee}

The balancing period of the emission saving has to be the same as the GHG balancing period for calculating the overall emissions of the relevant product. An assignment of emission saving from carbon capture and storage, carbon capture and replacement, soil carbon accumulation or excess electricity to individual batches or specific time periods is not allowed. Emission savings are 100% assigned to the main product.

In the latest update of the ISCC procedures these aspects and others in the context of actual GHG calculations have already been incorporated in more detail (see ISCC system update from 24/03/2015 archived in the client section of the ISCC website).

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Cancer Reductions from the Use of High-Octane Ethanol-Blended Gasoline with a Focus on Toxic Air Compounds

Prepared by: Steffen Mueller, PhD, Principal Economist,
University of Illinois at Chicago Energy Resources
Center

Prepared for: National Corn Growers Association

August 2019

This Study was conducted with substantial in-kind support from The Hormel Institute (THI), The University of Minnesota (UMN), and Oak Ridge National Laboratory (ORNL). ORNL supplied particulate filters from prior fuel economy and emissions tests to THI. THI prepared the samples for further analysis in the UMN gas chromatograph/mass spectrometer. O'Shea Environmental conducted the MOVES2014b and Atmospheric Dispersion Modeling.

Funding was provided by The Hormel Foundation, the National Corn Growers Association, the Illinois Corn Marketing Board, and the Indiana Corn Marketing Board.

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Summary

This study lead by the University of Illinois at Chicago Energy Resources Center assesses the cancer reductions from the use of high-octane ethanol-blended gasoline with a focus on toxic air compounds. The present study follows a case study published by the United States Environmental Protection Agency (EPA) in 2011 for benzene-related cancer reductions resulting from the Clean Air Act, albeit with an updated model structure. The focus on toxic air compounds is based on the well-documented substitution and dilution effect of ethanol when blended with gasoline.

We combine pollutant vehicle emissions factor data for gasoline without ethanol (E0) from the MOVES2014b model which was parameterized for the local Chicago area with EPA's CAL3QHC air quality model to predict pollutant concentrations near highways. The resulting toxic air compound concentrations are further adjusted to reflect emissions reductions for high-octane fuels blended with twenty-five percent ethanol (E25).

The emissions factors used in this adjustment were developed from the scientific literature but also from recent vehicle tests conducted by Oak Ridge National Laboratory (ORNL): We obtained the particulate filters from these vehicle emissions tests at ORNL and collaborated with the The Hormel Institute-University of Minnesota-Mayo Clinic (THI) to analyze them in their gas chromatography/mass spectrometry unit. This closed a thin data gap in the scientific literature for a subset of air toxins called polycyclic aromatic hydrocarbons (PAHs). The toxic air compound concentrations reductions document for E25 in this effort where applied to the concentrations for E0 and then converted into a reduction in cancer cases using inhalation unit risk factors. Applying published values of a statistical life resulted in total avoided monetary damages.

Using data from this limited geographic area the study attempts to estimate an upper bound of cancer-related mortality impacts from toxic air compounds on a national level. Given the thin datasets on high octane fuel vehicle emissions studies and modeling limitations this number serves as an approximation of the air toxins health impacts from the use of high octane E25 fuels with clearly understood uncertainties. Besides cancer-related mortalities, toxic air compounds also have morbidity impacts which are not quantified.

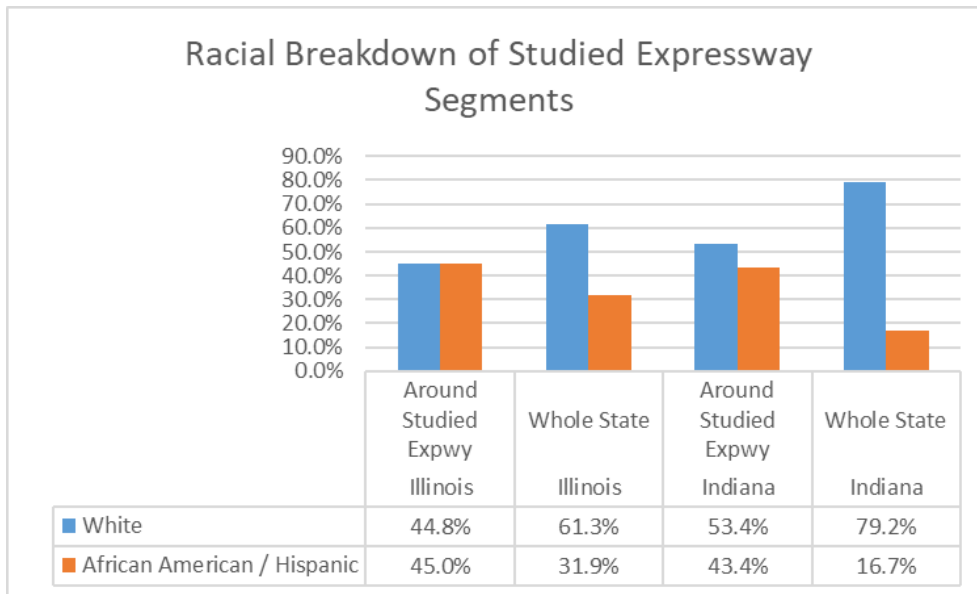
The study finds that for the 1.87 million people living next to the 500 miles of major expressways in the Chicago/NW Indiana region we expect a reduction of 9 lifetime cancer cases with a total lifetime savings in monetary damages of \$81 million. However, we only assessed cancer cases for selected toxic air compounds, exposed to a fraction (0.6 percent) of the US population. The total urban share of the US population is currently cited at 80.7 percent which would mean that 264 million of the current 327 million people in this country live in urban clusters. If we view our results as a first, approximate calibration of how urban areas are affected by air toxins then the extrapolation of this data would result in an upper bound cancer reduction for the studied toxic air compounds of 1,256 cases and avoided lifetime monetary damages of \$11.4 billion.

Summary of Health Impact and First Order Extrapolation

Cancer Case Reductions Chicago Major Expressway Area	9
Affected Population Chicago Major Expressway Area	1,873,456
Value of Statistical Life (VSL)	\$9,100,000
Monetary Damages Avoided Chicago Major Expressways Area	\$81,076,048
Urban Share of US Population	81%
US Population	327,200,000
US Urban Population	264,050,400
Upper Bound Extrapolation of Results	
Cancer Cases	1,256
Monetary Damages Avoided	\$11,427,096,739

Moreover, for the Chicago/NW Indiana region a significant upward adjustment can also be justified. With 9.5 million people living in the Chicago Metro area and many along other major roadways (in addition to the 1.87 million studied) the assessed cancer cases will also likely be a multiple of our selected modeling subset.

Importantly, the present study also documents that the share of minority groups living within the vicinity of polluting expressways is much higher than their respective share in each studied state (Indiana and Illinois). This means that the derived cancer reductions from ethanol-blended high-octane gasoline will likely over-proportionally benefit minority groups.



Racial Breakout Between State Totals and Studied Area

Introduction

The University of Illinois at Chicago Energy Resources Center has conducted a study to assess toxic air compound related cancer reductions from the use of high octane ethanol blended gasoline. The geographic focus of the study is along 500 miles of expressway segments in the Chicago and Northwest Indiana road corridor. Using data from this limited geographic area the study attempts to estimate an upper bound of health impacts on a national level. Given the thin datasets on high octane fuel vehicle emissions studies and modeling limitations this number serves as an approximation of the air toxins health impacts from the use of high-octane E25 fuels with clearly understood uncertainties.

Methodologically, the present study follows an EPA developed case study of the benefits of the Clean Air Act on benzene emissions in the Houston area but with newly developed, updated models.¹ The purpose of the EPA case study was to “demonstrate a methodology that could be used to generate human health benefits from the US Clean Air Act in an urban setting.”

EPA found that over a 30-year study period “the change in benzene-related population risk due to the 1990 CAAA programs would be equivalent to a total of four cases of leukemia in the Houston area” (see Appendix A). EPA states:

“Although the actual benefit results appear modest, we note that leukemia is a rare disease with a low baseline rate among the population - for people under 50, the baseline risk in the study area was generally less than 5 in 100,000. Therefore, even significant percentage reductions in the baseline leukemia mortality rate may translate to relatively small numbers of avoided cases. We also note that the cases avoided are associated with only three U.S. counties containing just over one percent of the total U.S. population. We would expect significantly higher numbers of leukemia cases avoided when looking nationally at benzene reductions.”

This EPA case study was chosen as a model because it quantifies the health benefits of a selected compound. In a similar way, ethanol adjusts the emissions profile of several, particularly carcinogenic toxic air compounds and following the EPA benzene modeling exercise therefore allows us to identify those benefits in a proven framework.

¹ https://www.epa.gov/sites/production/files/2015-07/documents/812caaa_benzene_houston_final_report_july_2009.pdf

Also detailed in: The Benefits and Costs of the Clean Air Act from 1990 to 2020; Final Report – Rev. A ; U.S. Environmental Protection Agency Office of Air and Radiation; April 2011)

Key Air Emissions Compounds Affected by Ethanol Blends

Gasoline contains a large amount of aromatic hydrocarbons that are added to gasoline because they have relatively high octane values and therefore serve as anti-knock agents in vehicle engines. Some aromatics are toxic compounds. Ethanol also has a high octane value and contains no aromatic compounds. It therefore substitutes and dilutes aromatics in gasoline. Moreover, ethanol also alters the distillation curve resulting in an adjustment of the distillation properties of the fuel with, for example a higher volume fraction of the fuel distilled at 200 degrees Fahrenheit. This effect further reduces the formation of toxic emissions in a vehicle.

Some of the most toxic air compounds from vehicle emissions include benzene, 1,3 butadiene, formaldehyde, acetaldehyde and a group of compounds called polycyclic aromatic hydrocarbons (PAHs). Some of these compounds are either in the vapor phase (benzene, 1,3 butadiene, formaldehyde, acetaldehyde) or the particulate phase. In general, PAHs with two or three benzene rings existed in the vapor phase, whereas PAHs with more than five rings were observed mainly in the particulate phase.² Benzo[a]pyrene, one of the most carcinogenic PAHs from vehicle exhaust has 5 fused benzene rings and is predominantly in the particulate phase. PAHs in the particulate phase are mostly bound to PM 2.5 and the ultrafine fraction of the airborne particulates that are reportedly known for their higher health risk.

The health impact of inhaling the considered toxic air compounds is summarized below:³

A) Emissions compounds in the volatile organic group:

Acetaldehyde. Acetaldehyde has been classified as *possibly carcinogenic to humans* (Group 2B) by the International Agency for Research on Cancer. The US EPA classifies acetaldehyde as a probable human carcinogen based on nasal and laryngeal tumors observed in rodents after inhalation exposure.

² Polycyclic Aromatic Hydrocarbons Bound to PM 2.5 in Urban Coimbatore, India with Emphasis on Source Apportionment; R. Mohanraj; ScientificWorldJournal; <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3350969/>

³ Multiple citations for this section:

- US EPA Integrated Risk Information System Chemical Assessment Summary: Acetaldehyde. https://cfpub.epa.gov/ncea/iris/iris_documents/documents/subst/0290_summary.pdf
- R Baan, Y Grosse, K Straif, B Secretan, F El Ghissassi, V Bouvard et al. (2009) A review of human carcinogens – Part F: Chemical agents and related occupations. Lancet 10(120): 1143-1144
- IARC Monographs Volume 100F. Chemical Agents and Related Occupations (2012) Lyon: France
- Toxicological Review of Benzo[a]pyrene: Executive Summary. EPA/635/6-17/003Fc (2017). https://cfpub.epa.gov/ncea/iris/iris_documents/documents/subst/0136_summary.pdf
- IARC Monographs Volume 100F. Chemical Agents and Related Occupations (2012) Lyon: France
- H Checkoway, P Boffetta, DJ Mundt, KA Mundt (2012) Critical review and synthesis of the epidemiologic evidence on formaldehyde exposure and risk of leukemia and other lymphohematopoietic malignancies. Cancer Causes Control 23(11): 1747-1766.
- L Zhang, C Steinmaus, DA Eastmond, XK Xin, MT Smith (2009) Formaldehyde exposure and leukemia: a new meta-analysis and potential mechanisms. Mut Res 681(2-3): 150-168.

Benzene. Benzene has been classified as *carcinogenic to humans* (Group 1) by the International Agency for Research on Cancer. Benzene causes acute myeloid leukemia (acute non-lymphocytic leukemia), and has been positively associated with acute lymphocytic leukemia, chronic lymphocytic leukemia, multiple myeloma and non-Hodgkin lymphoma.

Butadiene. 1,3-butadiene has been classified as *carcinogenic to humans* (Group 1) by the International Agency for Research on Cancer. 1,3-butadiene has been associated with cancer of the haematolymphatic organs, such as leukemia.

Formaldehyde. Formaldehyde has been classified as *carcinogenic to humans* (Group 1) by the International Agency for Research on Cancer. There is scientific consensus that formaldehyde contributes to the development of cancer in the nasal tissues, though the association with lymphohematopoietic cancers is more controversial.

B) Emissions compounds mostly in the particulate phase

Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs): This category is defined as hydrocarbons containing fused aromatic rings. These compounds can be measured in the gaseous phase, particulate phase, or both, depending on properties of the compound, particle characteristics and conditions in the exhaust stream or the atmosphere. Benzopyrene is one of the most carcinogenic PAHs. Appendix B indicates that Fluoranthene, Benzo[a]pyrene, Phenanthrene, Benzofluoranthene, and Chrysene/triphenylene are particularly dominant PAHs in vehicle exhaust.

Benzo[a]pyrene (BaP). BaP has been classified as *carcinogenic to humans* (Group 1) by the International Agency for Research on Cancer. The basis for this classification is a clear mechanism of genotoxicity that impacts lung tumors, though epidemiologic studies have observed increased lung and skin cancer risks. Animal studies have observed cancers at many locations after exposure to BaP in mixtures through multiple routes.

BaP is one of many polycyclic aromatic hydrocarbons (PAHs) emitted in vehicle exhaust, many of which are thought to be carcinogenic. For this analysis, BaP is used as an indicator of carcinogenic risk from PAHs because it is the most potent of the PAHs, and has been found to dominate the cancer risk posed by PAHs emitted by gasoline vehicles.

Many additional pollutants in vehicle exhaust adversely impact health, or are formed from vehicle emissions, but are not specifically quantified in this study.

Emissions Estimation

We employed the following modeling approach: In a first step the EPA MOVES2014b model was used to model emissions for gasoline without ethanol (E0) for the Chicago metro area and Northwest Indiana (Chicago-NWI) Expressway segments. From these model runs we extracted the resulting toxic air compound emissions rates in mass of emissions per distance driven (milligram/mile). In a next step the mass emissions were converted into concentrations using the CAL3QHC model for the Chicago-NWI expressway segments. CAL3QHC is an air quality model based on the CALINE3 model which can be used to predict the concentrations of select criteria pollutants and other user-defined inert pollutants near highways.⁴ Given source strength, meteorology and site geometry, the model can predict pollutant concentrations for receptors located within 500 meters of the roadway. Source strength is also a function of traffic totals.

The geographic area for the CAL3QHC parameterization is shown in Figure 1. The expressway segments cover a total of 500 miles bound by the Chicago suburb of Elgin in the North, Aurora to the West, South Bend, Indiana in the East, and Crown Point, Indiana in the South. The map below highlights the studied expressway segments and shows the approximate receptor distances from the road centerlines. For this study we divided the expressway system into 44 individual segments (see Appendix C for segment and traffic details). A sample CAL3QHC map for two of the expressway segments can be found in Appendix D. Using ARC-GIS we identified that 1.87 million people live within 0.6 miles on each side of these roadways. We also broke down the population by racial groups (see Table 1).

Population with 0.6 Miles of an Interstate in Chicago-land Area

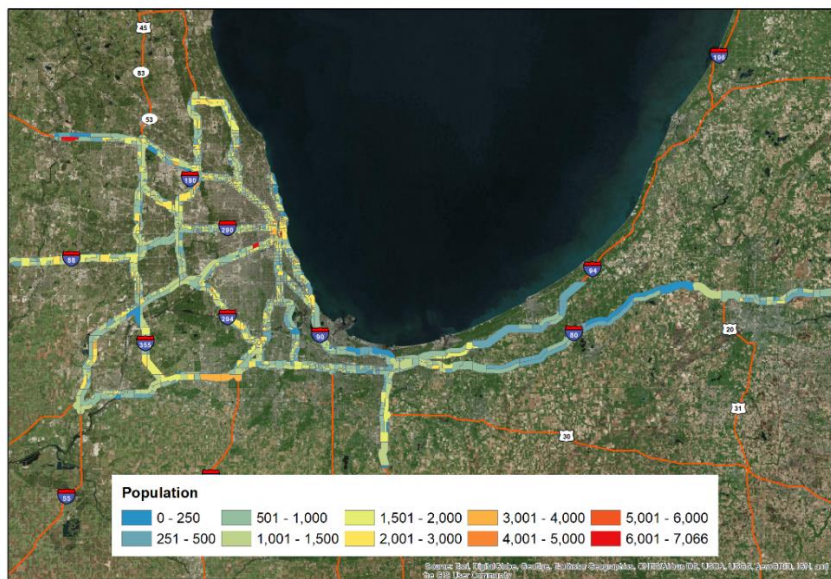


Figure 1: Population Across the Geographic Study Area

⁴EPA Air Quality Dispersion Modeling – Preferred and Recommended Models <https://www.epa.gov/scram/air-quality-dispersion-modeling-preferred-and-recommended-models>

Table 1: Population Characteristics Around Expressway Segments

	Illinois	Indiana	total
Expressway Miles Studied	338.1	162.27	500.37
Population Around Studied Expressways	1,724,877	148,579	1,873,456
White %	44.80%	53.40%	
Hispanic %	16.80%	17.80%	
African American %	28.20%	25.60%	
Statewide Population	12,741,080	6,691,878	
White %	61%	79%	
Hispanic %	17%	7%	
African American %	15%	10%	

The table below shows the derived pollutant concentrations from CAL3QHC averaged for all expressway segments. The spreadsheet model that is posted as supporting information to this report allows to disaggregate these concentrations by expressway segment.

Table 2: Modeled Pollutant Concentrations from E0 Along Chicago NW Indiana Expressways

	ug/m3
	E0
Benzene	0.256844
Formaldehyde	0.055661
1,3-Butadiene	0.031759
Acetaldehyde	0.023572
Acrolein	0.003929
Anthracene gas	0.000163
Anthracene particle	0.000003
Benz(a)anthracene gas	0.000026
Benz(a)anthracene particle	0.000026
Benzo(a)pyrene gas	0.000001
Benzo(a)pyrene particle	0.000064
Benzo(b)fluoranthene gas	0.000020
Benzo(b)fluoranthene particle	0.000031
Benzo(g,h,i)perylene particle	0.000174
Benzo(k)fluoranthene gas	0.000020
Benzo(k)fluoranthene particle	0.000031
Chrysene gas	0.000029
Chrysene particle	0.000022
Fluoranthene gas	0.000273
Fluoranthene particle	0.000010
Indeno(1,2,3,c,d)pyrene gas	0.000000
Indeno(1,2,3,c,d)pyrene particle	0.000065
Phenanthrene gas	0.001043
Phenanthrene particle	0.000010
Pyrene gas	0.000312
Pyrene particle	0.000011

Emissions Adjustments with E25

MOVES2014b is not set up for higher ethanol blends such as E25 so we had to rely on recent vehicle studies. Therefore, a thorough review of the global literature was conducted of emissions adjustments with E10 relative to E0 and studies using E20-E25 fuel blends relative to E0 (or E20/E25 blends relative to E10). We then averaged the emissions reductions for all vehicle studies. Table 3 below shows the result of the literature review.

Table 3: Emissions Adjustments from Ethanol Blends

Study Name	Pollutant	Karavalakis et al., 2012	Bertoa et al., 2015	SAE, 1992	NREL, 2009	Storey et al., 2010	ORNL 2012	Schifter et al., 2011	Graham et al., 2008	Bielaczyc et al., 2013	Knapp et al., 2011	Yao et al., 2011	Czerwinski et al., 2016	Martini et al., 2009	Munoz et al 2016 ES&T	MOVES 2014 Chicago	AVERAGE
Vehicles		1984-2007 Gasoline vehicles (Total 6), One additional 2007 Flex Fuel Vehicle	One Euro 5a flex-fuel light duty vehicle (FFV) equipped with a three way catalyst (TWC) and a turbo	Ford Valencia SI engine	1999-2007 Gasoline vehicles (Total 16)	2007 Pontiac Solstice	19 Tier 2 and 8 Tier 1/NLEV	4 vehicles older than 1992, 17 vehicles between 1993 - 1997 and 9 vehicles	Two 2002 LEV 1 LDT and One 2004 ULEV 1	One Euro V vehicle	1977 - 1994 Gasoline vehicle (Total 11 No.s)	2000 and 2005 passenger cars	new (Euro 5) flex fuel vehicle Volvo V60 (GDI)	Euro IV Ford Focus flexible fuel car	Flex fuel Euro-5 GDI vehicle		
Test cycle		FTP-75	WLTC		LA 92	FTP-75, US06	FTP-75	FTP-75	US06	NEDC	UDDS	FTP-75	WLTC	NEDC	WLTC		
Location		California	Italy	United States	United States	United States	United States	Mexico	Canada	Poland	Alaska	Taiwan	Switzerland	Italy	Switzerland		
E10 Relative to E0	PM					-6.0%				-19.7%					-26.0%		-17.2%
	Benzene	-29.0%	-56.0%	-11.5%				-10.0%	15.0%	-20.8%	-20.1%	-18.0%		17.9%			-14.7%
	1,3-butadiene	-30.0%		-5.8%				6.8%	16.0%		-14.3%			-63.6%			-15.2%
	Formaldehyde	-44.0%	-50.0%	19.3%	-85.0%	-29.0%	-96.0%	0.0%	5.0%	75.0%	-40.0%	11.2%	-17.2%	-5.0%			-19.7%
	Acetaldehyde	16.0%	133.0%	159.0%	9.0%	95.0%	17.0%	19.2%	108.0%	5.9%	#####	20.6%		149.0%			99.6%
	Fluoranthene														-60.9%	-8.6%	-34.7%
	Benzo(a)pyrene*														-27.6%	-8.6%	-18.1%
	Phenanthrene														-71.1%	-8.6%	-39.9%
	Benzo(b)fluoranthene														-81.0%	-8.6%	-44.8%
	Chrysene														-79.8%	-8.6%	-44.2%
E20/25 Relative to E0	PM					-29.0%											-29.0%
	Benzene	-36.0%							26.3%			-28.9%					-12.9%
	1,3-butadiene	-56.0%							0.0%								-28.0%
	Formaldehyde	-36.0%			-85.0%	-31.0%	-81.0%		61.5%			16.6%					-25.8%
	Acetaldehyde	101.0%			131.0%	250.0%	161.0%		200.0%			37.5%					146.8%
	Fluoranthene																-56.7%
	Benzo(a)pyrene*																-52.6%
	Phenanthrene																-82.6%
	Benzo(b)fluoranthene																-87.9%
	Chrysene																-89.4%

Only a couple of vehicle emissions studies have explored the impact of ethanol on PAH emissions. We combined PAH reductions documented in a study by the Swiss Federal Laboratories for Materials Science and Technology for E10 relative to E0 with very recent vehicle testing conducted by Oak Ridge National Laboratory for E25 relative to E10.⁵

Oak Ridge National Laboratory performed fuel economy and emissions tests for a GMC Terrain vehicle. The GMC Terrain vehicle emissions tests are based on 92-93 RON Tier 3 E10 and 99 RON E25 fuels. However, quantification of PAH emissions was not part of the original scope of

⁵ Bioethanol Blending Reduces Nanoparticle, PAH, and Alkyl- and Nitro-PAH Emissions and the Genotoxic Potential of Exhaust from a Gasoline Direct Injection Flex-Fuel Vehicle; Maria Muñoz et al. ; Swiss Federal Laboratories for Materials Science and Technology; Environ. Sci. Technol. 2016, 50, 11853–11861

that study. As part of the present study we obtained the filters and conducted a Gas Chromatography/Mass Spectrometry analysis for those filters at The Hormel Institute-University of Minnesota-Mayo Clinic (THI data).⁶ With that we documented additional emissions reductions for the most prevalent and carcinogenic PAHs from vehicle exhaust from adopting high octane E25 over E10. Table 4 shows that an increase in ethanol blends from E10 to E25 would further reduce selected PAHs by over 30 percent. Combining these results with the emissions reductions show from the Swiss study resulted in the overall expected reductions for E25 over E0 shown for PAHs in Table 3 (highlighted cells in blue).

Table 4: PAH Reduction from THI Analysis

PAH Compound	THI Data E25 over E10 Percent Reduction	Combined Data E25 over E0
Fluoranthene	-33.7%	-56.7%
Benzoapyrene*	-34.6%	-52.6%
Phenanthrene	-39.6%	-82.6%
Benzofluranthene	-36.3%	-87.9%
Chrysene/triphenylene	-47.5%	-89.4%

⁶ <https://www.hi.umn.edu/>

Cancer Outcomes and Impacts

We estimated the impact of ethanol fuels on cancer outcomes as follows: first we calculated the cancer risk for E0 by multiplying the affected population living around our studied expressway segments by inhalation unit risk factors for each pollutant. Then we quantified the percent reductions from E25 adoption (last column in Table 2).

The inhalation unit risk (IUR) factor is a standard metric for estimating excess lifetime cancer risk associated inhalation exposure, and assumes a lifetime of continuous exposure. The IUR factor has units of risk per 1 ug/m³ inhalation exposure. The IUR factors used in this study are shown in the table below, and were derived by the California Office of Environmental Health Hazard Assessment (OEHHA). The OEHHA values were selected because they tend to be more health-conservative than values derived by the US EPA.⁷

For polycyclic aromatic hydrocarbons additional clarification is required. Vehicle exhaust contains a host of PAHs which are more or less carcinogenic. The carcinogenicity of BaP is well studied and toxic equivalency factors to characterize other PAHs have been developed. However, the cancer risk is dominated by BaP for newer and older gasoline cars (see Appendix B). Therefore, we followed the approach described in Bostrom et al:⁸ “in the past, EPA has assessed risks posed by mixtures of PAHs by assuming that all carcinogenic PAHs are as potent as benzo[a]pyrene (B[a]P), one of the most potent PAHs.” We also acknowledge the statement in Bostrom et al that this approach is likely overestimating the risk.

Table 5. Inhalation Unit Risk (IUR) factors for selected carcinogens in vehicle exhaust

Pollutant	IUR Factor (risk per ug/m ³)	Relative Potency
Acetaldehyde	2.7×10^{-6}	0.002
Benzene	2.9×10^{-5}	0.026
Benzo[a]pyrene	1.1×10^{-3}	1.00
1,3-Butadiene	1.7×10^{-4}	0.155
Formaldehyde	6.0×10^{-6}	0.005

The change in the number of cases of cancer estimated to result from the introduction of ethanol fuels relative to the continued use of gasoline is shown in the table below. The emissions for the “possibly known carcinogen in humans” acetaldehyde is estimated to slightly increase with the use of ethanol fuels but the increase is very small relative to the decreases seen for other compounds.

⁷ OEHHA 2009. Air Toxics Hot Spots Program Technical Support Document for Cancer Potencies. Appendix B. Chemical-specific summaries of the information used to derive unit risk and cancer potency values. Updated 2011. <https://oehha.ca.gov/media/downloads/risk-assessment/report/appbraac.pdf>

⁸ Bostrom et al. (2002) Environmental Health Perspectives 110(S3): 451-488.

Table 6: Cancer Cases for E0 and E25 for Selected Pollutants

Pollutant	Cancer Cases	
	E0	E25
Benzene	14.60	12.7
Formaldehyde	0.65	0.5
1,3-Butadiene	10.58	7.6
Acetaldehyde	0.12	(0.1)
Acrolein		-
Anthracene gas	0.35	0.09
Anthracene particle	0.01	0.00
Benz(a)anthracene gas	0.06	0.01
Benz(a)anthracene particle	0.06	0.01
Benzo(a)pyrene gas	0.00	0.00
Benzo(a)pyrene particle	0.14	0.04
Benzo(b)fluoranthene gas	0.04	0.01
Benzo(b)fluoranthene particle	0.07	0.02
Benzo(g,h,i)perylene particle	0.37	0.10
Benzo(k)fluoranthene gas	0.04	0.01
Benzo(k)fluoranthene particle	0.07	0.02
Chrysene gas	0.06	0.02
Chrysene particle	0.05	0.01
Fluoranthene gas	0.59	0.15
Fluoranthene particle	0.02	0.01
Indeno(1,2,3,c,d)pyrene gas	0.00	-
Indeno(1,2,3,c,d)pyrene particle	0.14	0.04
Phenanthrene gas	2.25	0.59
Phenanthrene particle	0.02	0.01
Pyrene gas	0.67	0.18
Pyrene particle	0.02	0.01
	31	22
Difference	9	

As can be seen the adoption of E25 reduces cancers from the selected pollutants by 9 cases. Multiplied by the value of a statistical life of \$9.1 million, which measures the willingness to pay

to reduce the risk of death we derive total savings of \$81 million.^{9;10} Similarly to the EPA Houston Benzene Case Study the results appear, at first glance, modest.

However, we only assessed cancer cases for selected toxic air compounds for the 1.87 million people living next to the major expressways in the Chicago/NW Indiana region, which make up 0.6 percent of the US population. The total urban share of the US population is currently cited at 80.7 percent which would mean that 264 million of the current 327 million people in this country live in urban clusters.^{11;12} The visualization of traffic across urban clusters provided in Appendix E provides further support that the studied area is only a very small subset of the likely total US impact. If we view our results as a first approximate calibration, then the extrapolation of this data would result in an upper bound cancer reduction for the studied toxic air compounds of 1,256 cases and avoided lifetime monetary damages of \$11.4 billion.

Table 7: Summary of Health Impact and First Order Extrapolation

Cancer Case Reductions Chicago Major Expressway Area	9
Affected Population Chicago Major Expressway Area	1,873,456
Value of Statistical Life (VSL)	\$9,100,000
Monetary Damages Avoided Chicago Major Expressways Area	\$81,076,048
Urban Share of US Population	81%
US Population	327,200,000
US Urban Population	264,050,400
Upper Bound Extrapolation of Results	
Cancer Cases	1,256
Monetary Damages Avoided	\$ 11,427,096,739

Similarly, for the Chicago region an upward adjustment can be justified. With 9.5 million people living in the Chicago Metro area and many along other major roadways (in addition to the 1.87 million studied) the assessed cancer cases will also likely be a multiple of our selected modeling subset.¹³

For additional context, other regulatory actions have been taken to prevent numbers of cancers that seem modest relative to the total burden of disease. For example, in the reduction of the Permissible Exposure Limit for 1,3-butadiene in the United States to 1 ppm was estimated by the Occupational Safety and Health Administration to avoid 59 cancers among approximately 9000 exposed workers over a working lifetime of 45 years, or 1.3 cancers per year.¹⁴ Costs to

⁹ Technical Support Document. Estimating the Benefits per Ton of Reducing PM2.5 Precursors from 17 Sector. US EPA Office of Air and Radiation, 2013.

¹⁰ Guidelines for Preparing Economic Analyses; updated May 2014; National Center for Environmental Economics; U.S. Environmental Protection Agency <https://www.epa.gov/sites/production/files/2017-08/documents/ee-0568-50.pdf>

¹¹ https://en.wikipedia.org/wiki/Urbanization_in_the_United_States

¹² https://www.census.gov/history/www/programs/geography/urban_and_rural_areas.html

¹³ https://en.wikipedia.org/wiki/Chicago_metropolitan_area

¹⁴ Occupational Exposure to 1,3-butadiene. Final Rule. Federal Register 61: 56746-56856. (1996).

employers to comply with the new 1,3-butadiene standard was estimated to be \$2.9 million in 1996 dollars annually, or approximately \$2.3 million per cancer avoided per year. Similarly, the reduction in the Permissible Exposure Limit for benzene from 10 ppm to 1 ppm was estimated by the Occupational Safety and Health Administration to avoid 326 deaths from leukemia and other lymphohematopoietic cancers over 45 years, or 7.2 cancers per year; a reduction of similar magnitude to the presented ethanol blended gasoline efforts.¹⁵ Costs to employers to comply with the new benzene standard was estimated to be \$24 million in 1986 dollars annually, or \$3.3 million per cancer avoided per year.

Potential Impact on Racial Inequities

We also assessed the racial breakout within the studied road segment. The map below shows the amount of minorities (for simplification purposes defined as African Americans plus Hispanics) in census tracts within 0.6 miles on each side of these roadways.

Minority Population within 0.6 Miles of an Interstate in Chicago Area

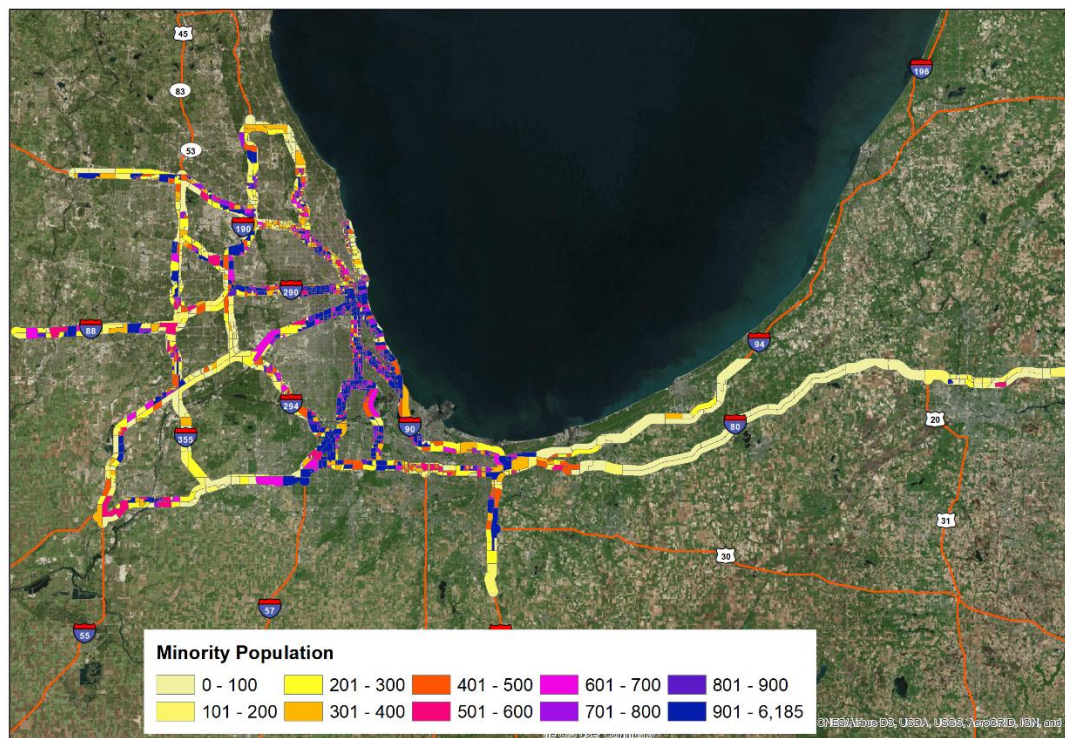


Figure 2: Racial Breakout Across the Study Area

The table and graph summarizes the racial breakouts. As can be seen statewide Illinois is home to 61.3% whites and 31.9% African-American/Hispanics but around the studied expressway segments in Illinois a much higher percentage of 45% is African Americans/Hispanics. Likewise, statewide Indiana is home to 79.2% whites and 16.7% African America/Hispanics but around the studied expressway segments in Indiana a much higher percentage of 43.4% is African

¹⁵ Occupational Exposure to Benzene: Final Rule. Federal Register 52(1786): 34460-34578 (1987)

Americans/Hispanics. This means that the derived cancer reductions from high-octane ethanol blended gasoline will likely over-proportionally benefit minority groups.

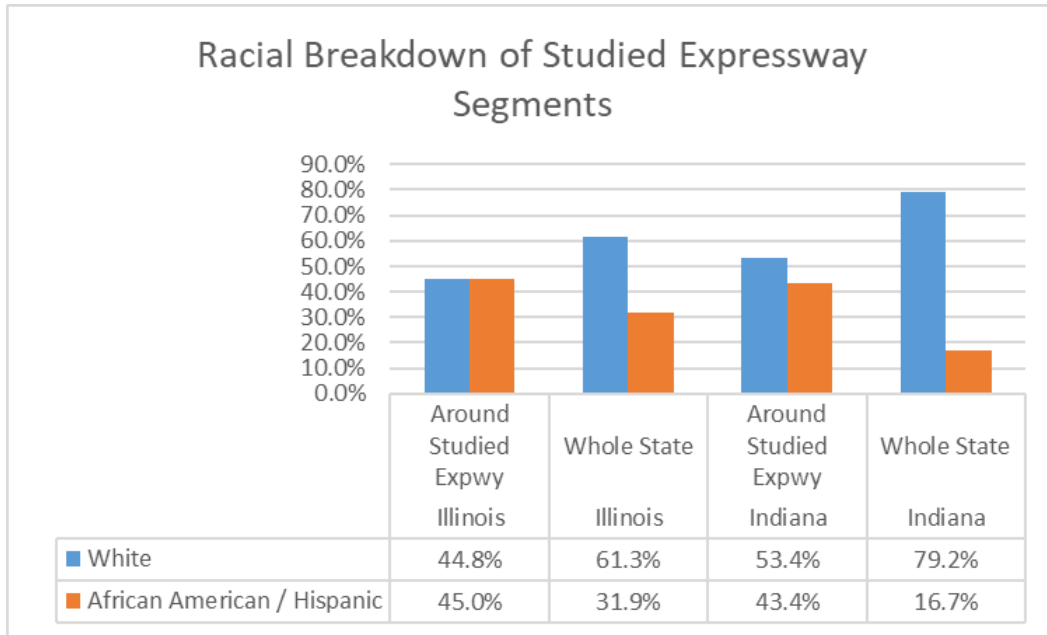



Figure 3: Racial Breakout Between State Totals and Studied Area

Appendix A: EPA Benzene Case Study

THE UNIVERSITY OF ILLINOIS AT CHICAGO



Benzene EPA Carcinogen Case Study

- Houston: 4 annual cases of Leukemia across 3 million people

TABLE 5-9. TOTAL ANNUAL BENEFITS FOR EACH STUDY YEAR FROM CAAA-RELATED CHANGES IN BENZENE EXPOSURE IN THE HOUSTON AREA

	ANNUAL AVOIDED CASES OF LEUKEMIA			TOTAL MONETARY BENEFITS, 1990 TO 2010 (1990 NPV, BILLIONS OF 2006\$, 5% DISCOUNT RATE)		
	AVOIDED FATAL CASES	AVOIDED NON-FATAL CASES	TOTAL AVOIDED CASES	BENEFITS FROM FATAL CASES OF LEUKEMIA	BENEFITS FROM NON-FATAL CASES OF LEUKEMIA	TOTAL BENEFITS
Results by Study Year						
2000	0.03	0.02	0.05	\$0.12	\$0.01 - 0.06	\$0.13 - 0.18
2010	0.09	0.07	0.2	\$0.27	\$0.01 - 0.13	\$0.28 - 0.40
2020	0.2	0.1	0.3	\$0.31	\$0.01 - 0.15	\$0.32 - 0.46
Cumulative Results						
Cumulative Cases Occurring within the Study Period	2	2	4	\$6.7	\$0.32 - 3.3	\$7.0 - 10
Additional Cumulative Cases Occurring after 2020*	1	1	2	\$1.8	\$0.08 - 0.8	\$1.9 - 2.6
Total Cumulative Cases	3	3	6	\$8.5	\$0.40 - 4.1	\$8.9 - 13

* Note: These avoided cases are due to changes in benzene exposure that took place within the study period. However, the cases occurred after 2020 due to lagging effects of these changes on leukemia risks, as described in the text.

Cancer Risk from PAHs for Emissions from Gasoline Vehicles

- Cancer risk is dominated by B[a]P

Table 15. The relative contribution of individual PAHs* to B[a]P equivalents calculated for emissions from gasoline and diesel engines.^b

PAH	TEF ^c	Light-duty vehicles			Heavy-duty trucks	
		Gasoline without catalytic converter	Gasoline + three-way catalytic converter	Diesel light (MKI) + oxidizing catalytic converter	Diesel (MKI) without catalytic converter	Diesel (MKI) without catalytic converter
		% of total B[a]P equivalents				
Anthracene	0.0005	0.2	0.4	0.1	0.3	0.1
Benzo[a]anthracene	0.005	0.3	0.3	0.1	0.4	0.1 ^d
B[a]P	1	77	43	5.3	4.2	7.1^d
Benzo[b]fluoranthene	0.005	4.4	11	1.6	0.8	0.5 ^d
Benzo[ghi]perylene	0.02	1.4	1.4	0.2	0.1 ^d	0.1 ^d
Chrysene/triphenylene	0.03 ^f	1.4	4.3	1.6	0.6	0.4
Fluoranthene	0.05	12	36	88	96	85
Indeno[1,2,3-cd]pyrene	0.1	2.3	1.4	0.5	0.2 ^d	0.7 ^d
Phenanthrene	0.0005	0.5	2.0	1.0	2.6	1.4
Pyrene	0.001	0.3	0.4	1.3	4.4	4.9
Total (pg/km)		8.6	0.7	1.9	4.8	1.4

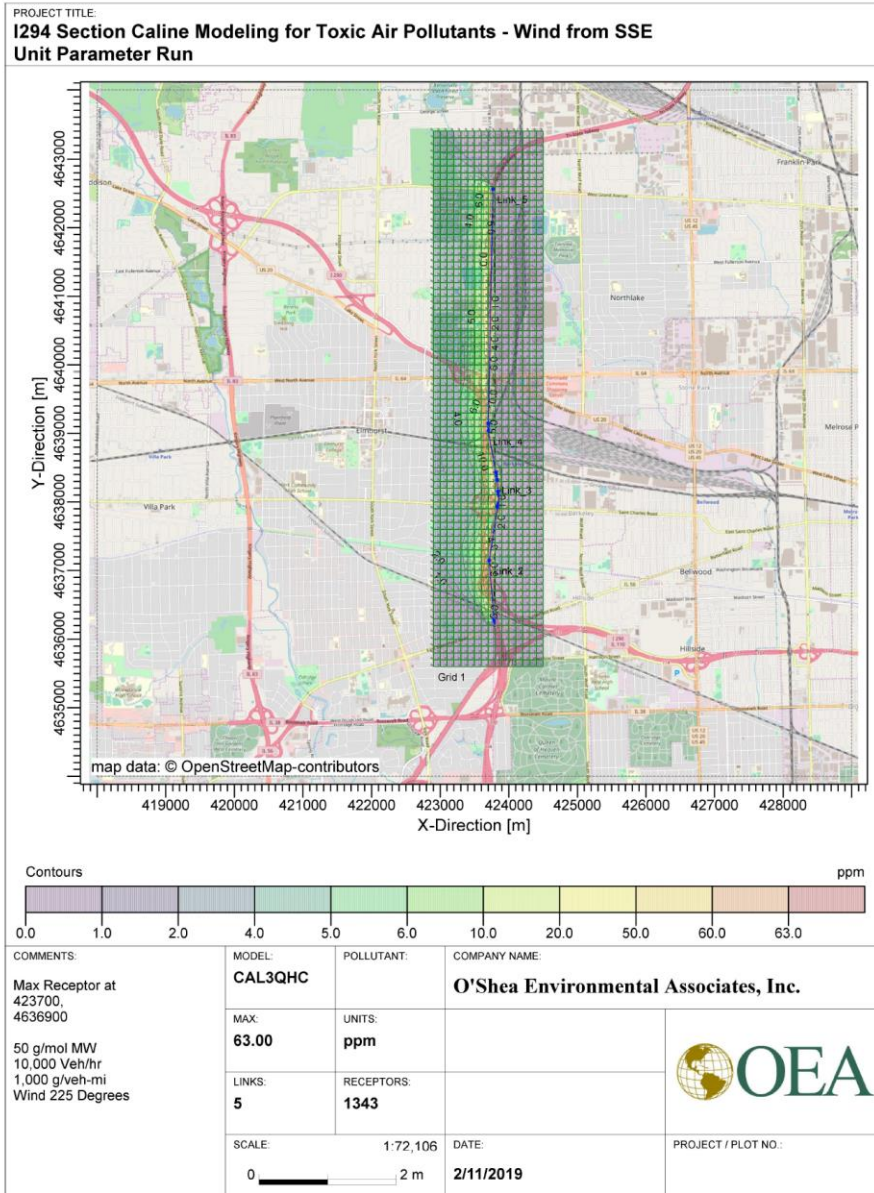
*Note that the sum is calculated for the given individual PAH only, although there are other PAHs present in the emissions that might also contribute to the carcinogenic risk of the emissions. ^bFor concentrations of individual PAHs, see Table 5. ^cData from Larsen and Larsen 1998. ^dConcentration below the detection limit. The detection limit is used for calculations. ^eBelow 0.1%. ^fTEF for chrysene.

Source: Cancer Risk Assessment, Indicators, and Guidelines for Polycyclic Aromatic Hydrocarbons in the Ambient Air
 Carl-Ellis Boström et al; Environmental Health Perspectives • VOLUME 110 | SUPPLEMENT 3 | JUNE 2002

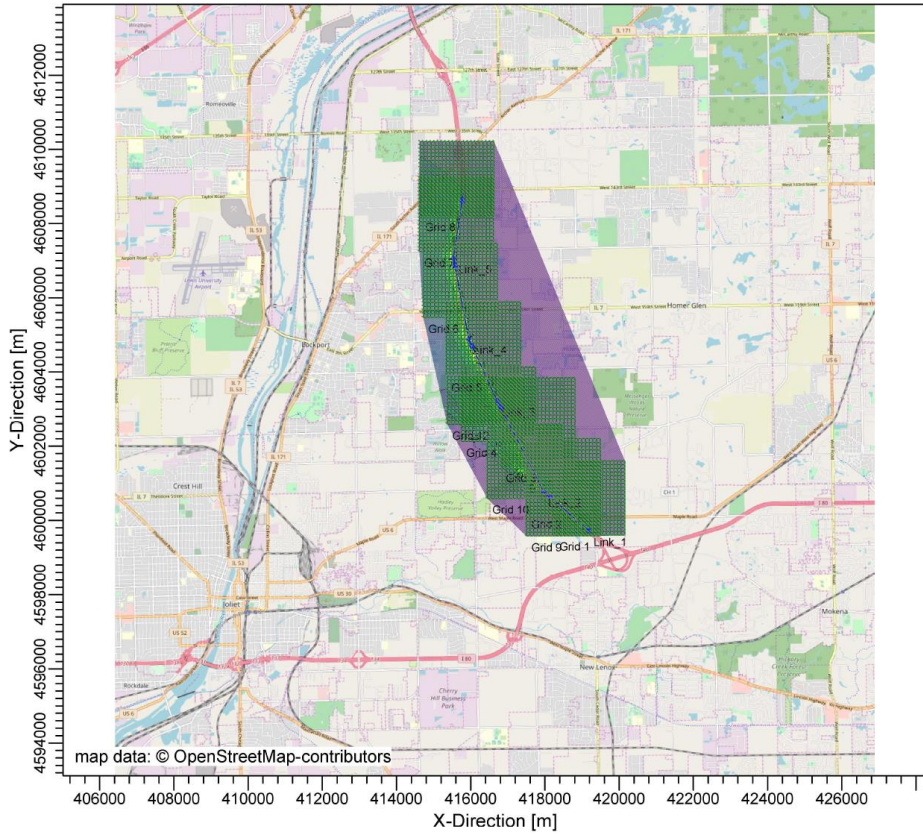
Appendix C: Traffic Totals by Expressway Segment



Highway Name	Map Segment	Average Daily Traffic Totals	Average Hourly Traffic Totals
Stevenson Expressway	I-355 to I-294	155,850	6,494
Stevenson Expressway	I-294 to Dan Ryan I-90 & I94	167,150	6,965
Stevenson Expressway	I-80 to I-355	100,542	4,189
I-57 Expressway	I-80 to Dan Ryan	131,350	5,473
I-80 Expressway	I-355 to I-57	98,800	4,117
I-80 Expressway	I-57 to I294	88,700	3,696
I-80 Expressway	I-55 to I-355	70,200	2,925
Kingery Expressway	I94 to Indiana State Line	149,600	6,233
Dan Ryan Expressway	I-90 Skyway to 95th Street	245,650	10,235
Dan Ryan Expressway	63rd Street to I-55	296,000	12,333
Kennedy Expressway	I-190 from Bessie Coleman to I-90	77,200	3,217
Kennedy Expressway	I-90 from Cumberland to Lawrence	171,250	7,135
Kennedy Expressway	I90/94 from Edens to Randolph	247,800	10,325
Bishop Ford Freeway	Route 394 to Dan Ryan	157,350	6,556
Edens Expressway	Clavey Rd to Kennedy Exp.	139,000	5,792
Eisenhower Expressway	I294 to I90/94	169,650	7,069
I-290 Extension	I-90 to I-290	140,900	5,871
Elgin O'Hare	US 20 to I-290 Thorndale	50,600	2,108
Illinois Route 53	I-90 Jane Addams Memorial Toll. to Thomdale Ave.	140,900	5,871
Veterans Memorial Tollway I-355	I-80 to I-55	73,890	3,079
Veterans Memorial Tollway I-355	I-55 to I-88	129,735	5,406
Veterans Memorial Tollway I-355	I-88 to Army Trail Road	142,010	5,917
Tri-State Tollway I-294	Bishop Ford to 95th Street	150,095	6,254
Tri-State Tollway I-294	95th Street to I-55	155,455	6,477
Tri-State Tollway I-294	I-55 to I-88	168,680	7,028
Tri-State Tollway I-294	I-88 to I-290	167,605	6,984
Tri-State Tollway I-294	I-290 to I-94	141,590	5,900
Reagan Memorial Tollway	I-355 to I-294	144,110	6,005
Reagan Memorial Tollway	Dekalb to I-355	49,280	2,053
Jane Addams Memorial Tollway	Tri State to Rt 53	259,740	10,823
Jane Addams Memorial Tollway	Rt. 53 to Elgin (Randall Rd.)	103,960	4,332
Lake Shore Drive	Hollywood to Balbo	133,650	5,569
Lake Shore Drive	Roosevelt Rd. to Jeffery Blvd.	85,950	3,581
Chicago Skyway	Dan Ryan to Indiana State Line	36,147	1,506
Indiana I-90	Indiana State Line to I-65	36,147	1,506
I-80 Expressway	Indiana State Line to I-65	175,818	7,326
I-80 Expressway	I-65 to Rt. 421	107,523	4,480
I-80 Expressway	Rt. 421 to Rt. 933	110,255	4,594
I-80 Expressway	Rt. 933 to US 35	74,494	3,104
I-94	I-65 to SR 49	70,157	2,923
I-94	SR 49 to US 35	59,008	2,459
I-94	US 35 to Michigan State Line	42,727	1,780
I-65	I-80 to US 30	99,427	4,143
I-65	US 30 South	55,908	2,330

Appendix D: Selected CALINE Runs



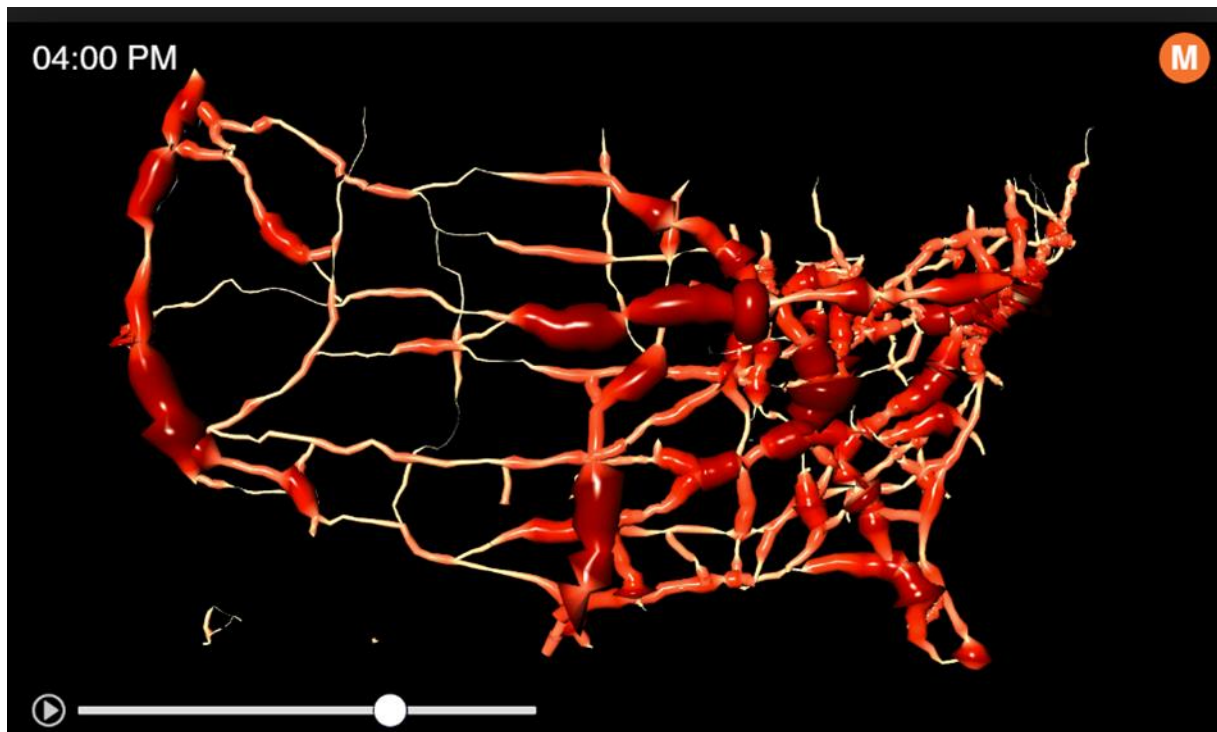
PROJECT TITLE
I355 Section Caline Modeling for Toxic Air Pollutants - Wind from SSE
Unit Parameter Model



<p>COMMENTS: Max Receptor at 417946 4600793 50 g/mol MW 10,000 Veh/hr 1,000 g/veh-mi Wind 135 Degrees</p>				<p>MODEL: CAL3QHC</p>	<p>POLLUTANT: </p>	<p>COMPANY NAME: O'Shea Environmental Associates, Inc.</p>
<p>MAX: 144.20</p>		<p>UNITS: ppm</p>				
<p>LINKS: 5</p>	<p>RECEPTORS: 4767</p>	<p>SCALE: 1:146,347</p> <p>0  5 m</p>		<p>DATE: 2/11/2019</p> <p>PROJECT / PLOT NO.:</p>		

CALRoads View - Lakes Environmental\355\I355\CALRoads View\CookCo_I294_Unit_225Wind\CookCo_I355_Unit_225Wind\CookCo_I355_Unit_135Wind\CookCo_I355_Unit_135Wind.clv

Appendix E: Visualization of US Traffic



Source: Visualized Department of Transportation Data <http://metrocosm.com/map-us-traffic/>

Avoided Mortalities from the Substitution of Ethanol for Aromatics in Gasoline with a Focus on Secondary Particulate Formation

Steffen Mueller, PhD

Principal Economist, University of Illinois at Chicago Energy Resources Center

August 12, 2019

In a previously released paper by this author titled “Cancer Reductions from the Use of High-Octane Ethanol-Blended Gasoline with a Focus on Toxic Air Compounds” we looked at selected toxic air compounds which are known to be carcinogenic and known to be reduced with ethanol blending into gasoline. The selected compounds were either in the volatile or particulate phase and mostly directly emitted from the tailpipe of vehicles. In the present examination we focus on avoided mortalities from the substitution of ethanol for aromatics in gasoline with a focus on secondary particulate formation (see Appendix A for a primer on direct and secondary PM emissions).

The following analysis is principally based on two reports: A publication by authors from the Harvard Risk Center co-authored with the US EPA and EPA’s Fuels Trend Report.

The first paper which is coauthored with US EPA (Stackelberg et al.) describes that secondary organic aerosols (SOAs) are a major contributor to PM_{2.5} with aromatics in gasoline being in turn the most effective precursors to SOAs:¹

“Field studies suggest 10% - 60% of fine particulate matter (PM_{2.5}) is comprised of organic compounds. This material may be directly emitted to the atmosphere (primary) or formed from the gas-phase oxidation of hydrocarbon molecules and subsequent absorption into the condensed phase (secondary). The latter portion, referred to as **secondary organic aerosol (SOA), is a major contributor to the PM_{2.5}**. Evidence is growing that **aromatics in gasoline exhaust are among the most efficient secondary organic matter precursors**. While the relative abundance of primary and secondary organic matter is the subject of ongoing debate, air quality models are continually updated to keep up with the latest scientific knowledge [...]. In the United States, gasoline-powered vehicles are the largest source of aromatic hydrocarbons to the atmosphere.”

Stackelberg et al. also suggest:

“In the United States, gasoline-powered vehicles are the largest source of aromatic hydrocarbons to the atmosphere. Most gasoline formulations consist of approximately 20% aromatic hydrocarbons, which are used in place of lead to boost octane. Therefore, it has been

¹ Public health impacts of secondary particulate formation from aromatic hydrocarbons in gasoline; Katherine von Stackelberg, Jonathan Buonocore, Prakash V Bhave & Joel A Schwartz Environmental Health Volume 12, Article number: 19 (2013) <https://ehjournal.biomedcentral.com/articles/10.1186/1476-069X-12-19#Tab5>



suggested that **removal of aromatics could reduce SOA concentrations and yield a substantial public health benefit.**"

The importance of aromatics to secondary PM2.5 formation is corroborated in a report prepared for the Federal Highway Administration.² Since a reduction in aromatics will lead to a reduction in SOA we look to the EPA Fuel Trends Report (released in November 2017) which shows the decrease in aromatics from the year 2000 was commensurate with an increase in ethanol blending (see Appendix B).³ On page 8 that report states: "Ethanol's high octane value has also allowed refiners to significantly reduce the aromatic content of the gasoline, a trend borne out in the data."

In their paper Stackelberg et al. use a) the EPA SPECIATE and National Emissions Inventory databases to estimate the nationwide proportion of aromatic VOCs attributable to emissions from gasoline vehicles (see Appendix C) and then b) the BenMap Model to quantify the health impact associated with exposures to the change in PM2.5 concentrations attributable to aromatic hydrocarbons. The results show 6,330 premature mortalities (upper range) from exposure to aromatic SOA in gasoline emissions.

The source-by-source breakdown of all aromatic hydrocarbon emissions is provided in the Additional File of the Stackelberg et al. paper: Gasoline-related aromatics emissions (Baseline Year 2005) totaled 2.47 million tons which are shown in that paper to result in 6,330 mortalities from exposure to PM2.5 originating from aromatics. From the EPA Fuel Trends Report we can correlate these emissions in tons and the mortalities with the average aromatics content in fuel for that year of 24.5% (Appendix B). If we assume a linear relationship between aromatics removal and a reduction in premature mortalities then we can calculate that the reduced aromatics from ethanol blending (as stated in the Fuel Trends Report) in 2016 will have resulted in proportionally lower mortalities of 4,986 incidents (see table below).

Table 1: Linear Regression Relating Mortalities to Aromatics Content

	Aromatics vol%	Ethanol vol%	Aromatic VOC (ton/year)	Mortalities (upper bound)	Monetary Damages
2005	24.5	2.23	2,469,970	6,330	\$ 57,603,000,000
2016	19.3	9.57	1,945,731.22	4,986	\$ 45,377,057,143
			Difference	1,344	\$ 12,225,942,857

Multiplying the reduction in mortalities from reduced exposure to PM2.5 originating from aromatic hydrocarbons in gasoline by the value of a statistical life of \$9.1 million (which measures the willingness to pay to reduce the risk of death) we derive total reduced monetary damages attributable to increased

² "The formation of PM2.5 from VOC Precursors is caused when volatile organic gases in secondary organic aerosol (SOA) are oxidized by species such as the hydroxyl radical (OH), ozone (O3), and nitrate (NO3). After oxidation of the VOC, some of the oxidation products have low volatilities and condense on available particles becoming part of the PM. VOCs from the **aromatic group** are the most significant contributor to SOA from anthropogenic sources." Source: William Hodan and William Barnard. "Evaluating the Contribution of M2.5 Precursor Gases and Re-entrained Road Emissions to Mobile Source PM2.5 Particulate Matter Emissions".

³ Fuel Trends Report: Gasoline 2006 - 2016 ; Office of Transportation and Air Quality; U.S. Environmental Protection Agency; EPA-420-R-17-005; October 2017; <https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100T5J6.pdf>



ethanol blending of \$12.2 billion.^{4;5} We can also calculate that **each one percent by vol. reduction in aromatics saves 258 mortalities from reduced exposure to PM2.5 originating from aromatic hydrocarbons in gasoline and \$2.35 billion avoided monetary damages.**⁶

A report by NREL details the aromatics content of several ethanol blended fuels.⁷ Table 2 in that report shows that flex fuels (E83) have aromatic contents below 2% which would constitute a reduction of 17% points over the 2016 aromatics content of fuels of 19.3%. Therefore, widespread flex fuel adoption would result in a reduction in 4,470 mortalities from reduced exposure to PM2.5 originating from aromatic hydrocarbons in gasoline and \$41 billion in avoided monetary damages. The NREL report also lists several E51 fuels at 6% aromatics content which would reduce mortalities by 3,440 incidents or 31 billion in avoided monetary damages.

Moreover, with this approach we can project the mortality/damages benefits that a new blend with aromatics limits could produce. An E25/E30 with 10% aromatics limits, for example, would result in avoided damages of \$22 billion whereas an E25/E30 blend with 15% aromatics limits would result in \$10 billion in avoided damages from reduced exposure to PM2.5 originating from aromatic hydrocarbons in gasoline.

Table 2: Avoided Mortalities and Monetary Damages for Different Ethanol Blend Levels

	Aromatics Content (%)	Aromatics Reduction (%)	Reduction in Mortalities	Avoided Monetary Damages
E83	2	17.3	4,469.76	\$40,674,771,429
E51	6	13.3	3,436.29	\$31,270,200,000
Assumed E25/E30	10	9.3	2,402.82	\$21,865,628,571
Assumed E25/E30	15	4.3	1,110.98	\$10,109,914,286

Importantly, one must keep in mind that ethanol has other emissions benefits including a reduction in direct PM2.5 emissions.^{8;9;10} In fact, the Honda PM Index developed by Aikawa and Jetter predicts PM formation in vehicle exhaust is correlated with the number of double bonds in gasoline hydrocarbons:

⁴ Technical Support Document. Estimating the Benefits per Ton of Reducing PM2.5 Precursors from 17 Sector. US EPA Office of Air and Radiation, 2013.

⁵ Guidelines for Preparing Economic Analyses; updated May 2014; National Center for Environmental Economics; U.S. Environmental Protection Agency <https://www.epa.gov/sites/production/files/2017-08/documents/ee-0568-50.pdf>

⁶ (6330-4987)/(24.5-19.3)

⁷ Property Analysis of Ethanol-Natural Gasoline-BOB Blends to Make Flex Fuel Alleman, Yanowitz; NREL Report, 2016. <https://www.nrel.gov/docs/fy17osti/67243.pdf>

⁸ Jin, D., Choi, K., Myung, C.L., Lim, Y., Lee, Y., Park, S., 2017. The impact of various ethanol-gasoline blends on particulates and unregulated gaseous emissions characteristics from a spark ignition direct injection (SID) passenger vehicle. Fuel. <http://dx.doi.org/10.1016/j.fuel.2017.08.063>.

⁹ Storey, J. M., Barone, T., Norman, K., and Lewis, S. 2010. Ethanol Blend Effects on Direct Injection Spark-Ignition Gasoline Vehicle Particulate Matter Emissions. SAE Technical Paper No. 2010-01-2129. SAE, Warrendale, PA.

¹⁰ Martini, G., Astorga, C., Adam, T., Farfaletti, A., Manfredi, U., Montero, L., Krasenbrink, A., Larsen, B. and De Santi, G. Effect of Fuel Ethanol Content on Exhaust Emissions of a Flexible Fuel Vehicle, JRC Report 2009



higher distillation aromatics (high molecular weight) have higher double-bond equivalents and therefore contribute directly to PM formation in exhaust emissions whereas ethanol has no double bonds.^{11,12}

Also, not all health outcomes were considered in this analysis. As Stackelberg et al state: "SOA from aromatics in gasoline are associated with other health outcomes, including exacerbation of asthma, upper respiratory symptoms, lost work days, and hospital emergency room visits."

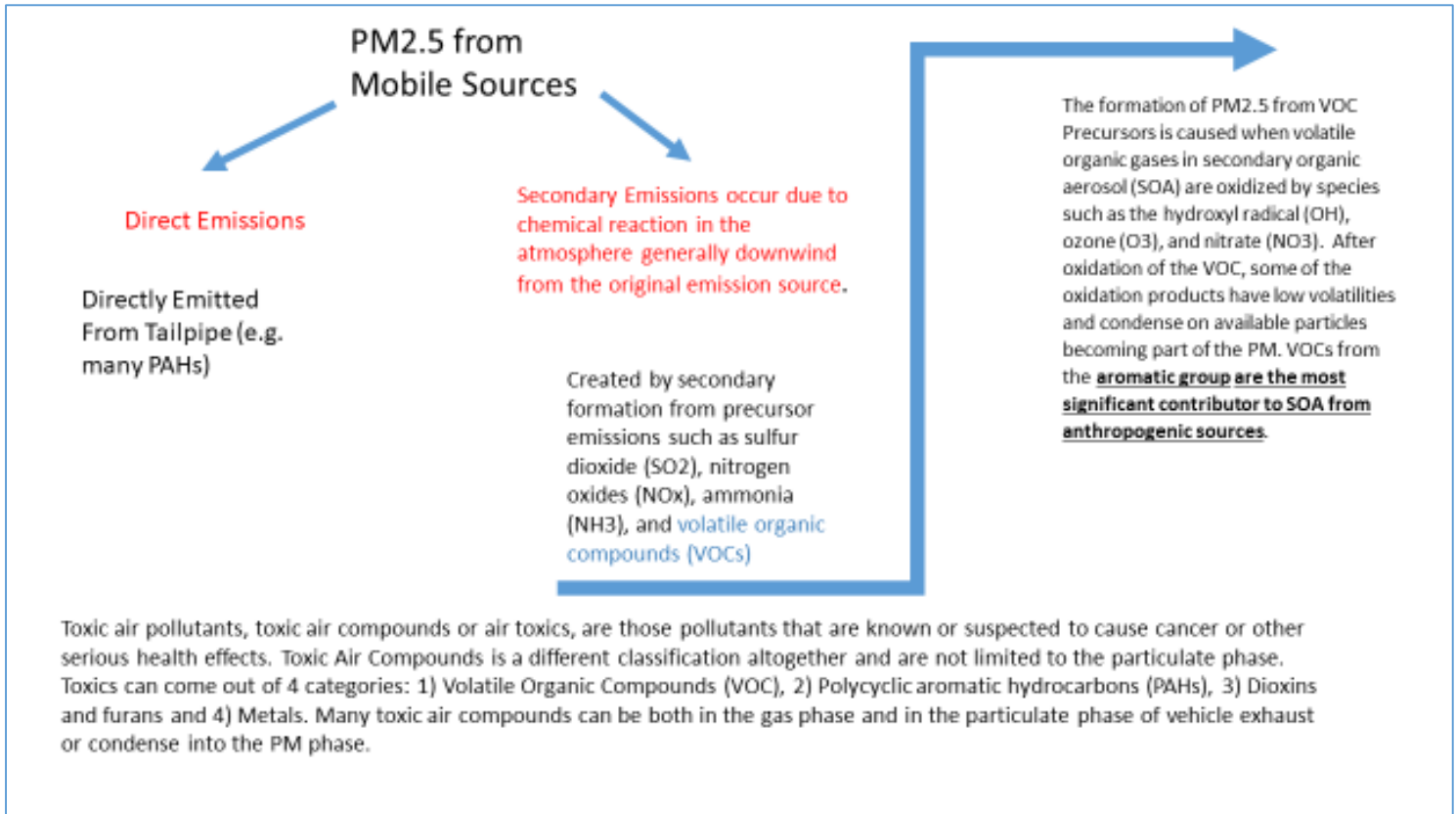
There are currently no federal limits on aromatics content in gasoline except for benzene which is regulated.¹³ Based on the significant mortalities associated with aromatics in gasoline we encourage the development of incentives or regulatory frameworks to reduce aromatics in our fuels.

¹¹ <https://www.sae.org/publications/technical-papers/content/2010-01-2115/>

¹² K. Aikawa and J. J. Jetter, "Impact of gasoline composition on particulate matter emissions from a direct-injection gasoline engine: Applicability of the particulate matter index," *International Journal of Engine Research*, vol. 15, no. 3, pp. 298-306, 24 June 2013.

¹³ <https://www.epa.gov/gasoline-standards/gasoline-mobile-source-air-toxics>

Appendix A: Direct and Secondary PM2.5 Emissions Primer Diagram



Appendix B: Table from EPA Fuel Trends Report

Year	Volume	Oxygen	API Gravity	Ethanol	MTBE	TAME	Sulfur	Aromatics	Olefins	Benzene	RVP	E200	E300	T50	T90
	Million Gallons	Wt%		Vol%	Vol%	Vol%	ppm	Vol%	Vol%	Vol%	Psi	Vol%	Vol%	F	F
1997	107,220	0.72	60.0	0.31	2.89	0.22	312.6	24.7	12.2	1.01	10.34	49.3	82.5	201.5	331.4
1998	112,950	1.05	60.0	0.80	3.65	0.36	272.7	24.8	11.2	1.00	10.35	49.0	82.6	202.0	329.5
1999	114,776	1.08	60.0	0.97	3.45	0.29	283.8	24.8	11.5	1.00	10.33	49.1	82.6	201.9	330.2
2000	115,574	1.07	60.0	1.07	3.27	0.35	270.2	24.6	11.7	0.99	10.23	49.2	83.0	201.7	327.8
2001	117,153	1.07	59.6	1.05	3.36	0.37	264.1	24.9	12.5	1.02	10.17	48.9	83.0	203.5	327.9
2002	120,802	1.08	59.8	1.14	3.27	0.39	259.4	24.7	11.7	0.97	10.16	48.9	82.8	203.5	329.1
2003	121,617	1.17	59.4	1.33	3.43	0.30	243.8	24.7	11.6	1.00	10.20	49.0	82.6	202.8	330.6
2004	122,166	1.39	60.1	2.02	3.35	0.24	112.0	24.5	11.3	0.98	10.21	49.3	82.7	202.3	330.0
2005	119,666	1.38	60.3	2.23	2.89	0.23	94.8	24.5	11.7	1.04	10.18	49.7	83.4	201.2	326.9
2006	123,178	1.19	60.1	2.91	0.64	<0.01	49.2	24.7	11.1	1.04	10.15	49.1	83.7	-	-
2007	122,403	1.27	60.2	3.44	0.02	<0.01	39.9	24.4	11.2	1.04	10.20	49.6	83.8	-	-
2008	114,032	2.02	60.8	5.54	<0.01	<0.01	34.2	22.5	10.5	1.02	10.33	52.0	85.8	-	-
2009	115,404	2.62	60.3	7.20	<0.01	<0.01	33.3	22.0	10.3	0.97	10.47	52.7	84.8	-	-
2010	116,286	3.13	60.4	8.65	<0.01	<0.01	32.4	21.2	10.0	0.89	10.54	53.8	85.3	-	-
2011	121,131	3.13	60.7	8.72	<0.01	<0.01	30.0	20.2	9.8	0.70	10.64	54.7	86.0	-	-
2012	119,696	3.24	61.0	9.01	<0.01	<0.01	29.4	19.6	9.6	0.63	10.73	55.2	86.3	-	-
2013	119,689	3.33	61.3	9.21	<0.01	<0.01	27.2	19.1	9.5	0.59	10.82	55.7	86.9	-	-
2014	123,005	3.34	61.4	9.23	<0.01	<0.01	25.3	18.8	9.3	0.59	10.95	55.6	87.0	-	-
2015	125,386	3.43	-	9.38	<0.01	<0.01	23.4	19.0	9.0	0.58	10.83	55.0	86.6	-	-
2016	125,000	3.48	-	9.57	<0.01	<0.01	23.1	19.3	8.6	0.58	10.60	54.4	85.9	-	-

Table 6 Summary of Annual Average Gasoline Properties Between 1997 and 2016

Appendix C: Extracted from Table S2 in Stackelberg et al. - US EPA's SPECIATE Database Used to Determine the Fraction of Anthropogenic SOA from Aromatic Hydrocarbons in Gasoline

tons/year

	Mobile Sources;Highway Vehicles - Gasoline	Mobile Sources;Pleasure Craft	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke	Mobile Sources;Off-highway Vehicle Gasoline, 2-Stroke
Aromatic VOC (ton/yr)	1,152,197	688,831	316,224	312,718
Toluene	401,877	219,848	106,474	99,571
M & p-xylene	219,739	126,730	58,810	57,337
Benzene	154,044	99,087	44,259	45,135
Isomers of xylene	0	0	0	0
Ethylbenzene	86,959	48,721	22,809	21,969
O-xylene	82,018	49,019	22,343	22,220
1-Methyl-3-ethylbenzene (3-Ethyltoluene)	59,118	38,254	16,769	17,417
1,2,4-trimethylbenzene (1,3,4-trimethylbenzene)	52,962	32,798	14,716	14,905
1,3,5-trimethylbenzene	22,856	17,116	7,035	7,854
1-Methyl-4-ethylbenzene	24,276	16,980	7,161	7,756
1-Methyl-2-ethylbenzene	16,859	13,868	5,478	6,392
N-propylbenzene	13,888	10,961	4,419	5,046
Benzaldehyde	9,885	9,774	3,574	4,505
Ethylene glycol	0	0	0	0
Phenol (carbolic acid)	0	0	0	0
1,2,3-trimethylbenzene	7,715	5,677	2,377	2,611

Environmental Benefits of Ethanol Blended Fuels

September 2019

**THE
UNIVERSITY OF
ILLINOIS
AT
CHICAGO**

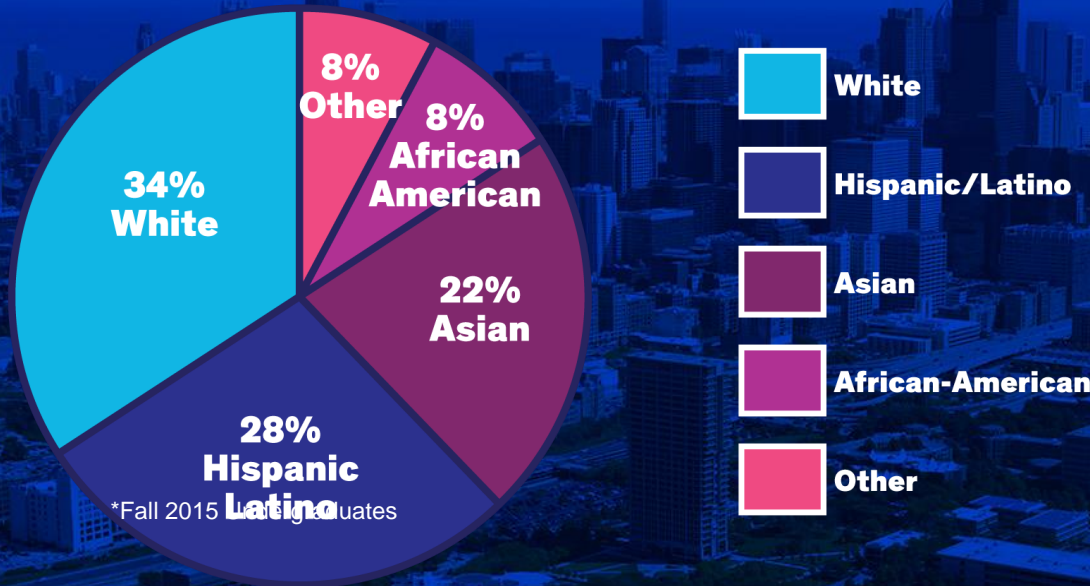


Presented to:
Chile Fuels Specification Committee
Hyatt Centric Las Condes Santiago, Chile

Steffen Mueller, PhD
Principal Economist
UIC Energy Resources Center

University of Illinois at Chicago Diverse Student Body 29,000 students

000096 vta



conducting
\$368M
total research
expenditures

40th
among public
universities



Biofuels and Sustainable Landscapes Research Center

000097



- 2 Senior Scientists – 5 Students/Interns – Large Network of Cooperators
- Fuel Ethanol life cycle and combustion emissions modeling
- New biofuels technology evaluation/commercialization
- Land use research using Remote Sensing/Satellite tools
- Pollinator habitat conservation

Presentation Overview: Emissions Reductions with Ethanol Blended Gasoline



- Tailpipe Emissions: Assess Local Air Emissions Impact
 - Carbon Monoxide, Nitrogen Oxides, Volatile Organics
 - Particulate Matter
 - Direct
 - Indirect via Secondary Organic Aerosols
 - Air Toxins and Polycyclic Aromatic Hydrocarbons
 - Aldehydes
 - High altitude considerations
- Life Cycle Emissions Greenhouse Gas Emissions: Assess Global Climate Change Impact
- Refinery Profitability Considerations
- Biofuels Sustainability Considerations

Tailpipe Emissions Reductions Start at ⁰⁰⁰⁰⁹⁸ the Refinery Level

- Gasoline contains a large amount of aromatic hydrocarbons that are added to gasoline because they have relatively high octane values and therefore serve as anti-knock agents in vehicle engines.
- Some aromatics are highly toxic compounds.
- Ethanol also has a high octane value and contains no aromatic compounds.
 - It therefore substitutes and dilutes aromatics in gasoline.
 - Moreover, ethanol also alters the distillation curve resulting in an adjustment of the distillation properties of the fuel with, for example a higher volume fraction of the fuel distilled at 200 degrees Fahrenheit.
 - This effect further reduces the formation of many emissions compounds from a vehicle.



Definitions and Key Emissions Terms



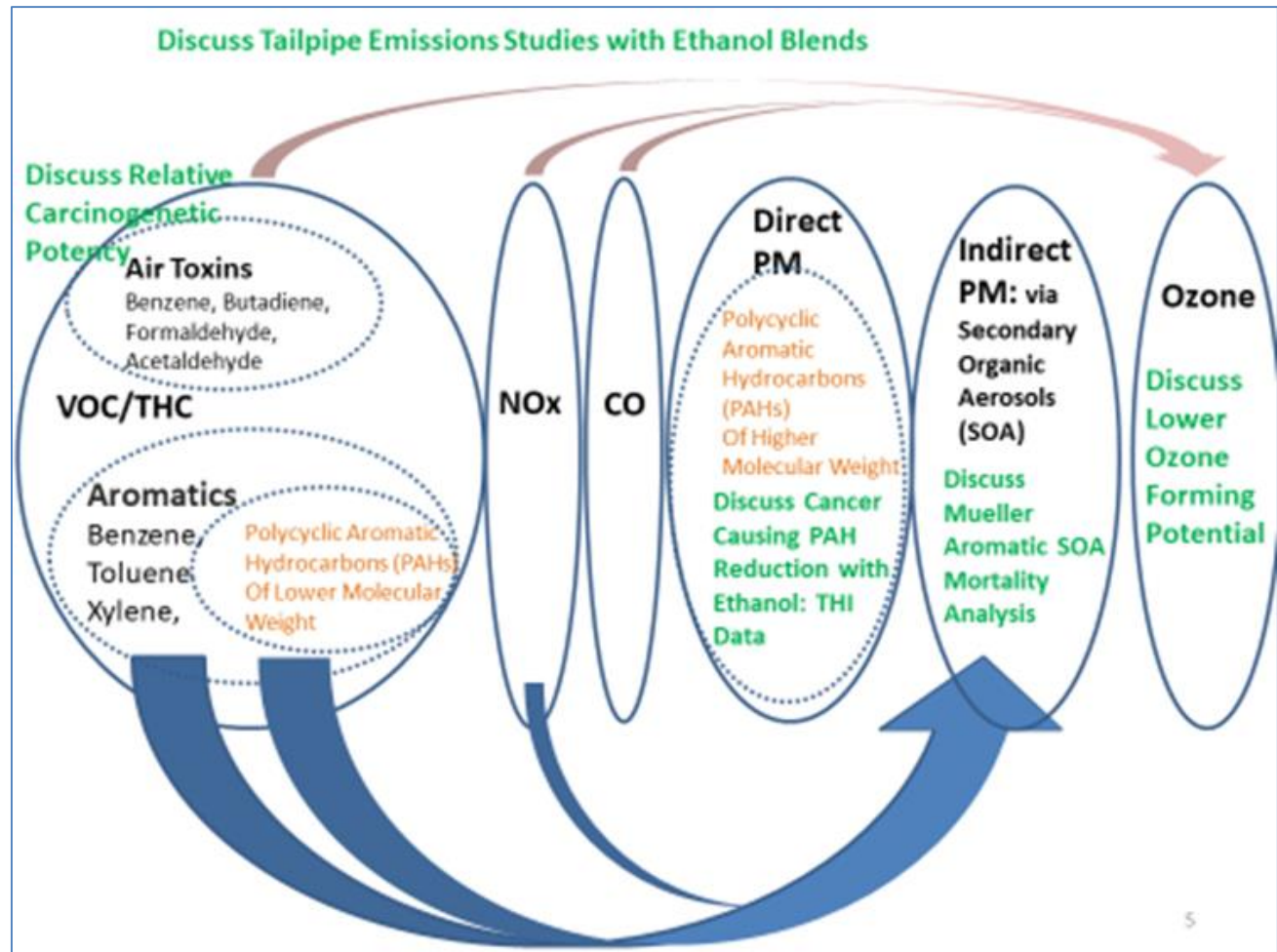
Definitions

- Volatile Organic Compounds (VOC): EPA defines VOC as any compound of carbon, excluding carbon monoxide, carbon dioxide, (some other exclusions)
- Toxic air pollutants, toxic air compounds or air toxics, are those pollutants that are known or suspected to cause cancer or other serious health effects. Toxics can come out of 4 categories: 1) Volatile Organic Compounds (VOC), 2) Polycyclic aromatic hydrocarbons (PAHs), 3) Dioxins and furans and 4) Metals. Many toxic air compounds **can be both in the gas phase and in the particulate phase of vehicle exhaust or condense into the PM phase (as secondary organic aerosol formation.**
- Polycyclic aromatic hydrocarbons (PAHs): This category is defined as hydrocarbons containing fused aromatic rings. These compounds can be measured in the **gaseous phase, particulate phase, or both**, depending on properties of the compound, particle characteristics and conditions in the exhaust stream or the atmosphere.
 - Benzo[a]pyrene one of the most carcinogenic PAHs from vehicle exhaust has 5 fused benzene rings and is mostly in the particulate phase.
 - PAHs in the particulate phase are mostly bound to PM 2.5 and ultrafine fraction of the airborne particulates that are reportedly known for their higher health risk

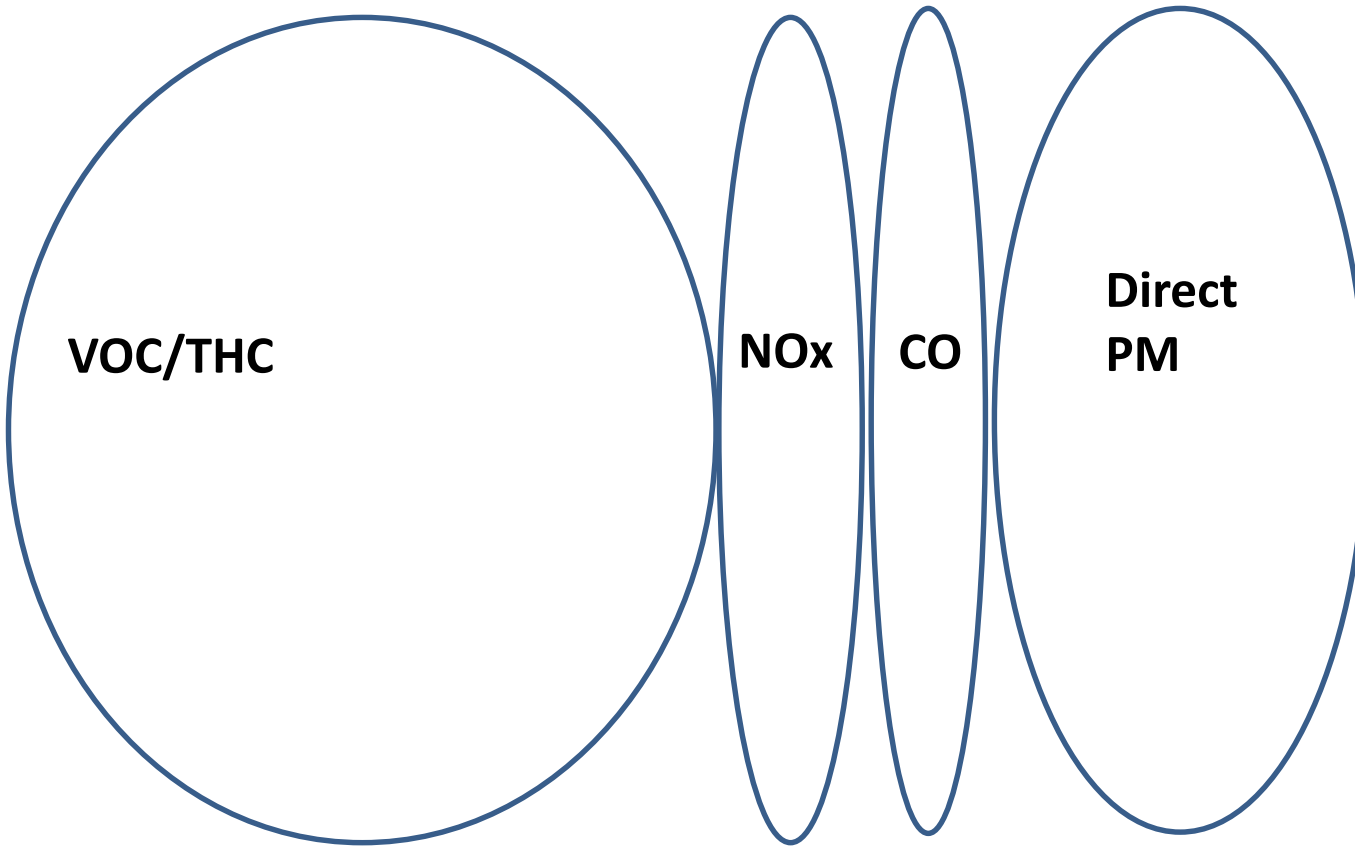
How does Ethanol Reduce Air Emissions in Gasoline Blends

Over the next Slides we will be building the below diagram step by step

It is important to look at the major pollutant groups of VOC, NO_x, PM **but it is even more important to understand the adjustments in key individual pollutants that are particularly harmful**



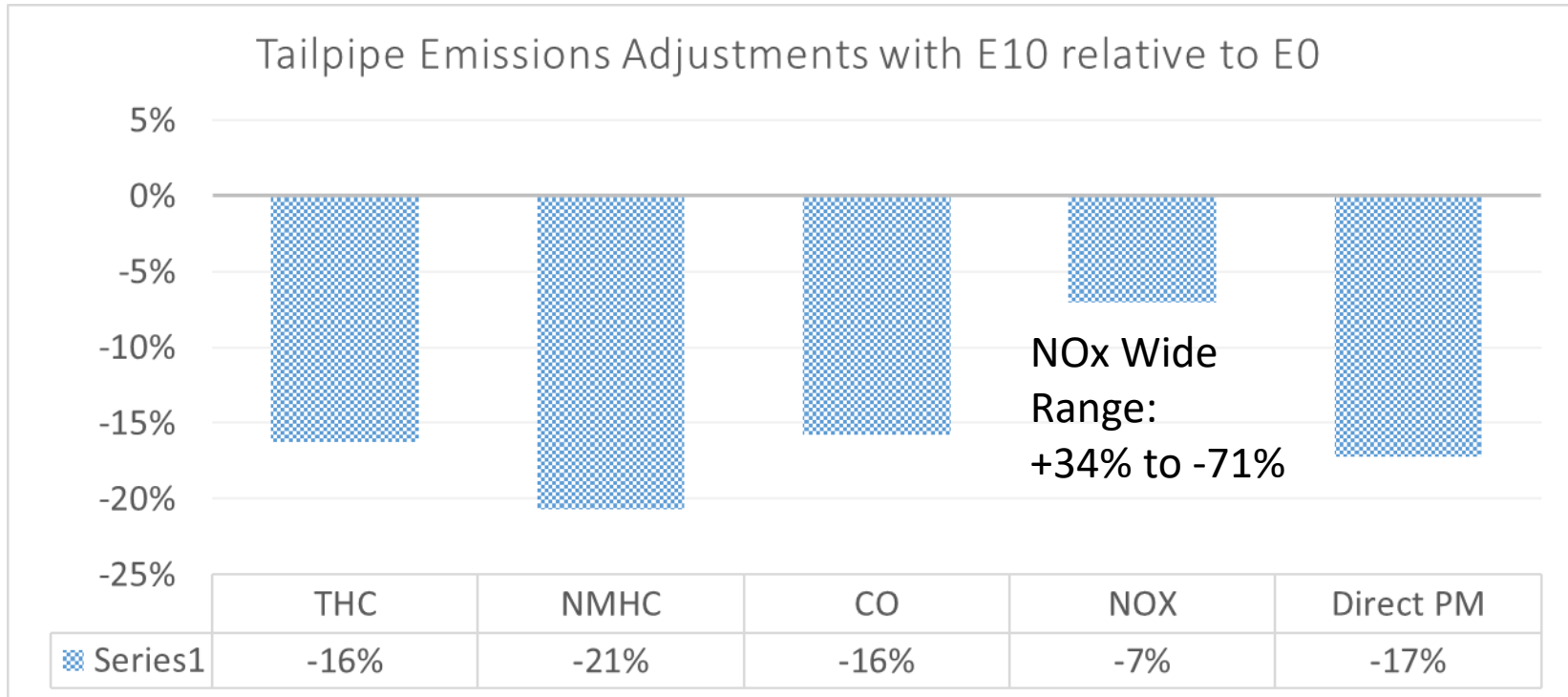
Discuss Tailpipe Emissions Studies with Ethanol Blends



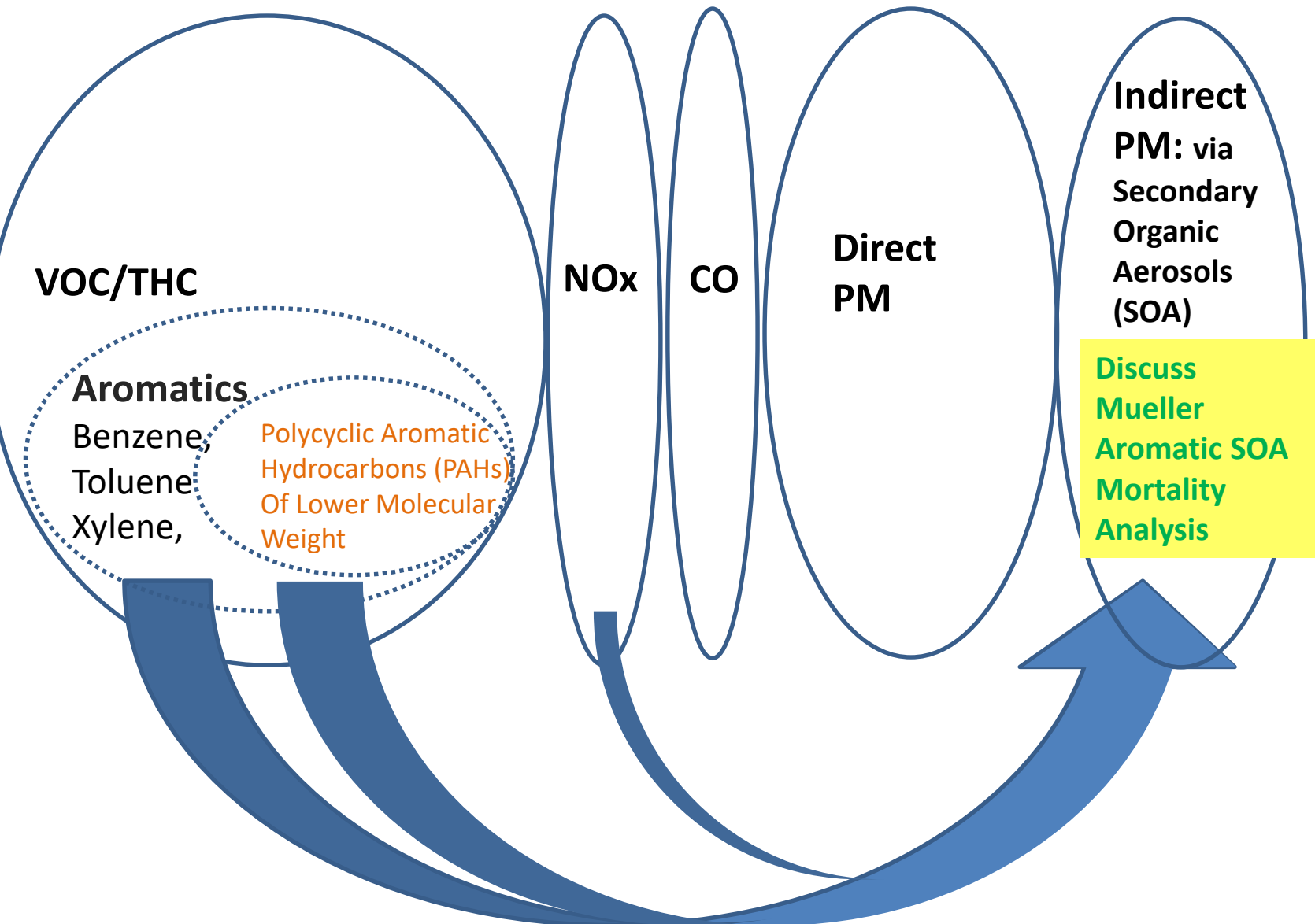
Thorough Literature Review of Vehicle Emissions Studies with E10; by Pollutant Groups

Study Name	Vehicles	Test cycle	Location	Relative to E0				
				THC	NMHC	CO	NOX	PM
Karavalakis et al., 2012	1984-2007 Gasoline vehicles (Total 6), One additional 2007 Flex Fuel Vehicle	FTP-75	California	-12.80%			13.60%	
Bertoa et al., 2015	One Euro 5a flex-fuel light duty vehicle (FFV) equipped with a three way catalyst (TWC) and a turbo charged air intake system	WLTC	Italy	-65%	-68%	13%	-24%	
SAE, 1992	Ford Valencia SI engine		United States	-4.90%	-5.90%	-13.40%	5.10%	
NREL, 2009	1999-2007 Gasoline vehicles (Total 16)	LA 92	United States		-12%	-15%	-5.50%	
Storey et al., 2010	2007 Pontiac Solstice	FTP-75, US06	United States		-20%	3%	-42%	-6%
ORNL 2012	19 Tier 2 and 8 Tier 1/NLEV	FTP-75	United States		-7.02%	-2.36%	34.26%	
Ozsezen et al. 2011	Test Vehicle - 1.4i SI engine, Water-cooled, four stroke, multi point injection	wide-open throttle conditions and at the vehicle speeds of 40, 60, 80 and 100 kmph	Turkey	-14%		-2.60%	-1.30%	
Schifter et al., 2011	4 vehicles older than 1992, 17 vehicles between 1993 - 1997 and 9 vehicles 2000-2004	FTP-75	Mexico	-5%		-13.70%	-2.70%	
Zhu et al., 2017	Two China IV vehicles and one Tier 2 vehicle	WLTC	China	-6%		-22.70%		
Graham et al., 2008	Two 2002 LEV 1 LDT and One 2004 ULEV 1	FTP-75, US06	Canada	9%		-10%	3%	
Bielaczyc et al., 2013	One Euro V vehicle	NEDC	Poland	23%		13.30%	7.80%	-19.70%
Knapp et al. 2011	1977 - 1994 Gasoline vehicles (Total 11 No.s)	UDDS	Alaska	-6.50%		-8.30%	-0.70%	
Canakci et al., 2013	1.4i SI engine Honda Civic Water-cooled, four-stroke, multi-point injection	two different vehicle speeds (80 km/h and 100 km/h), and four different wheel powers	Turkey	-41%		-24.20%	-18.50%	
Yao et al., 2011	2000 and 2005 passenger cars	FTP-75	Taiwan	-13%	-11.50%	-10%	-4.40%	
Czerwinski et al., 2016	new (Euro 5) flex fuel vehicle Volvo V60 (GDI)	WLTC	Switzerland	-1%		-16%	-25%	
Martini et al., 2009	Euro IV Ford Focus flexible fuel car	NEDC	Italy	-49%		-77%	1%	-26%
Truyen et al., 2012	2001 Fuel Injected Car	ECE15+EUDC	Vietnam	-4%		-8%	10.70%	
Munoz et al., 2019	Euro-5 flex-fuel GDI vehicle (Volvo V60) with a 1.6 L engine	WLTC	Switzerland	-53%		-75%	-71.23%	
AVERAGE				-16%	-21%	-16%	-7%	-17%

Mass Reductions of Emissions Groups with Ethanol: Thorough Literature Review of Vehicle Emissions Studies with E10



Increases in Acetaldehyde Possible with Ethanol but this is insignificant in Health Impact Assessments when weighted by its Low Relative Cancer Potential

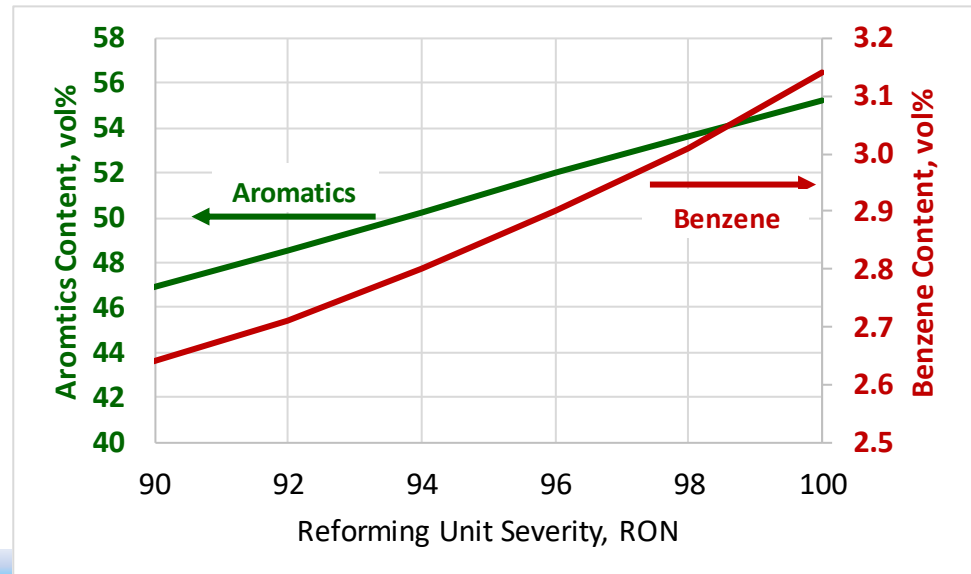


Aromatics Reductions from Blending Corn Ethanol

What happens at the Refinery when we produce Fuels that Meet Octane Specifications for our Car Engines?

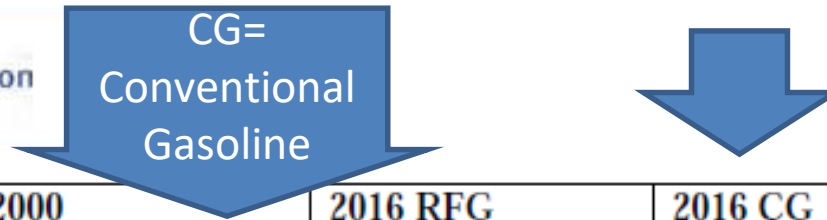
- The Catalytic Reforming Unit within a Refinery is the major producer of high octane (measured in research octane number “RON”) for gasoline blending.
- Generally the higher the desired RON number the more aromatics are added.
- With ethanol blended into gasoline the reforming unit severity is adjusted to lower RON numbers, which generally results in lower benzene and aromatics content

Many aromatics are toxics, carcinogenic, and have other adverse health effects.



U.S. Domestic Blending Behavior

- United States Environmental Protection Agency “Fuel Trends Report” (Released October 2017) <https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100T5J6.pdf>,
- Page 8: "Ethanol’s high octane value has also allowed refiners to **significantly reduce the aromatic content of the gasoline**, a trend borne out in the data. Other direct effects of blending in ethanol are described below."



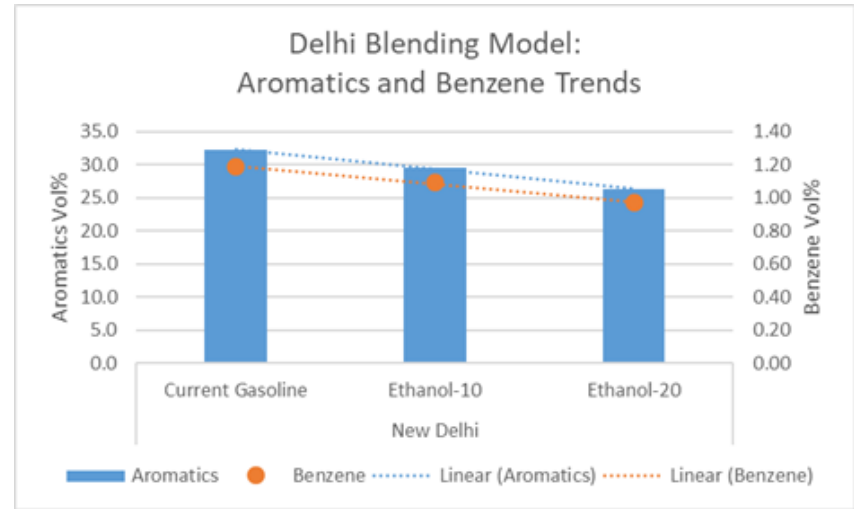
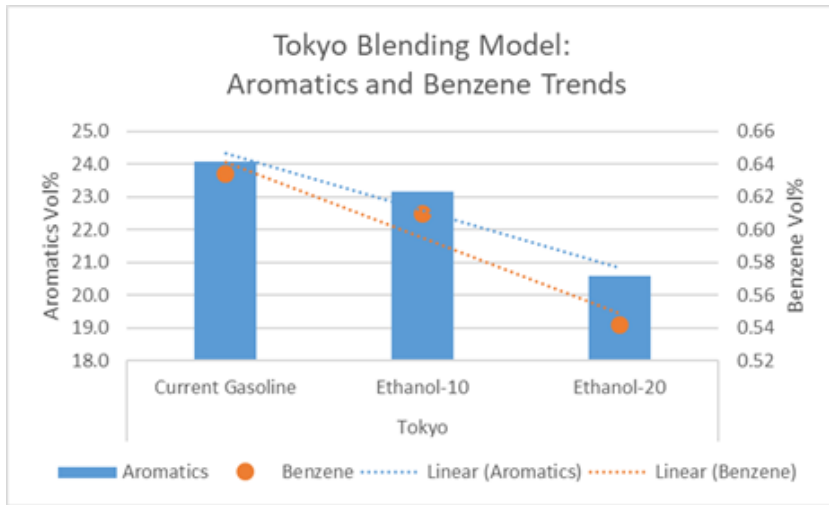
Property	1990	2000		2016 RFG		2016 CG	
	Baseline	RFG Average	CG Average	Average	95%	Average	95%
Sulfur (ppm)	339	126	324	23.1	48.2	22.5	51.0
Benzene (vol%)	1.53	0.59	1.15	0.51	0.86	0.63	1.27
RVP (psi)	8.7	6.78	8.27	7.1	7.47	9.08	10.0
Aromatics (vol%)	32	19.3	28.5	17.12	27.3	21.76	32.1
E200 (vol%)	41	47.6	45.2	47.9	54.8	55.0	61.4
E300 (vol%)	83	84.7	80.7	85.6	92.0	84.8	91.1
Olefins (vol%)	13.1	10.6	11.8	10.5	18.7	8.38	16.4
Ethanol (vol%)	0.6	1.14	0.84	9.61	9.97	9.28	9.8

Winter gasoline

CG= Conventional Gasoline; RFG= Reformulated Gasoline

International Blending Behavior

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International Blending Model confirms that ethanol blended into gasoline reduces the reforming unit severity at refineries which results in lower benzene and aromatics content

Preventing SOA with Ethanol

Public health impacts of secondary particulate formation from aromatic hydrocarbons in gasoline

Katherine von Stackelberg^{1†}, Jonathan Buonocore^{1†}, Prakash V Bhave² and Joel A Schwartz¹

- Harvard/EPA Paper: <https://ehjournal.biomedcentral.com/articles/10.1186/1476-069X-12-19#Tab5>
 - “Secondary organic aerosol (SOA), is a major contributor to the PM2.5. Evidence is growing that aromatics in gasoline exhaust are among the most efficient secondary organic matter precursors. “
 - “Most gasoline formulations consist of approximately 20% aromatic hydrocarbons, which are used in place of lead to boost octane. Therefore, it has been suggested that removal of aromatics could reduce SOA concentrations and yield a substantial public health benefit.”
- EPA Fuel Trends Report: “Ethanol’s high octane value has also allowed refiners to significantly reduce the aromatic content of the gasoline, a trend borne out in the data.” ; <https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100T5J6.pdf>
- Mueller Analysis: **Each one percent by vol. reduction in aromatics saves 258 mortalities from reduced exposure to PM2.5 originating from aromatic hydrocarbons in gasoline and \$2.35 billion avoided monetary damages.**
[http://www.erc.uic.edu/assets/pdf/UIC Indirect Aromatics SOA Paper FINAL 8 12 2019.pdf](http://www.erc.uic.edu/assets/pdf/UIC%20Indirect%20Aromatics%20SOA%20Paper%20FINAL%208%2012%202019.pdf)

	Aromatics vol%	Ethanol vol%	Aromatic VOC (ton/year)	Mortalities (upper bound)	Monetary Damages
2005	24.5	2.23	2,469,970	6,330	\$ 57,603,000,000
2016	19.3	9.57	1,945,731.22	4,986	\$ 45,377,057,143
			Difference	1,344	\$ 12,225,942,857

Secondary Organic Aerosols Study by Harvard, Mario Molina/Chile and U of Sao Paulo/Brazil

Environmental Research 177 (2019) 108661

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

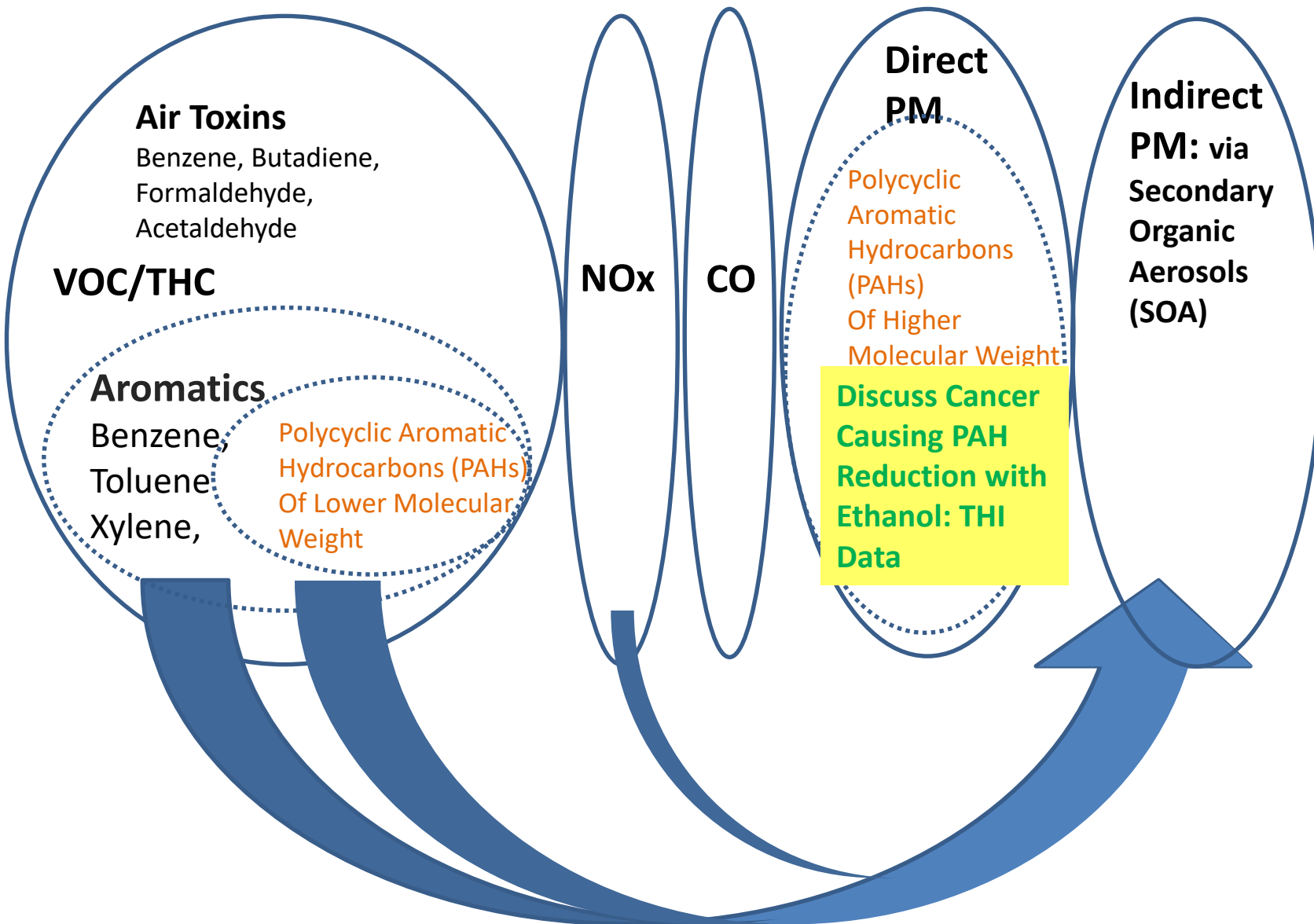


Secondary particles formed from the exhaust of vehicles using ethanol-gasoline blends increase the production of pulmonary and cardiac reactive oxygen species and induce pulmonary inflammation

Reactive oxygen species (ROS)
Bronchoalveolar lavages (BAL).

Study Set Up: Exhaust emissions from vehicles using ethanol blends were delivered to a photochemical chamber and reacted to produce Secondary Organic Aerosols . The aerosol samples were collected on filters and subjected to animal tests.

Overall, the results obtained in this study suggest that gasoline, followed by fuels E85 (both winter and summer formulations) are those with greater toxic potential. Based on chemiluminescence in the lungs, gasoline has a higher potential to generate an acute toxic response (45 min) measured as ROS production. Considering the number and cells identified in BAL, a greater ability to induce inflammation by SOA derived from gasoline was noted. At 4 h after the exposure, the most significant comparison between gasoline and ethanol was observed. The total number of lymphocytes observed in animals exposed to SOA from gasoline was significantly higher than that found in pure ethanol ($p = 0.0006$), in a ratio of approximately 1:4. This fuel was also associated higher number of macrophages and lymphocytes when compared to other exposure groups.



Swiss Study: Ethanol and Gasoline Direct Injection Engines

Bioethanol Blending Reduces Nanoparticle, PAH, and Alkyl- and Nitro-PAH Emissions and the Genotoxic Potential of Exhaust from a Gasoline Direct Injection Flex-Fuel Vehicle

Maria Muñoz,^{*,†} Norbert V. Heeb,[†] Regula Haag,[†] Peter Honegger,[‡] Kerstin Zeyer,[‡] Joachim Mohn,[‡] Pierre Comte,[§] and Jan Czerwinski[§]

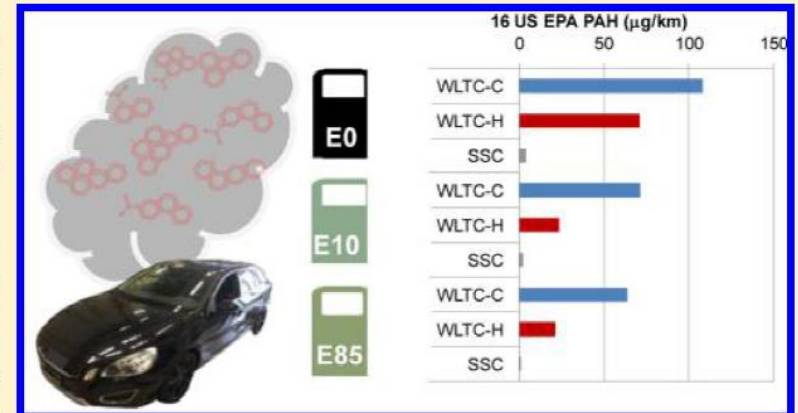
[†]Laboratory for Advanced Analytical Technologies and [‡]Laboratory for Air Pollution/Environmental Technology, EMPA, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

“emissions of selected PAHs were lowered by 67-96% with E10”

Oct 2016

ABSTRACT: Bioethanol as an alternative fuel is widely used as a substitute for gasoline and also in gasoline direct injection (GDI) vehicles, which are quickly replacing traditional port-fuel injection (PFI) vehicles. Better fuel efficiency and increased engine power are reported advantages of GDI vehicles. However, increased emissions of soot-like nanoparticles are also associated with GDI technology with yet unknown health impacts. In this study, we compare emissions of a flex-fuel Euro-5 GDI vehicle operated with gasoline (E0) and two ethanol/gasoline blends (E10 and E85) under transient and steady driving conditions and report effects on particle, polycyclic aromatic hydrocarbon (PAH), and alkyl- and nitro-PAH emissions and assess their genotoxic potential.

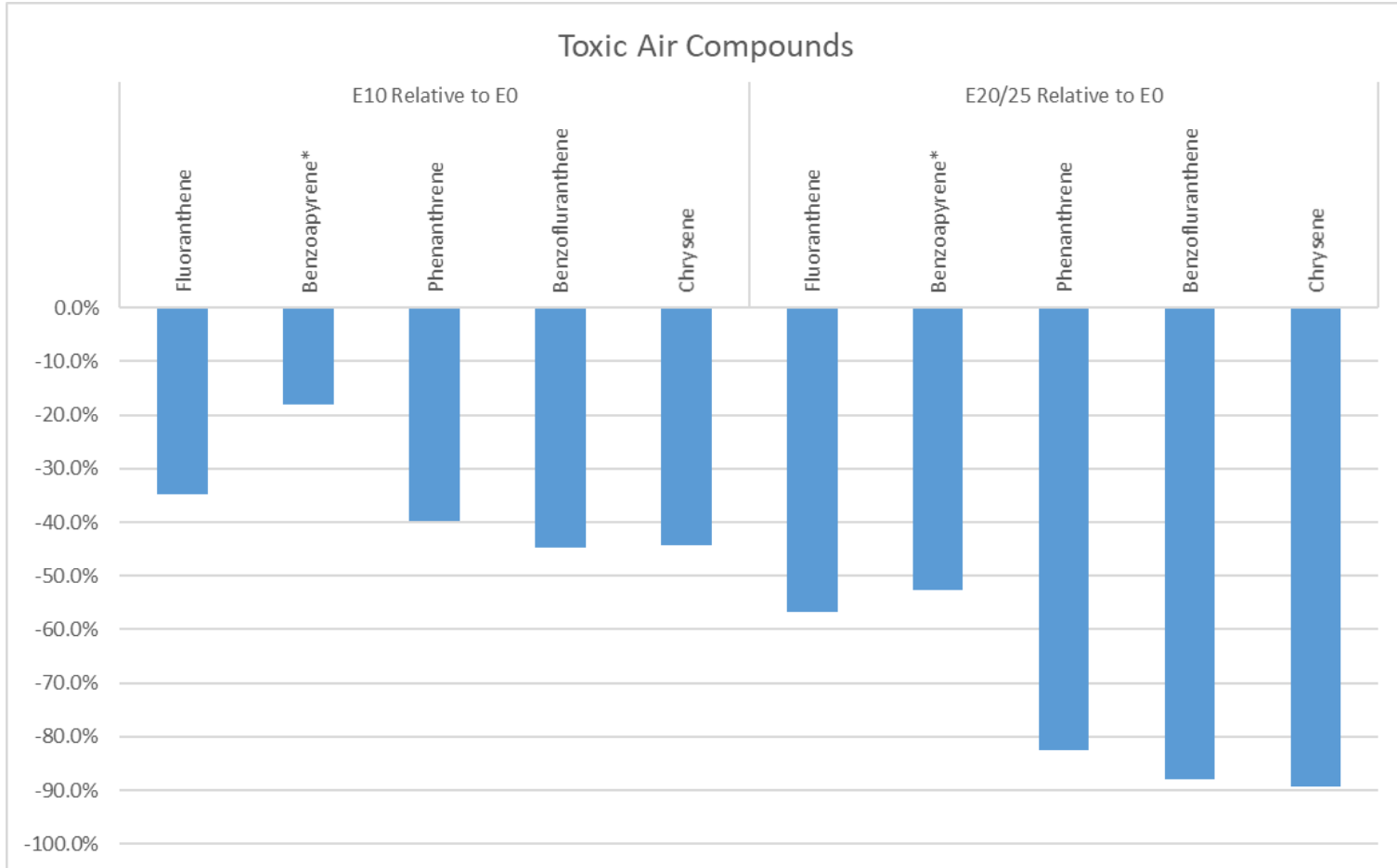
Particle number emissions when operating the vehicle in the hWLTC (hot started worldwide harmonized light-duty vehicle test cycle) with E10 and E85 were lowered by 97 and 96% compared with that of E0. CO emissions dropped by 81 and 87%, while CO₂ emissions were reduced by 13 and 17%. Emissions of selected PAHs were lowered by 67–96% with E10 and by 82–96% with E85, and the genotoxic potentials dropped by 72 and 83%, respectively. Ethanol blending appears to reduce genotoxic emissions on this specific flex-fuel GDI vehicle; however, other GDI vehicle types should be analyzed.



PAH Reduction with Ethanol: ORNL/THI Data Set

- Only a couple of vehicle emissions studies have explored the impact of ethanol on PAH emissions.
- We combined PAH reductions documented in a study by the Swiss Federal Laboratories for Materials Science and Technology for E10 relative to E0 with very recent vehicle testing conducted by Oak Ridge National Laboratory for E25 relative to E10.
- Oak Ridge National Laboratory performed fuel economy and emissions tests for a GMC Terrain vehicle. The GMC Terrain vehicle emissions tests are based on 92-93 RON Tier 3 E10 and 99 RON E25 fuels.
- However, quantification of PAH emissions was not part of the original scope of that study. As part of the present study we obtained the filters and conducted a Gas Chromatography/Mass Spectrometry analysis for those filters at The Hormel Institute-University of Minnesota-Mayo Clinic (THI data).
- With that we documented additional emissions reductions for the most prevalent and carcinogenic PAHs from vehicle exhaust from adopting high octane E25 over E10.
- Combining these results with the emissions reductions show from the Swiss study resulted in the overall expected reductions for E25 over E0 shown for PAHs in the next slide....

Mass Reductions of Toxic Air Compounds and Polycyclic Aromatic Hydrocarbons with Ethanol



Source: Cancer Reductions from the Use of High-Octane Ethanol-Blended Gasoline with a Focus on Toxic Air Compounds; Mueller, August 2019

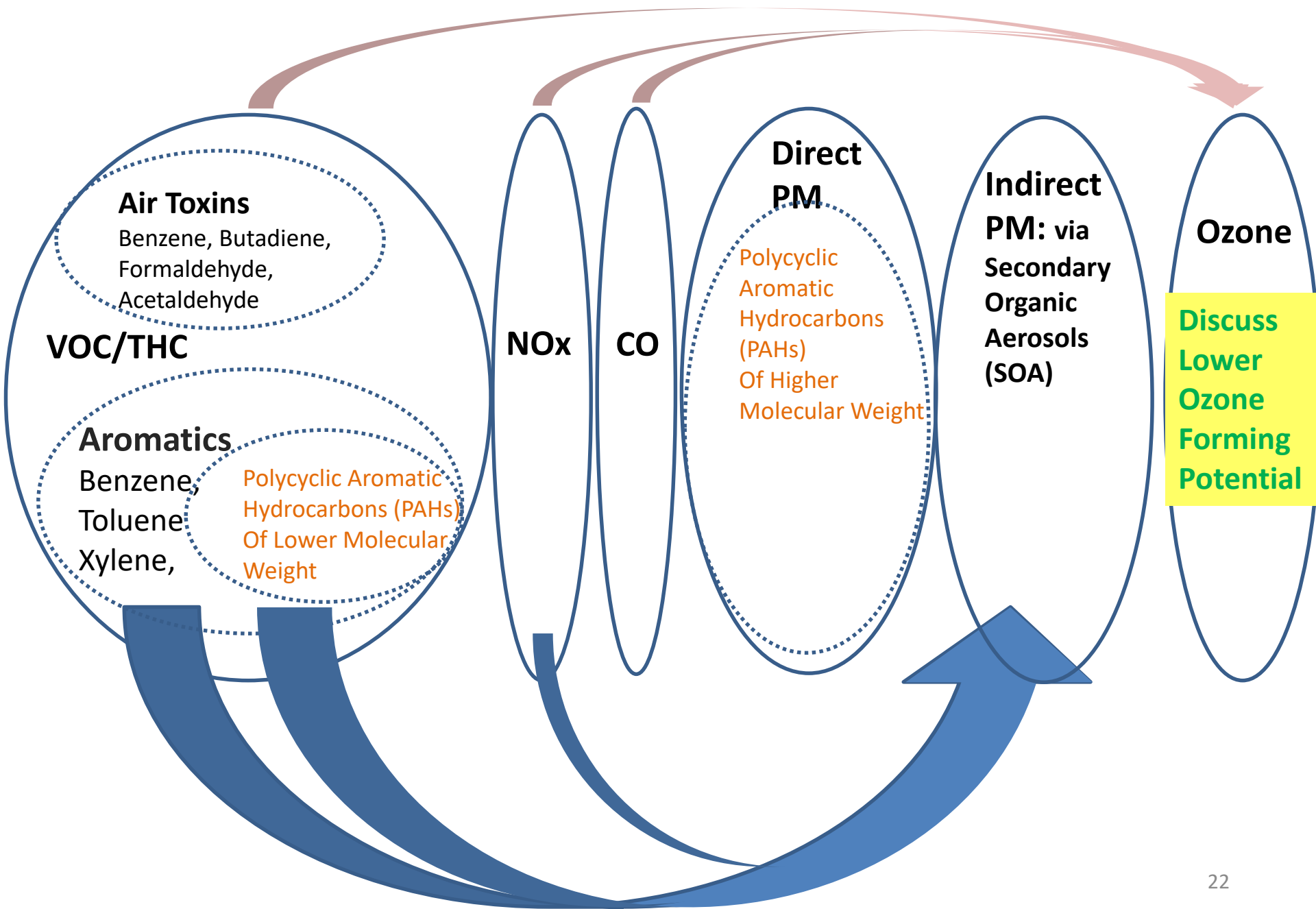
EPA CAL3QHC Atmospheric Modeling



- Parametrized MOVES and CAL3QHC Atmospheric model to assess reduction in cancer cases from high octane E25 adoption.
- Included Benzene, Butadiene, Formaldehyde, Acetaldehyde, PAHs.
- Model was set up for Chicago region and then results extrapolated to whole United States.
- If we view our results as a first, approximate calibration of how urban areas are affected by air toxins then the extrapolation of this data to the **whole United States would result in an upper bound cancer reduction for the studied toxic air compounds of 1,256 cases and avoided lifetime monetary damages of \$11.4 billion.**








Population with 0.6 Miles of an Interstate in Chicago-land Area





Ozone

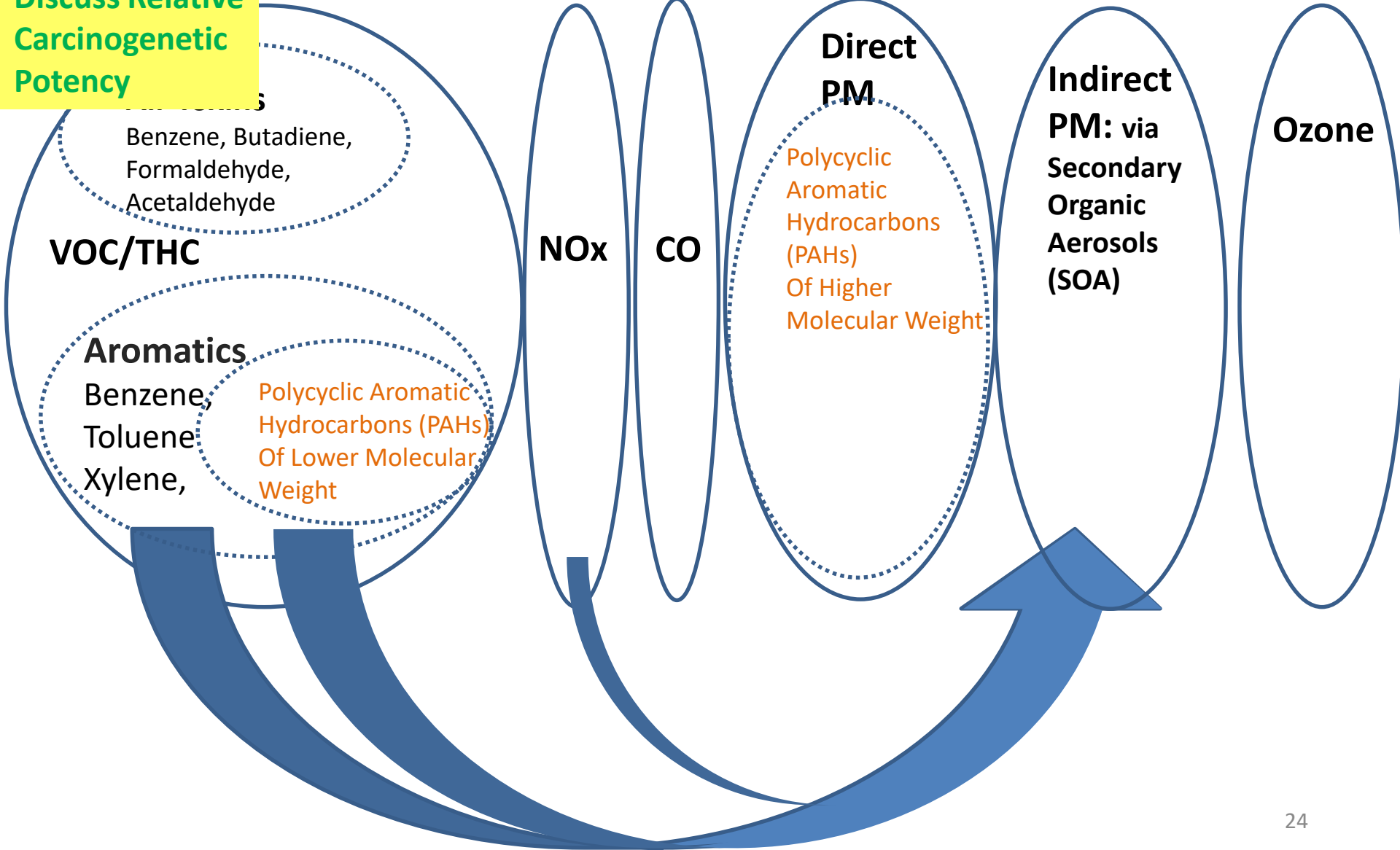
- Ozone potential provides a **measure of the smog forming potential** of organic compounds
 - **Different species have different ozone potential**
- Maximum Incremental Reactivity (MIR) is used by government regulators to evaluate fuels
- Ozone potential based on:
 - MIR × tons/year for each species
- MIR for many compounds is reduced with ethanol substituting for them. Only Acetaldehyde would go up but MIR is substantially below Xylene and Butadiene.

Species	MIR
 MTBE	0.78
 Benzene	0.69
Hexane	1.15
Misc Hydrocarbon	3
2,2,4-Trimethylpentane	1.2
Ethanol	1.45
Styrene	1.65
Ethyl Benzene	2.93
 Toluene	3.88
 Acetaldehyde	6.34
Propionaldehyde	6.83
Acrolein	7.24
 Xylene	7.44
 Formaldehyde	9.24
 1,3-Butadiene	12.21

Sources: Carter, W. P. (2010) Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales. California Air Resources Board Contracts 02-318 and 07-730

Unnasch, S., Browning, L., & Kassoy, E. (2001). Refinement of Selected Fuel-Cycle Emissions Analyses. California Air Resources Board Contract No. 98-338

Discuss Relative Carcinogenetic Potency





From Emissions to Health Impacts: Carcinogenicity of Selected Toxics Affected by Ethanol Blends

- **Benzene**
 - is a well-established cause of cancer in humans. The International Agency for Research on Cancer has classified benzene as carcinogenic to humans (Group 1). Benzene causes **acute myeloid leukemia** (acute non-lymphocytic leukemia), and there is limited evidence that benzene may also cause acute and chronic lymphocytic leukemia, **non-Hodgkin's lymphoma** and multiple myeloma.
Source: World health organization
- **1,3-butadiene**
 - “Studies have consistently shown an association between occupational exposure to 1,3-butadiene and an increased incidence of **leukemia**.” Source: <https://www.cancer.gov/about-cancer/causes-prevention/risk/substances/butadiene>
 - The Department of Health and Human Services (DHHS), IARC, and EPA have determined that 1,3-butadiene is a human carcinogen. Studies have shown that workers exposed to 1,3-butadiene may have an increased risk of cancers of the stomach, blood, and lymphatic system. Source: CDC ATSDR Database
- **Formaldehyde**
 - **Probable human carcinogen, based on limited evidence in humans**, and sufficient evidence in animals. IARC: Carcinogenic to humans . NTP: Reasonably anticipated to be a human
Source: CDC ATSDR Database
- **Acetaldehyde**
 - Based on increased evidence of **nasal tumors in animals** and adenocarcinomas.
Source: US EPA
 - Note: adenocarcinomas are most prevalent in esophageal cancer, pancreas, prostate cancer.
- **Benzo[a]pyrene (BaP); a polycyclic aromatic hydrocarbon PAH**
 - The carcinogenicity of certain PAHs is well established in laboratory animals. Researchers have reported increased incidences of skin, lung, bladder, liver, and stomach cancers, as well as injection-site sarcomas, in animals. Animal studies show that certain PAHs also can affect the hematopoietic and immune systems (ATSDR)
 - Tumor site(s): **Lung**, Gastrointestinal, Respiratory
 - Tumor type(s): **Squamous cell neoplasia in the larynx, pharynx, trachea, nasal cavity, esophagus, and forestomach**. (Thyssen et al., 1981). Source: https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=136

Converting Emissions Mass Reductions to Cancer Risk Reductions

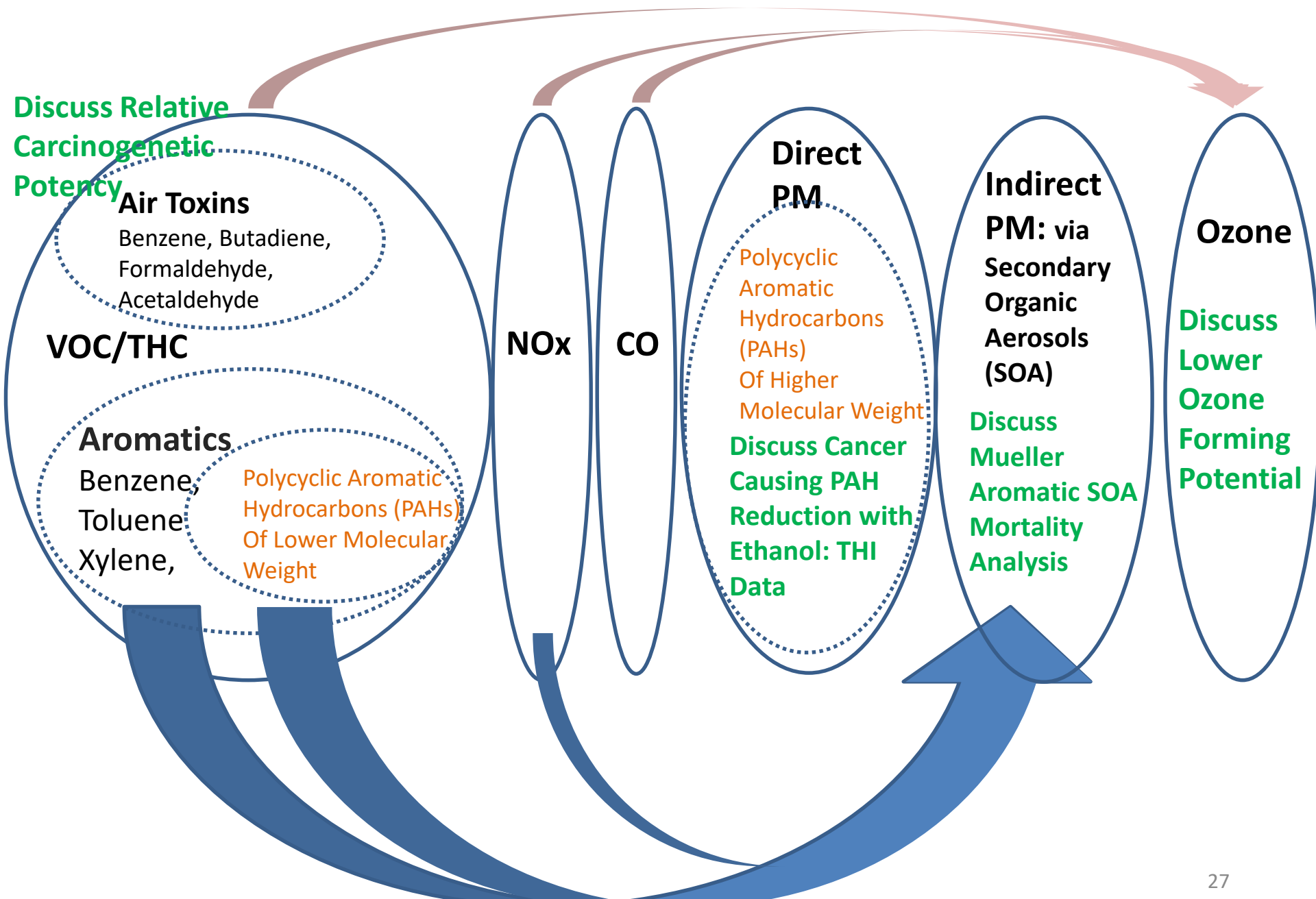
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- Convert emissions mass reductions to concentration reductions using atmospheric model (box model)
- Apply Inhalation Unit Risk Factors: excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 microgram/m³ air.
- Butadiene and Benzopyrene are very carcinogenic; Acetaldehyde has very low relative potency.
- Key unit is “Weighted Air Toxins” taking relative potency into account.

Pollutant	IUR Factor (risk per ug/m ³)	Relative Potency
Acetaldehyde	2.7×10^{-6}	0.002
Benzene	2.9×10^{-5}	0.026
Benzo[a]pyrene	1.1×10^{-3}	1.00
1,3-Butadiene	1.7×10^{-4}	0.155
Formaldehyde	6.0×10^{-6}	0.005



Source: California Environmental Protection Agency



UIC/US Grains Council 5 Cities Study

Tailpipe Emissions Modeling

Contributors

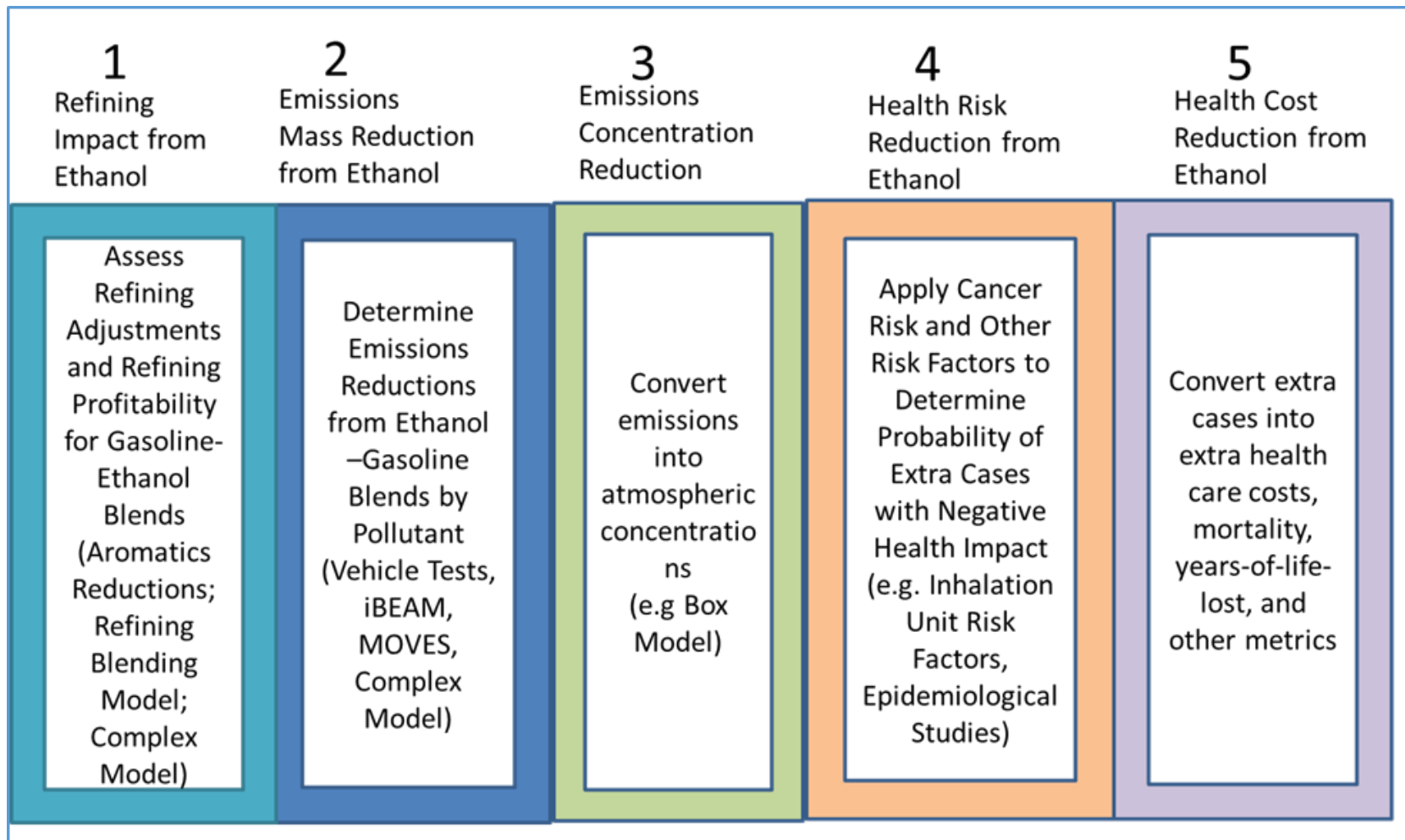
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- Professor Jane Lin; University of Illinois at Chicago. Department of Civil Engineering.
- Kristi Moore; Fueltech Service.
- Jordan Rockensuess, Intertek Laboratories. Intertek is a leading global testing, inspection, and certification laboratory.

Multi Step Modeling Process



Annual Total Vehicle Distance Travelled

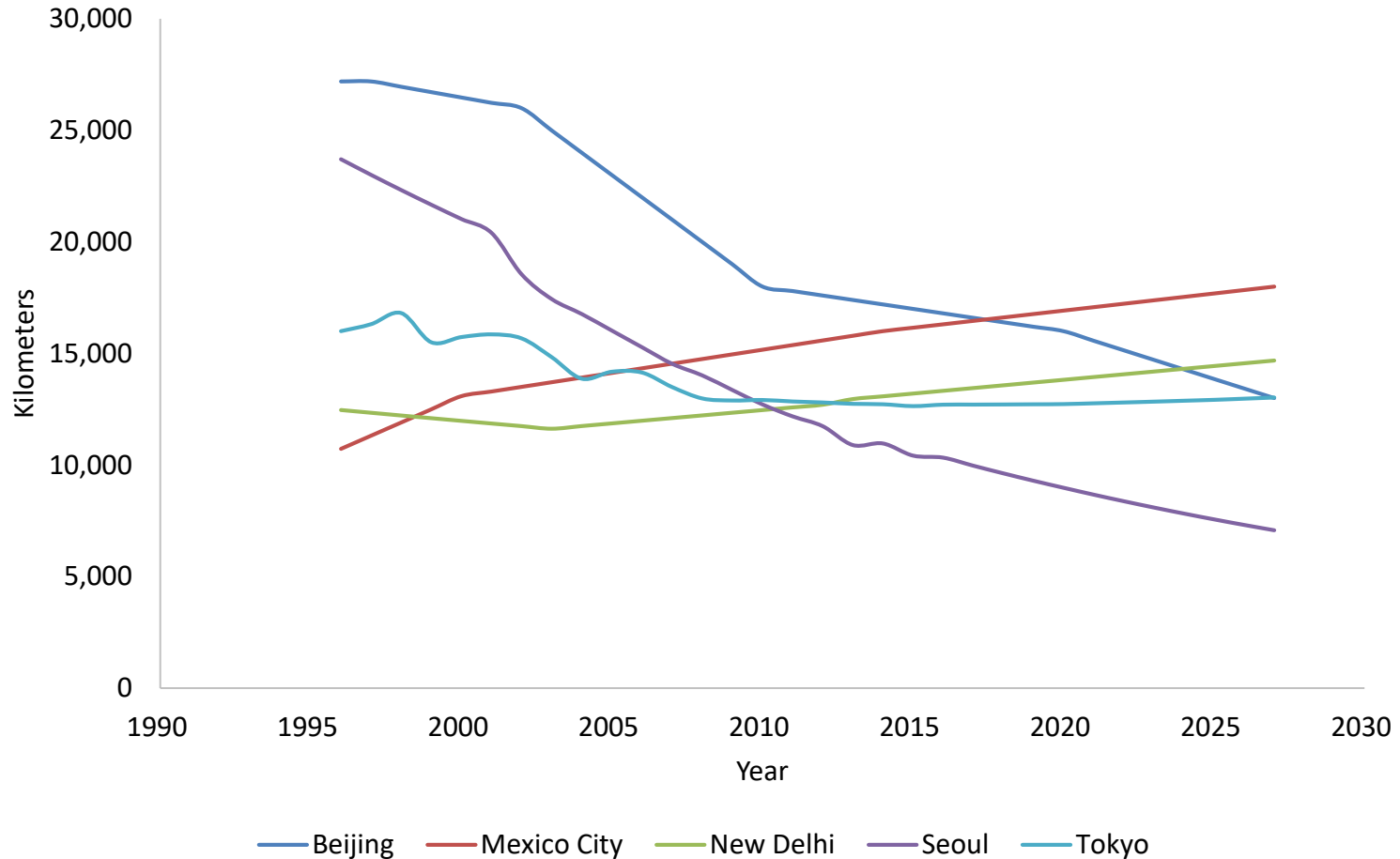
1. Project Annual Gasoline Passenger Car Population for each City (based on extrapolation of vehicle saturation levels complemented with literature citations)
2. Account for Electric Vehicle Share
3. Project vehicle distance traveled per gasoline passenger car per year
4. Multiply 1,2,3 to derive total kilometers driven by passenger cars in the city (Annual Vehicle Distance Travelled [km/year])
5. Also: Project Vehicle Retirement over time to derive new vehicles added each year.



Annual vehicle distance travelled per car



Annual Vehicle Distance Travelled per Car





5 Cities Study Model Modeled Emissions Reductions

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iBEAM Emissions Results by City and Ethanol Blend (7% EV, 50% GDI Share by 2027)

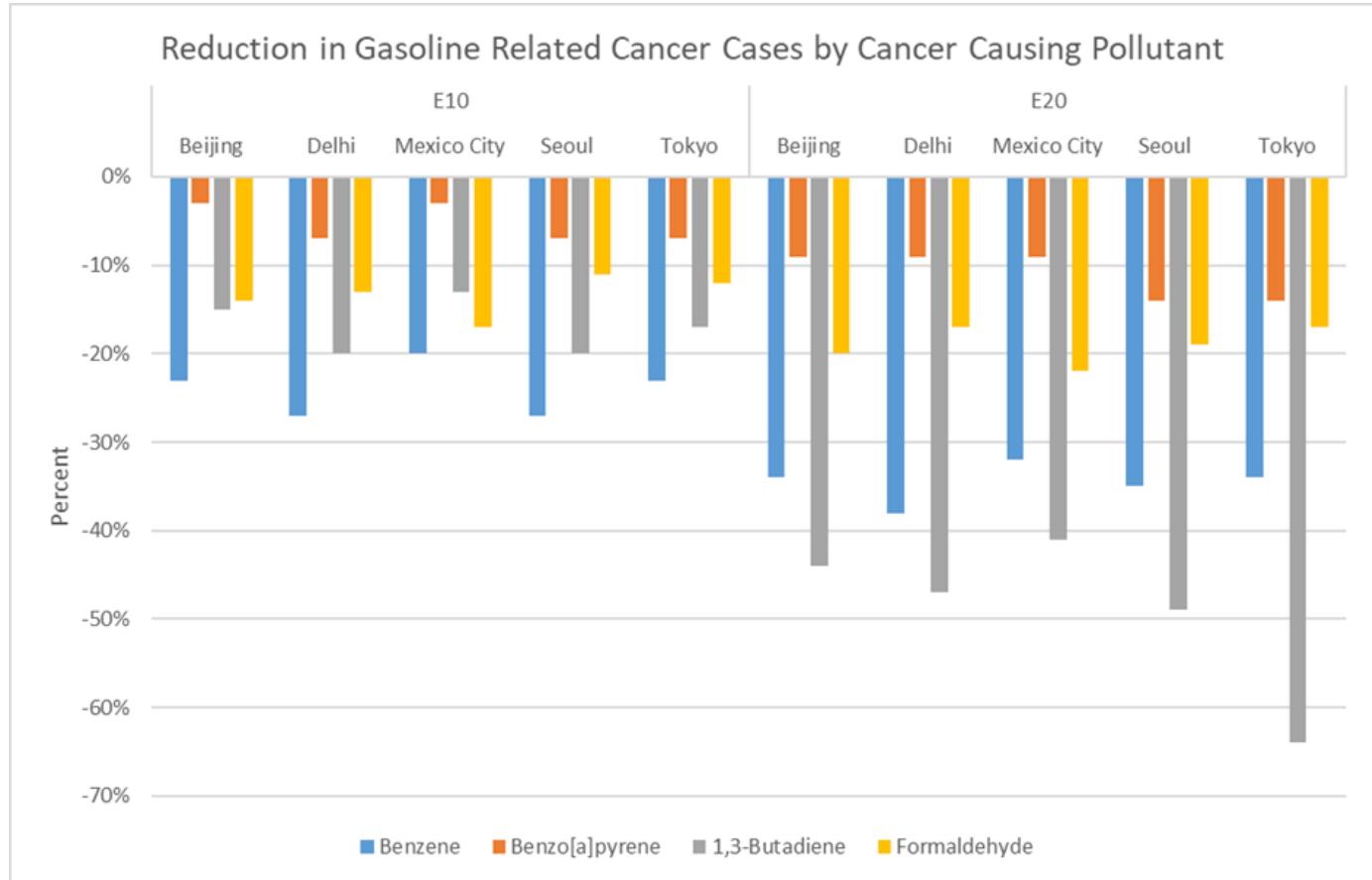


- Polycyclics and Weighted Toxins Reductions. Resulting in Lower Cancer Risk for the Cities
- Reduced CO Emissions reduces heart disease and other health effects
- No effect on NOx
- Total Hydrocarbon Reductions (THC, VOC). Resulting in likely reduced risk of Ozone Formation for the Cities

UIC International Ethanol Health Impact Study

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- Our study shows that across five global cities higher blends of ethanol achieve high reductions in cancer cases from these pollutants

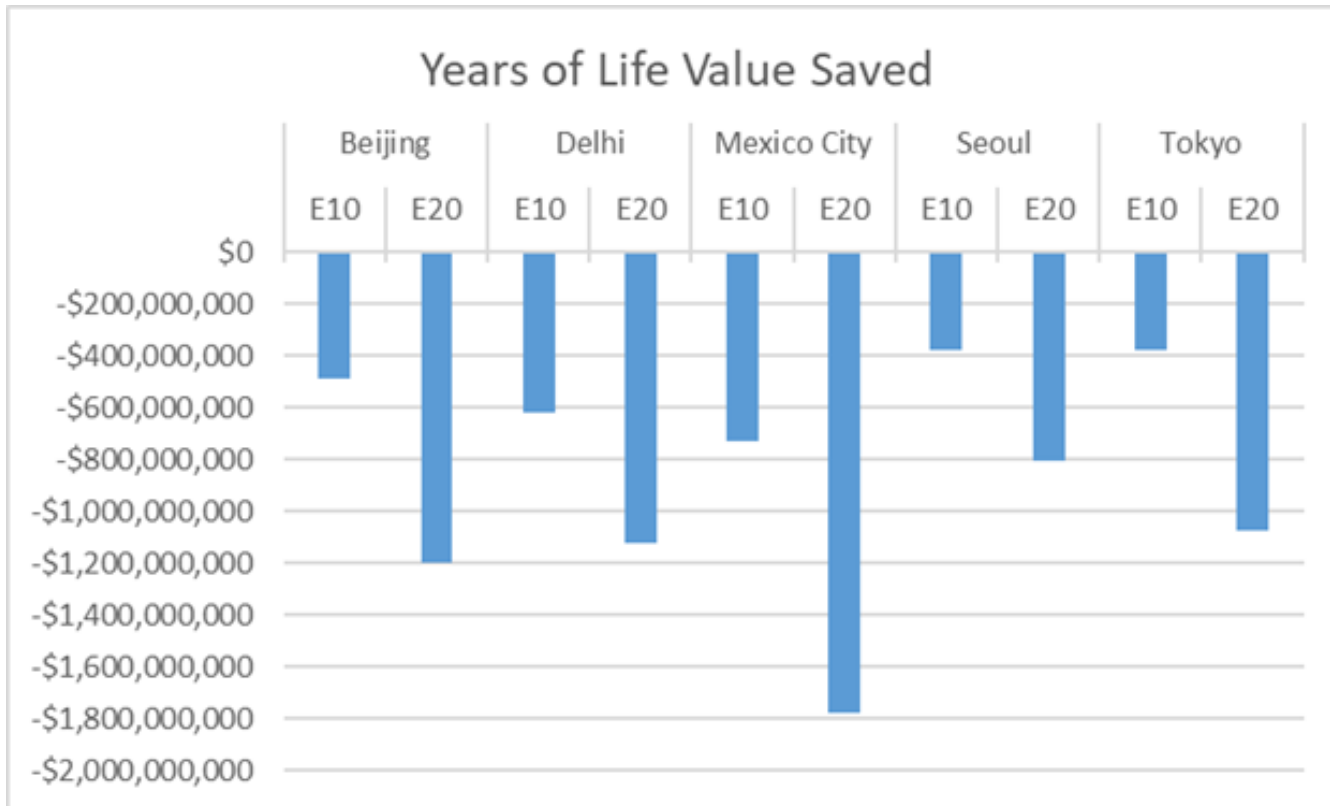


Note: Study performed in collaboration with Dr. Zigang Dong (Executive Director) and Dr. K. S. Reddy, The Hormel Institute for Cancer Research, University of Minnesota. Additional contributions were provided by Dr. Rachel Jones, Associate Professor of Environmental and Occupational Health Sciences, UIC School of Public Health.



Study Results: Reduction in Total Years of Life Lost and Reduction in Cost to Economy with Ethanol Blends

- Air Toxins Cause Years of Life Lost and with that economic damage from lost productivity
- Ethanol Overall Reduces Years of Life Lost and Reduces Economic Damage.

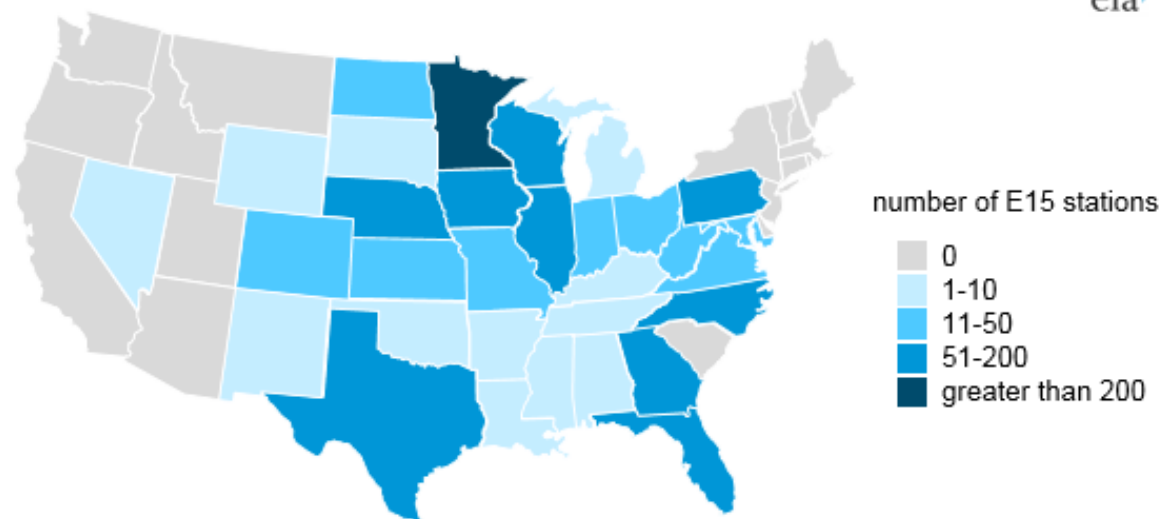


High Altitude Considerations

E10 and E15 in High Altitude States

- E10 is used in all US states including major high altitude cities like Denver, Colorado (5280 feet or 1609.3 meters)
- Colorado is also a E15 market
- Studies for Mexican market show no deteriorations of emissions group

Number of E15 stations in the U.S. Lower 48 states

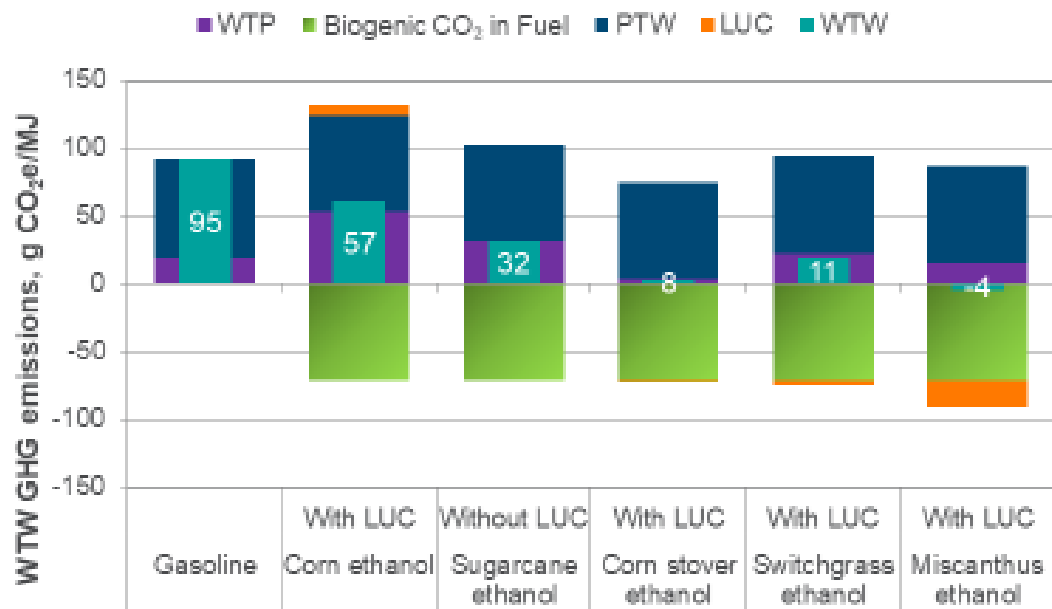


Source: US Department of Energy, July 2019:
<https://www.eia.gov/todayinenergy/detail.php?id=40095>

Greenhouse Gas Life Cycle Modeling

Comparison of Life Cycle GHG Emissions for Ethanol from Different Feedstocks Compared to Gasoline

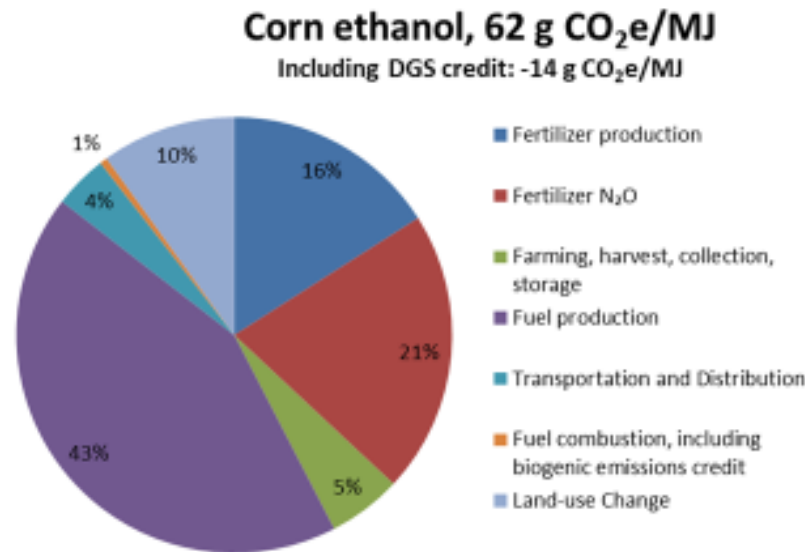
REET life-cycle GHG emissions of ethanol: feedstock is a main driver



Life Cycle GHG Emissions for Corn Ethanol by Emissions Source

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Emission breakout for corn ethanol GHGs



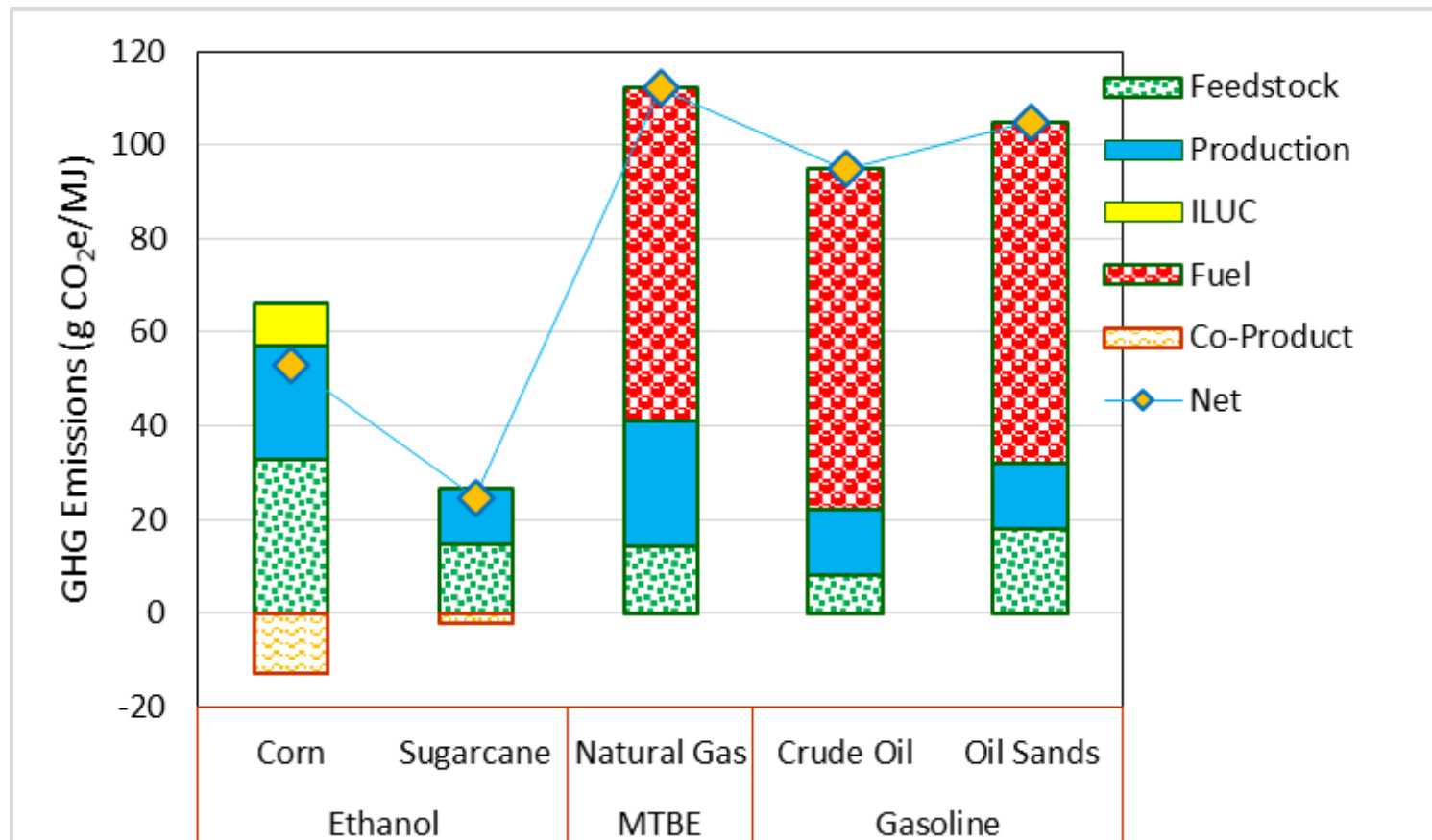
Source: Wang 2019

GHG Models Used

- The UIC ibeam model displays the energy inputs and emissions from corn ethanol over the life cycle from farming to end use. The carbon in the corn is treated as biogenic carbon neutral and the approach follows the methods for ANL's GREET model and the Biograce Model
 - The **GREET model developed by Argonne National Laboratory** is the gold standard for U.S. based life cycle analysis and contains the most up to date information on corn ethanol production. A California version of the GREET model is used for the Low Carbon Fuel Standard. An earlier version was used by the US Environmental Protection Agency for the Renewable Fuel Standard modeling.
 - **The Biograce Model** is a European life cycle model that evaluates European fuel pathways under the Renewable Energy Directive (RED). Current Japanese modeling efforts are also closely aligned with the EU RED methodology.

GHG Emissions of Pure Ethanol vs Pure MTBE

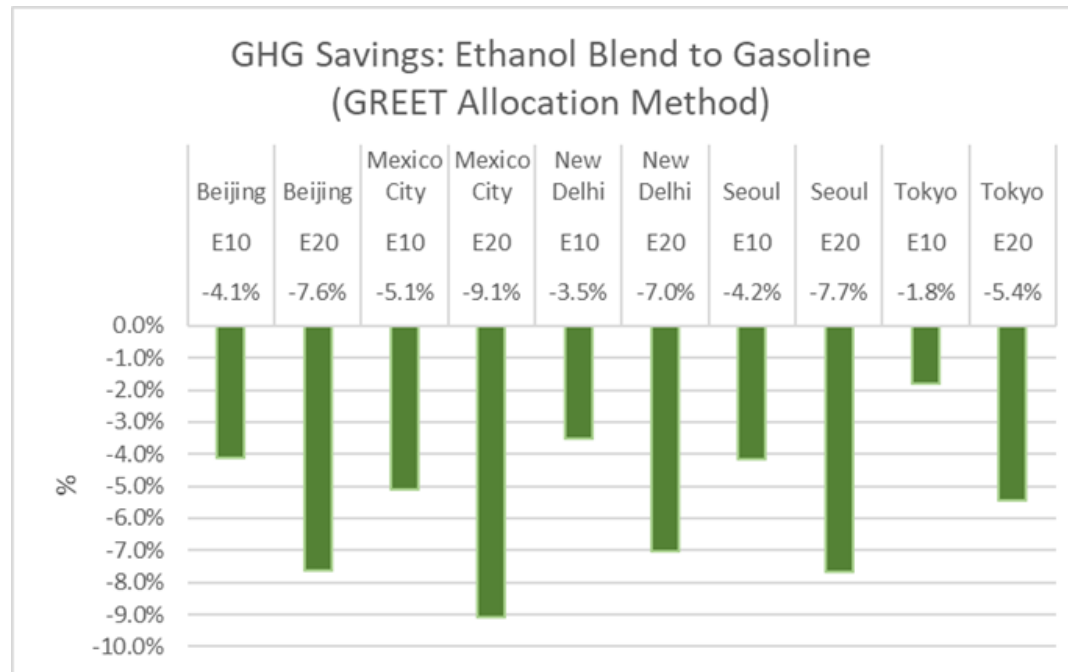
- Corn Ethanol by itself has about half the greenhouse gas emissions of MTBE



5 Cities Study GHG Summary

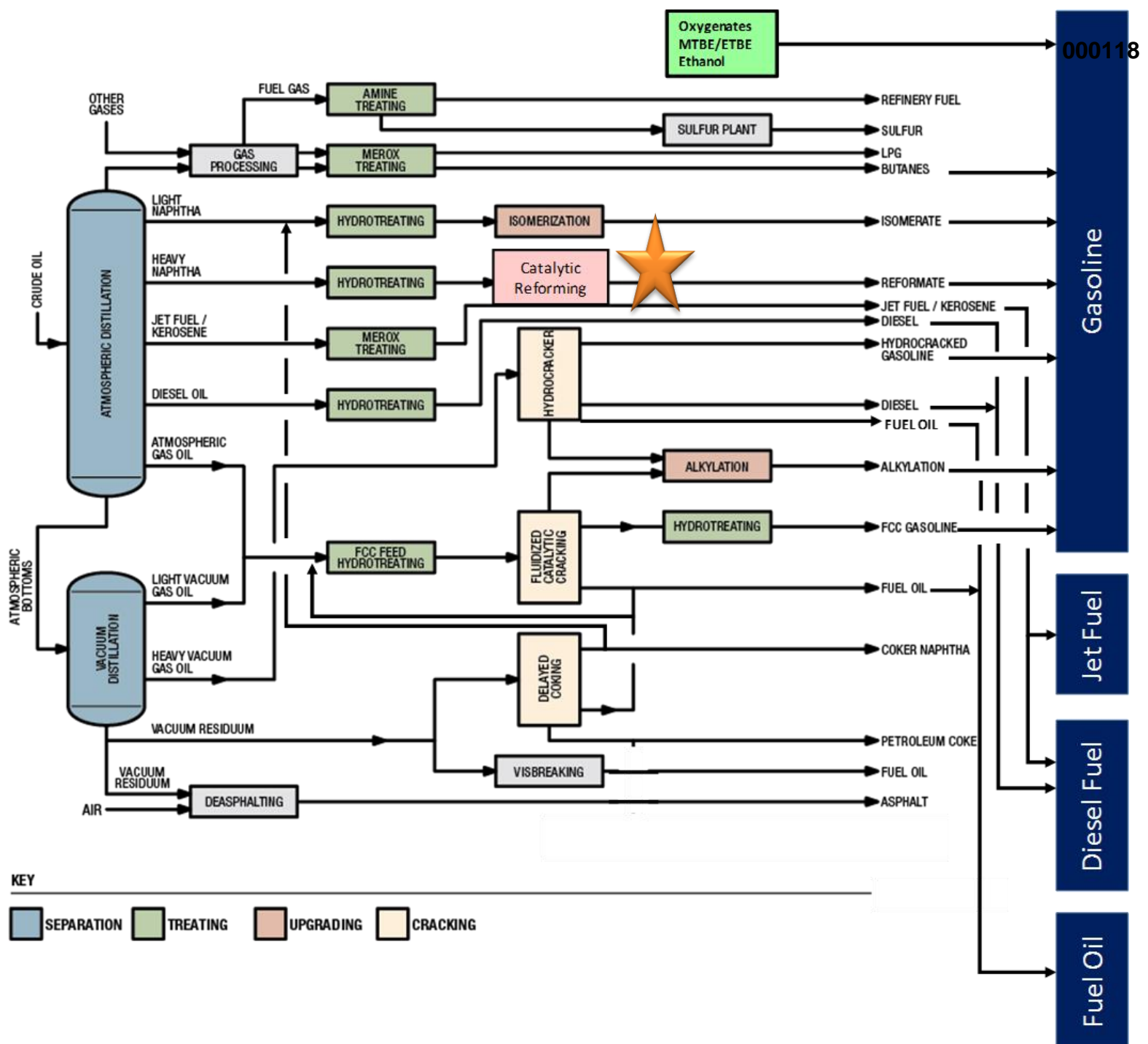


- On a total tonnage and percentage basis the study shows sizable greenhouse gas reductions for all cities and ethanol blends.
 - Cities with high fuel demand and current MTBE use can realize large GHG savings due to the high GHG intensity of the MTBE production pathway.
 - Beijing and Mexico City, for example, can save 10 and 15 million metric tonnes of CO₂ emissions, respectively, from E10 blends through 2027.
- EV Adoption: We looked at projected global EV Vehicle Stock Turnover which projected to be about 6% by 2027.
 - Ethanol adoption into the existing fleet provides about the same benefits **but right now.**



Country-Specific Refinery Profitability Considerations

First Approximation



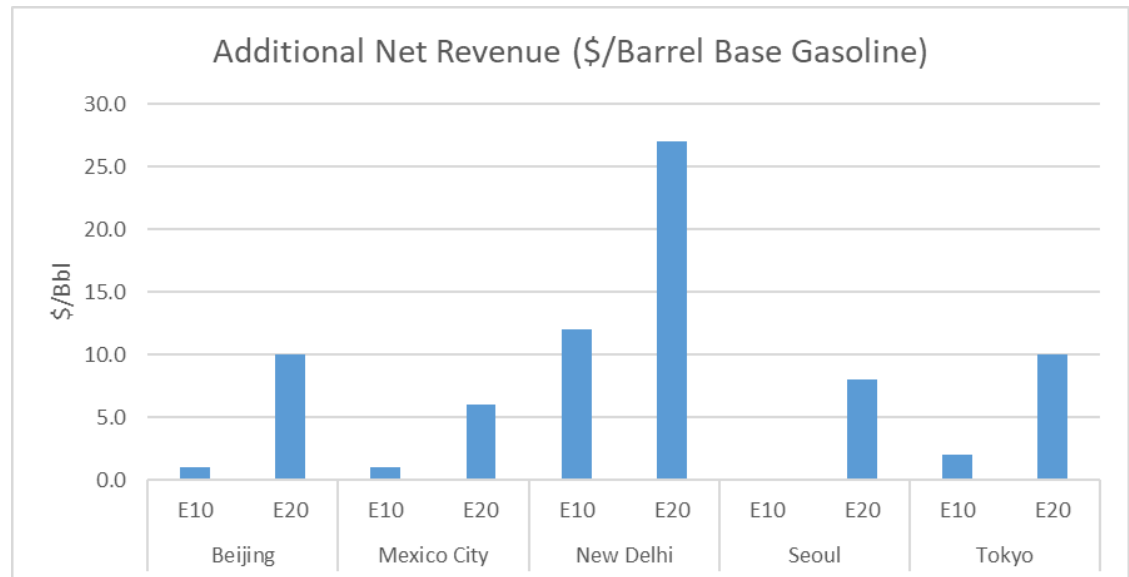
Catalytic Reforming Unit or Reformer

- When oxygenates (like ethanol in E10 or E20) are added in gasoline blending, there is less need for octane from the catalytic reforming unit and more hydrotreated naphtha feed to the catalytic reforming unit can be bypassed around this unit and blended directly to gasoline and/or the severity (RON) of the catalytic reforming unit can be reduced.
- The result is more gasoline production as a result of adding oxygenates and less processing in the catalytic reforming unit.
- However, as a result of operating at lower severity and processing less feed, there is less hydrogen produced from this unit.

Net Revenue Impact for Refiners in Each Country From Ethanol Use

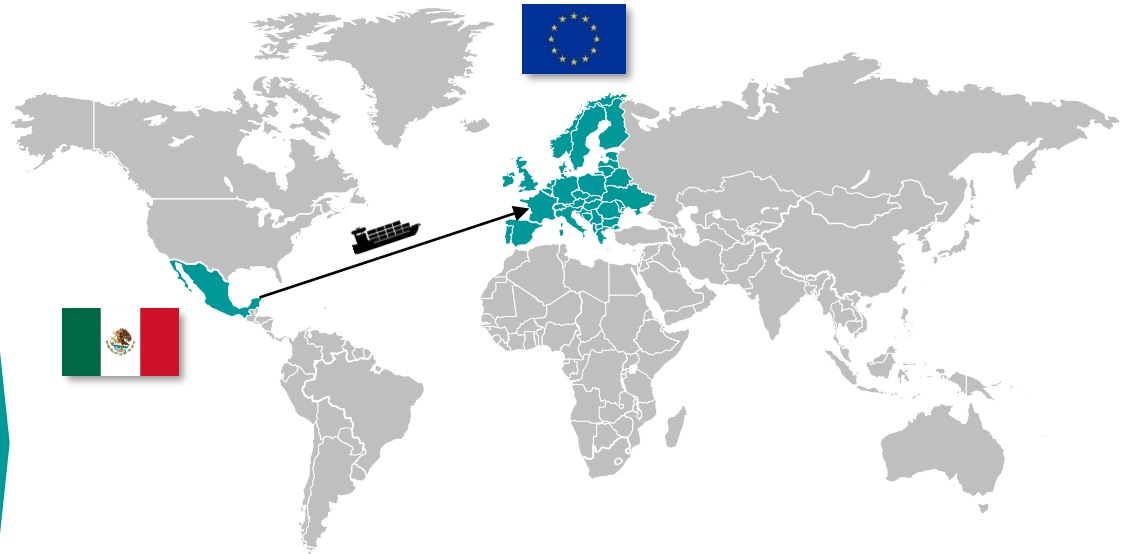


- Based on Refinery Profile the Incremental hydrogen and incremental gasoline were determined for each case vs. the Base Case for each city.
- Net revenue impact from changes in hydrogen and gasoline production relative to the Base Case for each city.
- The cost of hydrogen was calculated from the cost of natural gas using yields from a steam methane reforming unit hydrogen plant model operating on natural gas and steam.
- An estimate of additional operating costs for the hydrogen plant is included.
- The results are shown on the basis of barrels of gasoline in the Base Case for each city.
- As can be seen all ethanol blended fuels return equal or increased revenue for refiners. This is a first approximation.



Sustainability Certification

ISCC opens European Market



ISCC certificates prove compliance with European legislation under the Renewable Energy Directive and the Fuel Quality Directive.

ISCC enables certified companies to export bioenergy to the European Union.



ISCC Certification Approach for Japan

Dr Norbert Schmitz, Managing Director, ISCC System GmbH
7th ISCC Regional Stakeholder Committee North America, Las Vegas, 27 November 2018



New biofuel mandate in Japan for 2018 – 2022 (I)

- ISCC PLUS is recognised by the Japanese government to **verify compliance with sustainability requirements** for biofuels
- The recognition was announced by METI (Japanese Ministry of Trade and Industry) in the framework of presenting the **new biofuel mandate for Japan for 2018 – 2022**
- Most important changes in the new mandate:
 - GHG emission reduction target for ethanol **raised from 50% to 55%**
 - Markets opened for **U.S. corn-based ethanol** (previously, only Brazilian sugarcane-based ETBE and ethanol allowed)
 - Rationale is to **lower the overall sourcing costs** and **improve energy security** of Japan

ISCC in the USA: 76 ISCC certificates have been issued for ethanol plants

Selection



MARQUIS ENERGY

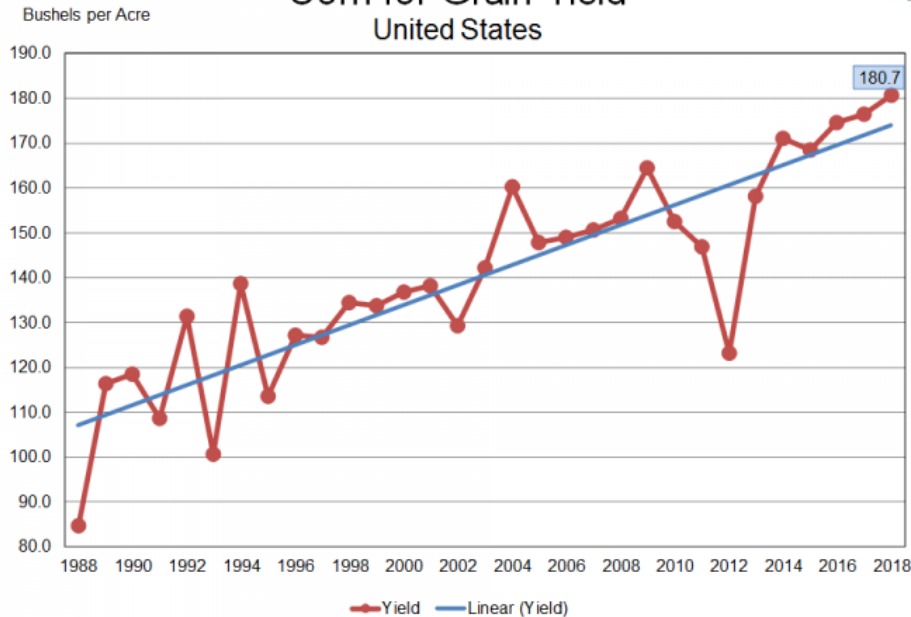


Ethanol Feedstock Flexibility

Corn Ethanol



Corn for Grain Yield
United States



USDA-NASS
10-11-18

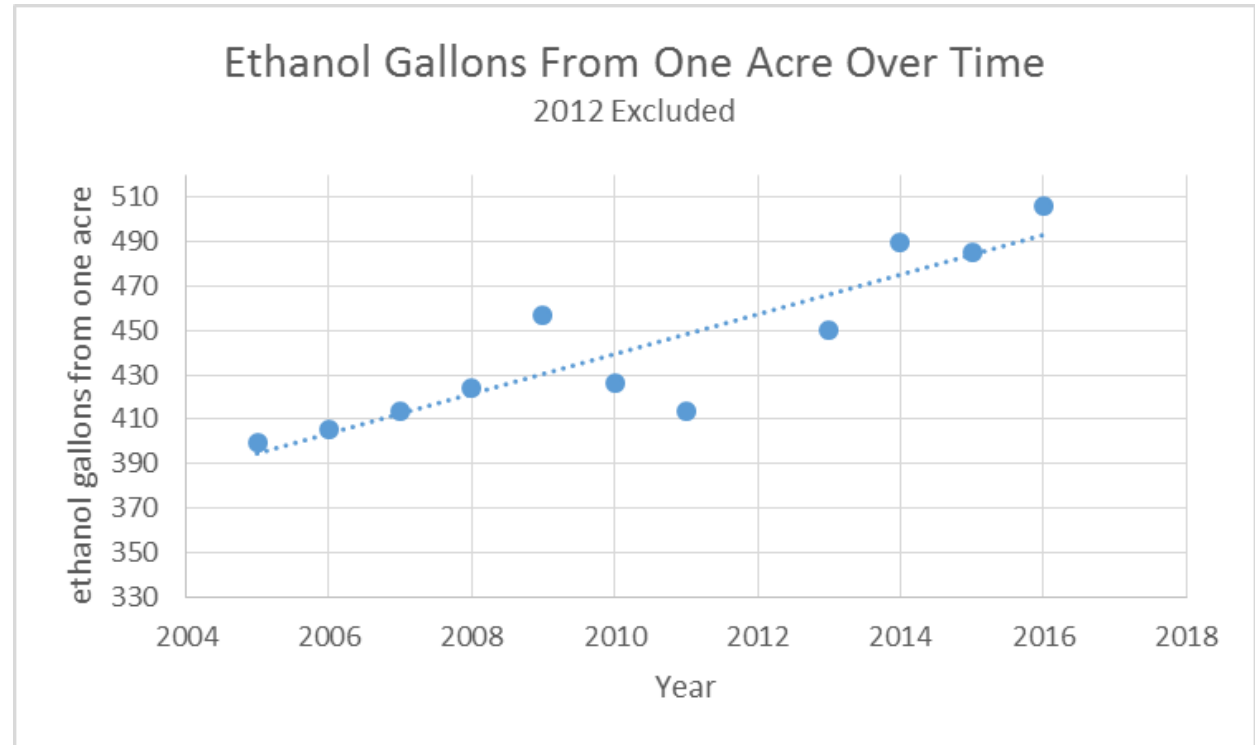
- Nearly 100 years of infrastructure build-up, research and experience
- High starch content
- Relatively easy to convert to ethanol with animal feed co-production at the ethanol plant (distillers dried grains DDG)



Due to the infrastructure and the grower intelligence, corn is a highly suitable crop for expanded uses such as bioethanol

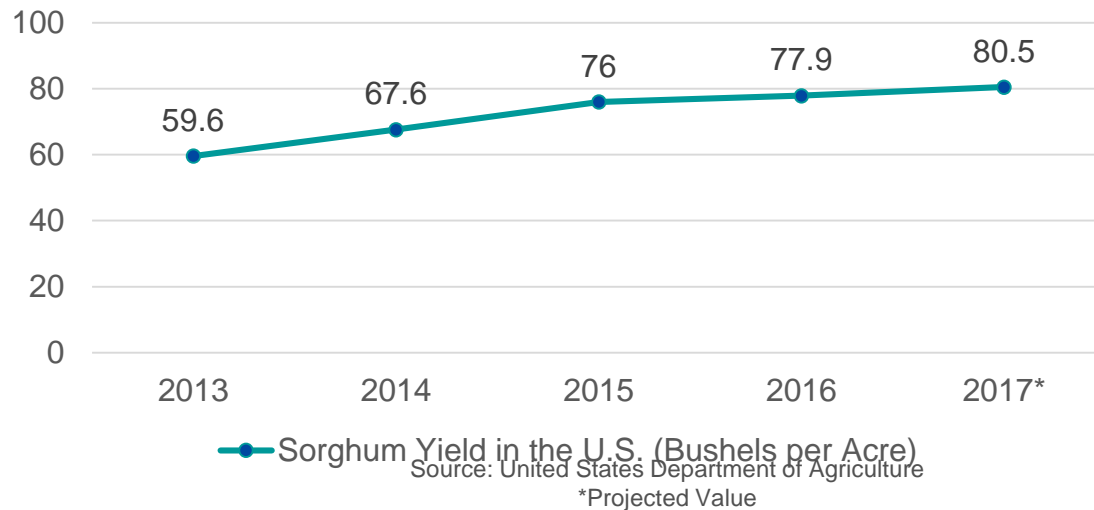
Corn Ethanol: Ethanol Gallons from One Acre Over time

- Compound effect: corn yield increases **and** ethanol output per bushel increases result in more gallons of ethanol “harvested” from one acre
- Biofuels production drives agricultural investment



Sorghum Ethanol

Sorghum Yield in the U.S. (Bushels per Acre)



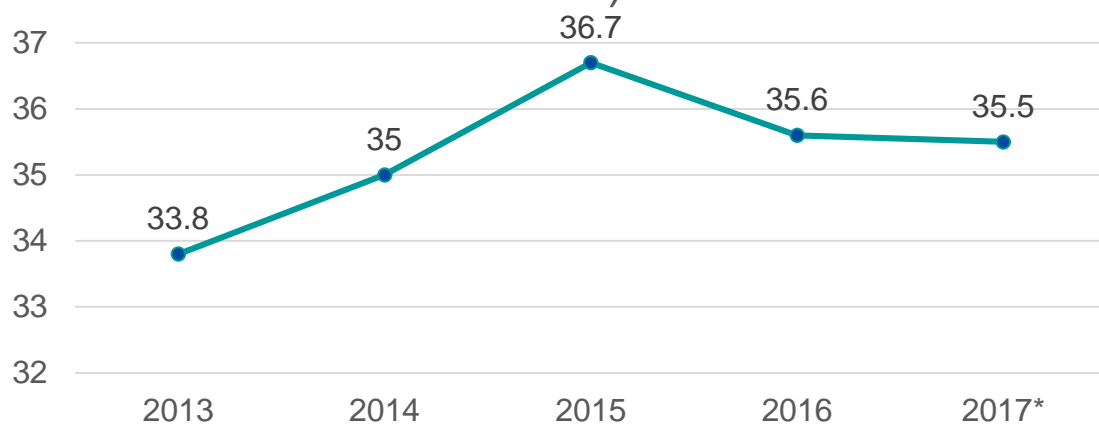
- **Drought** Tolerant
- Grows in temperate to tropical climate
- Suitable to grow on **over 80% of the world's agricultural land**
- Lower bushel yield per acre but same ethanol yield per bushel at the plant
- In ethanol production: virtually **interchangeable feedstock with corn** at the ethanol plant
- Sorghum DDGS tend to be **higher in protein and slightly lower in fat** than corn DDGS, while starch content remains **basically the same.**

Sorghum is a tolerant crop to both marginal lands and environmental conditions and therefore highly important as high yield bioethanol feedstock



Sugarcane Ethanol

Sugarcane Yield in the U.S. (Tons per Acre)



—●— Sugarcane Yield in the U.S. (Tons per Acre)

Source: United States Department of Agriculture

*Projected Value

- Efficient bioenergy crop for the tropical and subtropical regions
- Sugarcane ethanol plant produce excess electricity



Sugarcane is a highly efficient crop that is suitable for the production of affordable and low-carbon biofuel

Summary Points

- Corn ethanol in gasoline blends...
 - reduces Greenhouse Gas Emissions on a life cycle basis .
 - Particularly high GHG reductions where ethanol replaces MTBE because of the high GHG intensity of those compounds.
 - Continued advances in agriculture including conservation management practices as well as advances in biorefining continuously reduces GHG emissions of corn ethanol relative to gasoline.
 - reduces tailpipe emissions of key pollutant groups and individual, high impact pollutants such as PAHs and weighted air toxins
 - Reduces cancer cases and treatment costs
- Reduces tailpipe and Greenhouse Gas Emissions right now with the existing vehicle fleet. With electric vehicles we have to wait a long time to realize emissions reductions since the vehicle stock needs to change.
- Sustainability of bioethanol feedstock production can be verified.

The 5 Cities Study

UIC ENGINEERING

**THE
UNIVERSITY OF
ILLINOIS
AT
CHICAGO**



**US Grains Council
March 2019**

Steffen Mueller, PhD, Principal Economist

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Primer: Vehicle Emissions of Toxic Compounds

EPA-420-R-16-016
November 2016

Tailpipe Emissions Reductions Start at the Refinery Level

- Gasoline contains a large amount of aromatic hydrocarbons that are added to gasoline because they have relatively high octane values and therefore serve as anti-knock agents in vehicle engines.
- Some aromatics are highly **toxic compounds**.
- Ethanol also has a high octane value and contains no aromatic compounds.
 - It therefore **substitutes and dilutes** aromatics in gasoline.
 - Moreover, ethanol also **alters the distillation curve** resulting in an adjustment of the distillation properties of the fuel with, for example a higher volume fraction of the fuel distilled at 200 degrees Fahrenheit.
 - This effect further **reduces tailpipe emissions** in a vehicle.

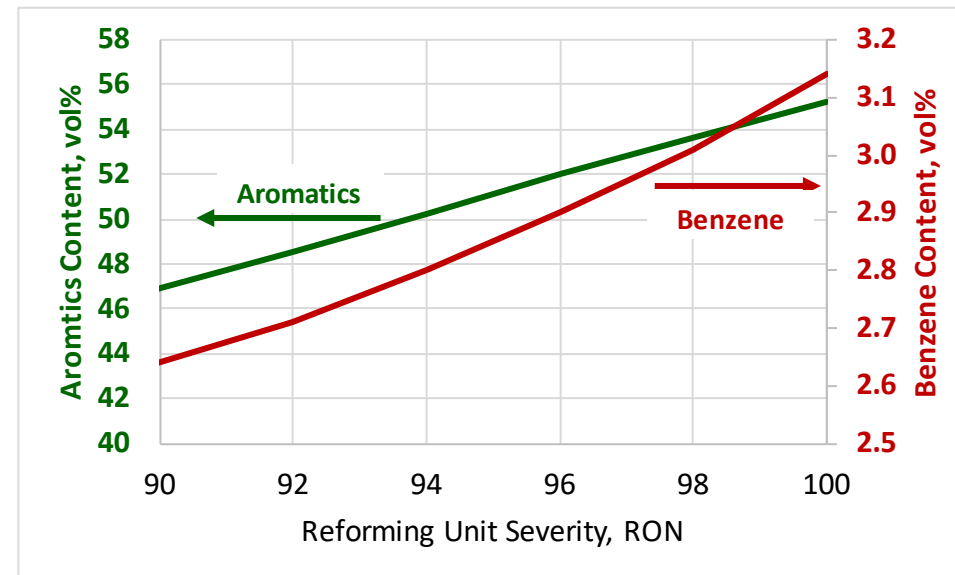


Tailpipe Emissions Reductions from Corn Ethanol

What happens at the Refinery when we produce Fuels that Meet Octane Specifications for our Car Engines?


- The Catalytic Reforming Unit within a Refinery is the major producer of high octane (measured in research octane number “RON”) for gasoline blending.
- Generally the higher the desired RON number the more aromatics are added.
- With ethanol blended into gasoline the reforming unit severity is adjusted to lower RON numbers, which generally results in lower benzene and aromatics content

Many aromatics are toxics, carcinogenic, and have other adverse health effects.



U.S. Domestic Blending Behavior

- United States Environmental Protection Agency “Fuel Trends Report” (Released October 2017) <https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockkey=P100T5J6.pdf>,
- Page 8: "Ethanol's high octane value has also allowed refiners to **significantly reduce the aromatic content of the gasoline**, a trend borne out in the data. Other direct effects of blending in ethanol are described below."



United States Environmental Protection Agency

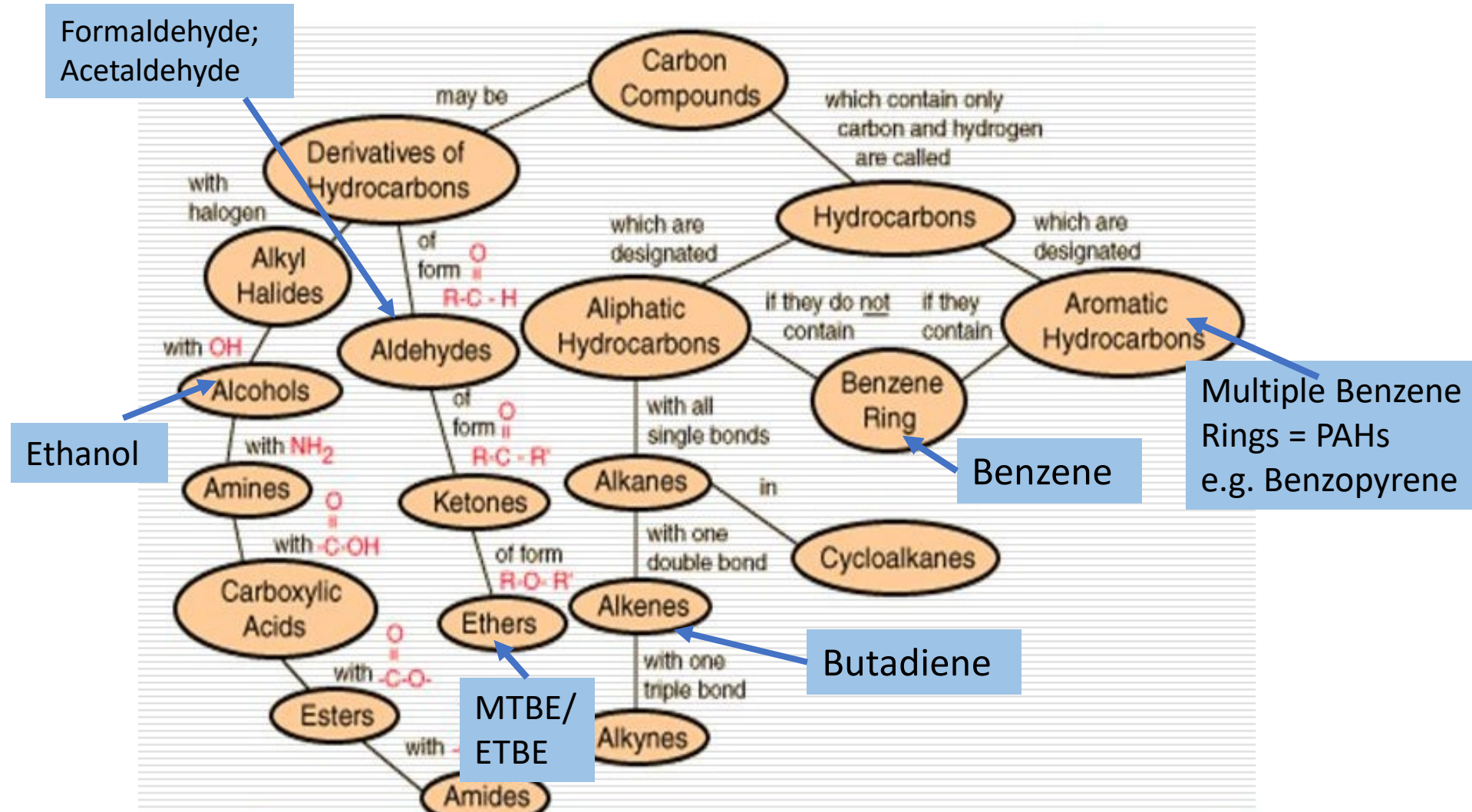
CG= Conventional Gasoline

Property	1990	2000		2016 RFG		2016 CG	
	Baseline	RFG Average	CG Average	Average	95%	Average	95%
Sulfur (ppm)	339	126	324	23.1	48.2	22.5	51.0
Benzene (vol%)	1.53	0.59	1.15	0.51	0.86	0.63	1.27
RVP (psi)	8.7	6.78	8.27	7.1	7.47	9.08	10.0
Aromatics (vol%)	32	19.3	28.5	17.12	27.3	21.76	32.1
E200 (vol%)	41	47.6	45.2	47.9	54.8	53.0	61.4
E300 (vol%)	83	84.7	80.7	85.6	92.0	84.8	91.1
Olefins (vol%)	13.1	10.6	11.8	10.5	18.7	8.38	16.4
Ethanol (vol%)	0.6	1.14	0.84	9.61	9.97	9.28	9.8

Winter gasoline

CG= Conventional Gasoline; RFG= Reformulated Gasoline

Groups and Derivatives of Hydrocarbons



<https://slideplayer.com/slide/4217696/>

Primer

- Aldehyde:
an organic compound containing the group —CHO , formed by the oxidation of alcohols. Typical aldehydes include methanal (formaldehyde) and ethanal (acetaldehyde). Many aldehydes are either gases or volatile liquids.
- Aromatic Hydrocarbons:
Aromatic hydrocarbons are those which contain one or more benzene rings. The name of the class comes from the fact that many of them have strong, pungent aromas.
 - Polycyclic aromatic hydrocarbons (PAHs, also polyaromatic hydrocarbons or polynuclear aromatic hydrocarbons):
Are hydrocarbons—organic compounds containing only carbon and hydrogen—that are composed of multiple aromatic rings (organic rings in which the electrons are delocalized). The simplest such chemicals are naphthalene, having two aromatic rings, and the three-ring compounds anthracene and phenanthrene. Benzopyrene is one of the most carcinogenic PAHs.
- Butadiene, either of two aliphatic organic compounds that have the formula C_4H_6 . At atmospheric conditions, 1,3-butadiene exists as a colorless gas.

Vehicle Emissions of Toxic Compounds

Many vehicle emissions compounds identified as air toxics in the National Emission Inventory (NEI) and National Air Toxics Assessment (NATA). Toxics can come out of 4 categories:

- 1) Volatile Organic Compounds (VOC): EPA defines VOC as any compound of carbon, excluding carbon monoxide, carbon dioxide, (some other exclusions)
- 2) Polycyclic aromatic hydrocarbons (PAHs): This category is defined as hydrocarbons containing fused aromatic rings. These compounds can be measured in the **gaseous phase, particulate phase, or both**, depending on properties of the compound, particle characteristics and conditions in the exhaust stream or the atmosphere.
- 3) Dioxins and furans and
- 4) Metals

EPA-420-R-16-016
November 2016

Vehicle Emissions of Toxic Compounds

- Selected Volatile Organic Compounds

Pollutant
Benzene
Ethanol
1,3-Butadiene
Formaldehyde
Acetaldehyde
Acrolein
Methyl-Tertiary-Butyl Ether (MTBE)
2,2,4-Trimethylpentane
Ethyl Benzene
Hexane
Propionaldehyde
Styrene
Toluene
Xylene(s) ¹

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Vehicle Emissions of Toxic Compounds

- Polycyclic Aromatic Hydrocarbons (PAHs)

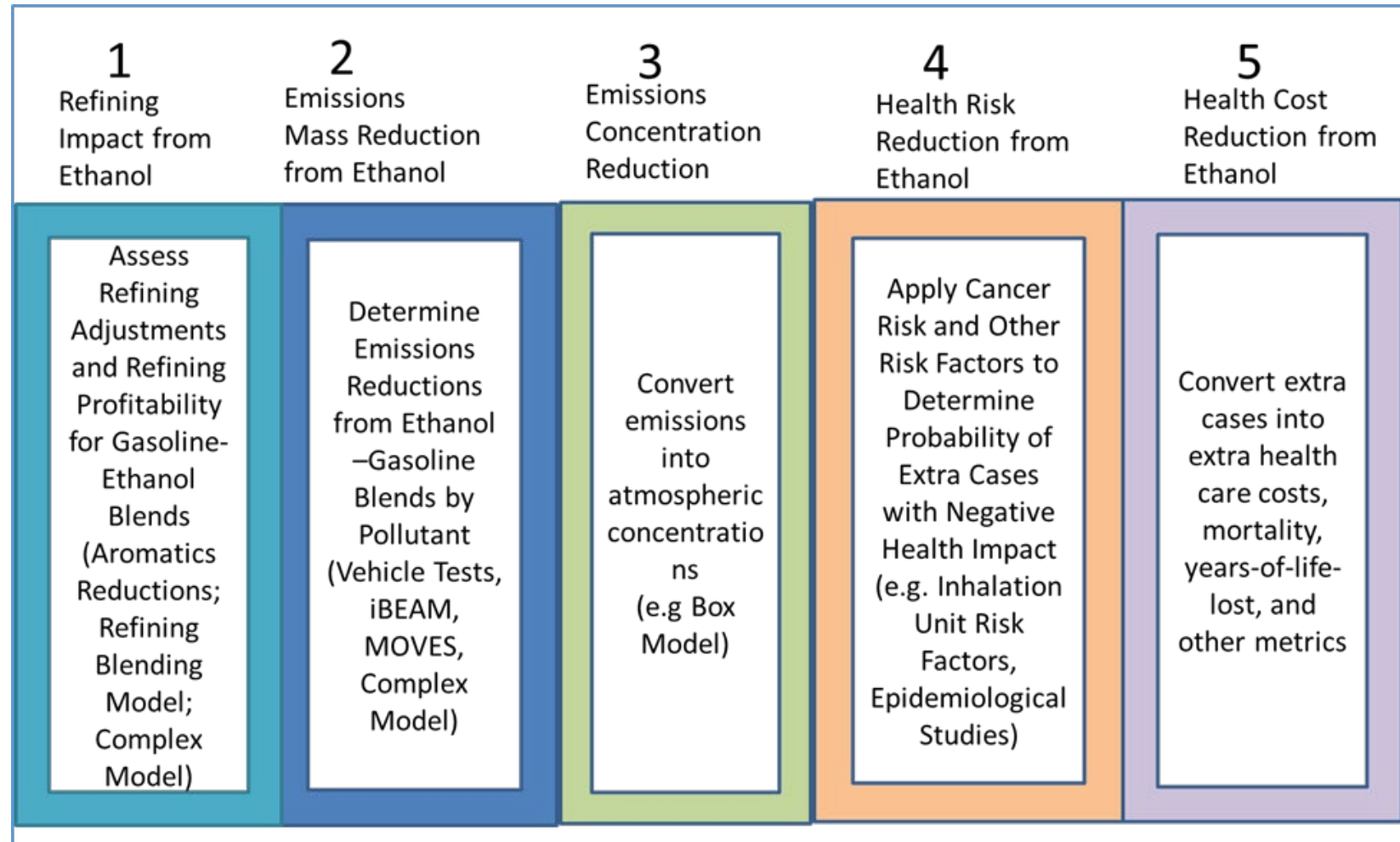
Pollutant
Acenaphthene
Acenaphthylene
Anthracene
Benzo(<i>a</i>)anthracene
Benzo(<i>a</i>)pyrene
Benzo(<i>b</i>)fluoranthene
Benzo(<i>g,h,i</i>)perylene
Benzo(<i>k</i>)fluoranthene
Chrysene
Dibenzo(<i>a,h</i>)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3, <i>c,d</i>)pyrene
Naphthalene
Phenanthrene
Pyrene

EPA-420-R-16-016
November 2016

Vehicle Emissions of Toxic Compounds

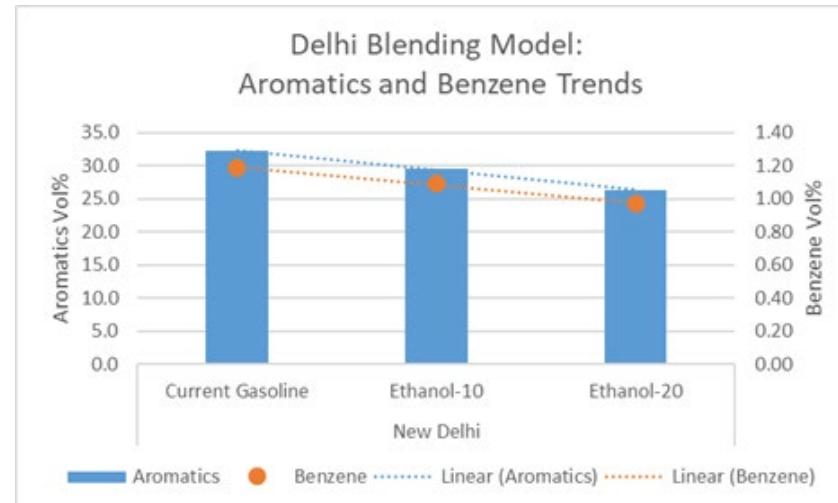
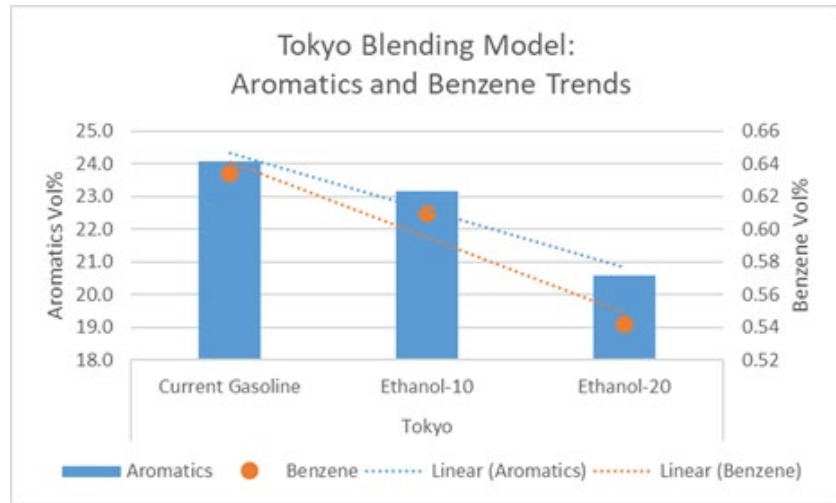
- Toxics are emitted through exhaust, crankcase and evaporative processes, and by both light-duty and heavy-duty vehicles, operating on gasoline, diesel and compressed natural gas (CNG) fuels.
- In emissions inventory models such as MOVES emissions of toxic compounds (except for metals and dioxins/furans), are estimated as
 - fractions of the emissions of VOC, or
 - for toxic species in the particulate phase, fractions of total organic carbon < 2.5 μm (OC2.5).

Multi Step Modeling Process

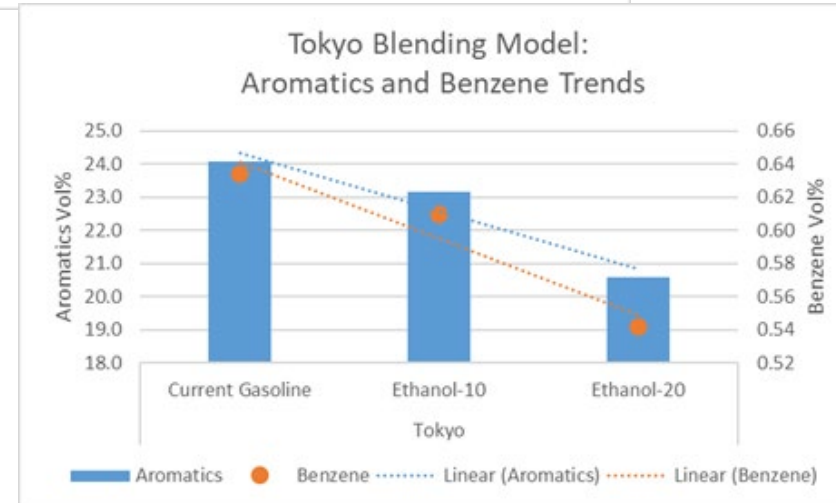




Refining Impact

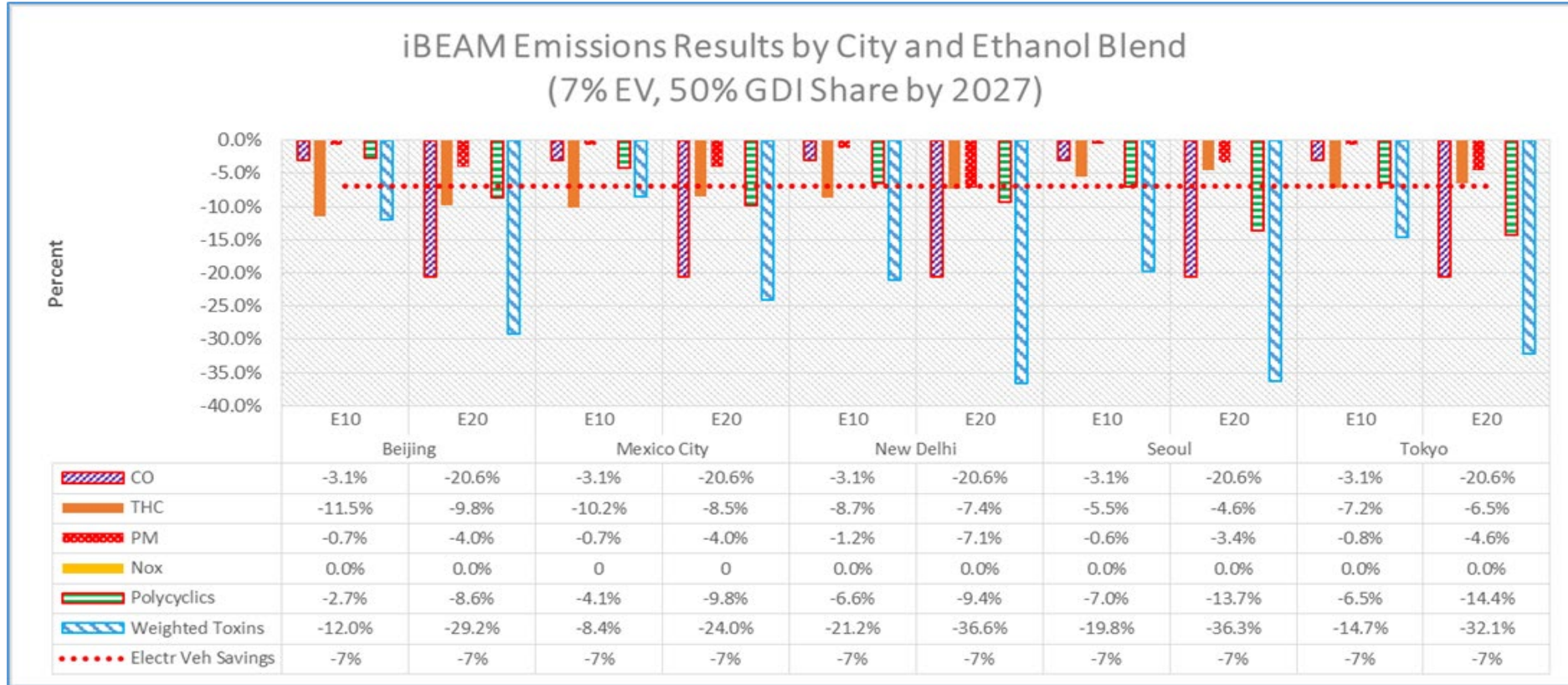


International Blending Model confirms that ethanol blended into gasoline reduces the reforming unit severity at refineries which results in lower benzene and aromatics content





5 Cities Study Model Modeled Emissions Reductions



- Polycyclics and Weighted Toxins Reductions. Resulting in Lower Cancer Risk for the Cities
- Reduced CO Emissions reduces heart disease and other health effects
- No effect on NOx
- Total Hydrocarbon Reductions (THC, VOC).
Resulting in likely reduced risk of Ozone Formation for the Cities



From Emissions to Health Impacts: Carcinogenicity of Selected Toxics Affected by Ethanol Blends

000132 vta

- **Benzene**
 - is a well-established cause of cancer in humans. The International Agency for Research on Cancer has classified benzene as carcinogenic to humans (Group 1). Benzene causes **acute myeloid leukemia** (acute non-lymphocytic leukemia), and there is limited evidence that benzene may also cause acute and chronic lymphocytic leukemia, **non-Hodgkin's lymphoma** and multiple myeloma.
Source: World health organization
- **1,3-butadiene**
 - “Studies have consistently shown an association between occupational exposure to 1,3-butadiene and an increased incidence of **leukemia**.” Source: <https://www.cancer.gov/about-cancer/causes-prevention/risk/substances/butadiene>
 - The Department of Health and Human Services (DHHS), IARC, and EPA have determined that 1,3-butadiene is a human carcinogen. Studies have shown that workers exposed to 1,3-butadiene may have an increased risk of cancers of the stomach, blood, and lymphatic system. Source: CDC ATSDR Database
- **Formaldehyde**
 - **Probable human carcinogen, based on limited evidence in humans**, and sufficient evidence in animals. IARC: Carcinogenic to humans . NTP: Reasonably anticipated to be a human
Source: CDC ATSDR Database
- **Acetaldehyde**
 - Based on increased evidence of **nasal tumors in animals** and adenocarcinomas.
Source: US EPA
 - Note: adenocarcinomas are most prevalent in esophageal cancer, pancreas, prostate cancer.
- **Benzo[a]pyrene (BaP); a polycyclic aromatic hydrocarbon PAH**
 - The carcinogenicity of certain PAHs is well established in laboratory animals. Researchers have reported increased incidences of skin, lung, bladder, liver, and stomach cancers, as well as injection-site sarcomas, in animals. Animal studies show that certain PAHs also can affect the hematopoietic and immune systems (ATSDR)
 - Tumor site(s): **Lung**, Gastrointestinal, Respiratory
 - Tumor type(s): **Squamous cell neoplasia in the larynx, pharynx, trachea, nasal cavity, esophagus, and forestomach**. (Thyssen et al., 1981). Source: https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=136



Converting Emissions Mass Reductions to Cancer Risk Reductions

- Convert emissions mass reductions to concentration reductions using atmospheric model (box model)
- Apply Inhalation Unit Risk Factors: excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 microgram/m³ air.

Pollutant	IUR Factor (risk per ug/m ³)	Relative Potency
Acetaldehyde	2.7×10^{-6}	0.002
Benzene	2.9×10^{-5}	0.026
Benzo[a]pyrene	1.1×10^{-3}	1.00
1,3-Butadiene	1.7×10^{-4}	0.155
Formaldehyde	6.0×10^{-6}	0.005



Source: California Environmental Protection Agency



Study Results: Reduction in Lifetime Cancer Cases with Ethanol Blends

- Air Toxins Cause Increases Cancer Cases
- Ethanol Overall Reduces Cancer Cases from Selected Pollutants. Note slight increase in cancer cases from acetaldehyde is outweighed by significant decreases from other pollutants.

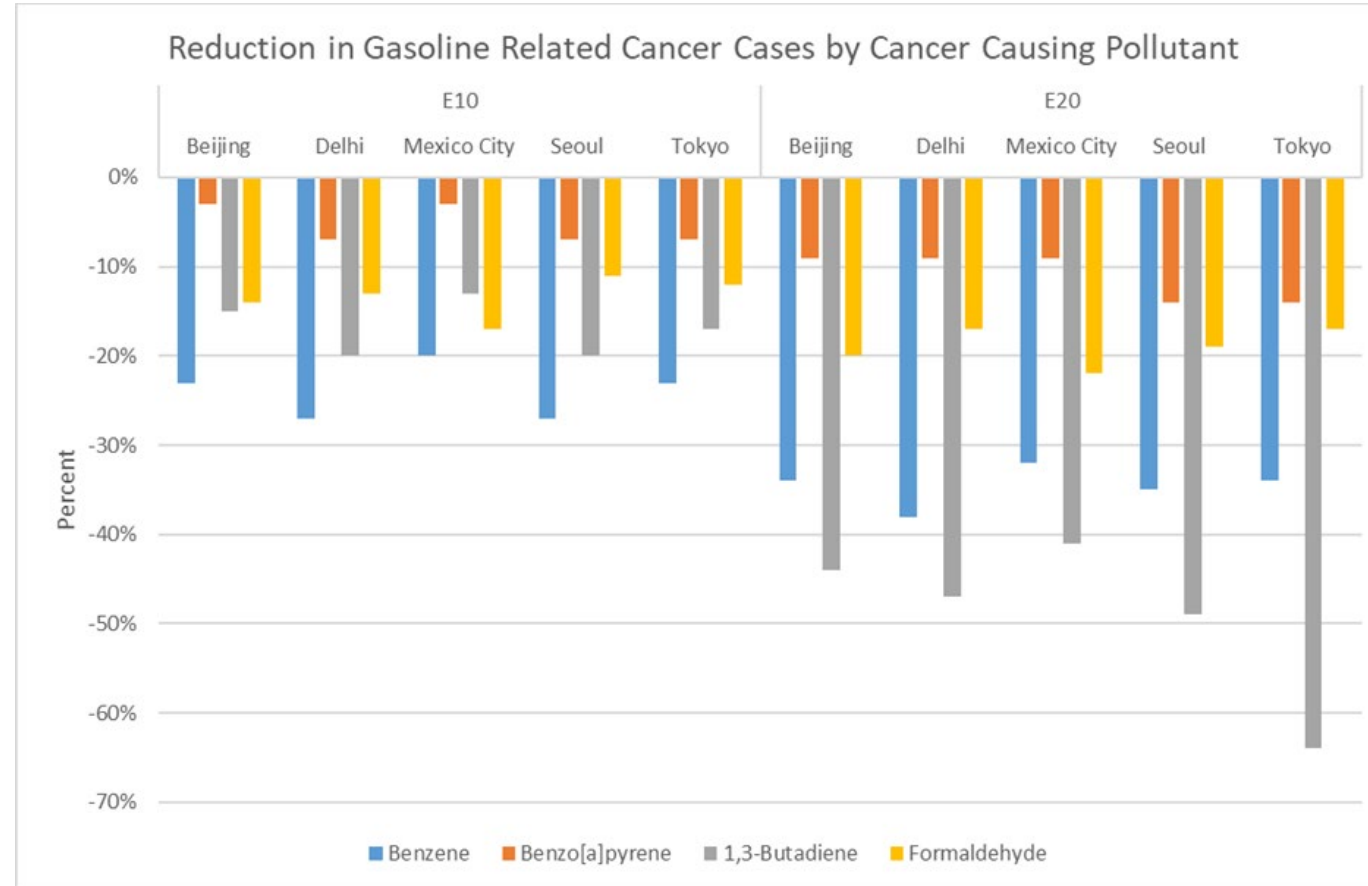
	Change in Number of Cancer Cases by Pollutant				
	Acetaldehyde	Benzene	Polycyclics	1,3-Butadiene	Formaldehyde
<i>E10 Fuel</i>					
Beijing	5.2	-79.0	-30.6	-97.9	-3.3
Delhi	3.9	-95.7	-59.8	-107.8	-2.2
Mexico City	10.5	-123.2	-43.5	-142.8	-9.5
Seoul	2.9	-33.9	-40.3	-83.5	-1.4
Tokyo	2.7	-39.4	-42.5	-76.5	-1.5
<i>E20 Fuel</i>					
Beijing	13.7	-116.3	-99.6	-287.4	-4.6
Delhi	10.7	-136.9	-85.4	-251.7	-2.8
Mexico City	27.5	-192.6	-95.7	-456.7	-12.5
Seoul	7.3	-44.4	-79.2	-207.7	-2.4
Tokyo	7.3	-57.6	-93.4	-288.9	-2.1



UIC International Ethanol Health Impact Study

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- Our study shows that across five global cities higher blends of ethanol achieve high reductions in cancer cases from these pollutants

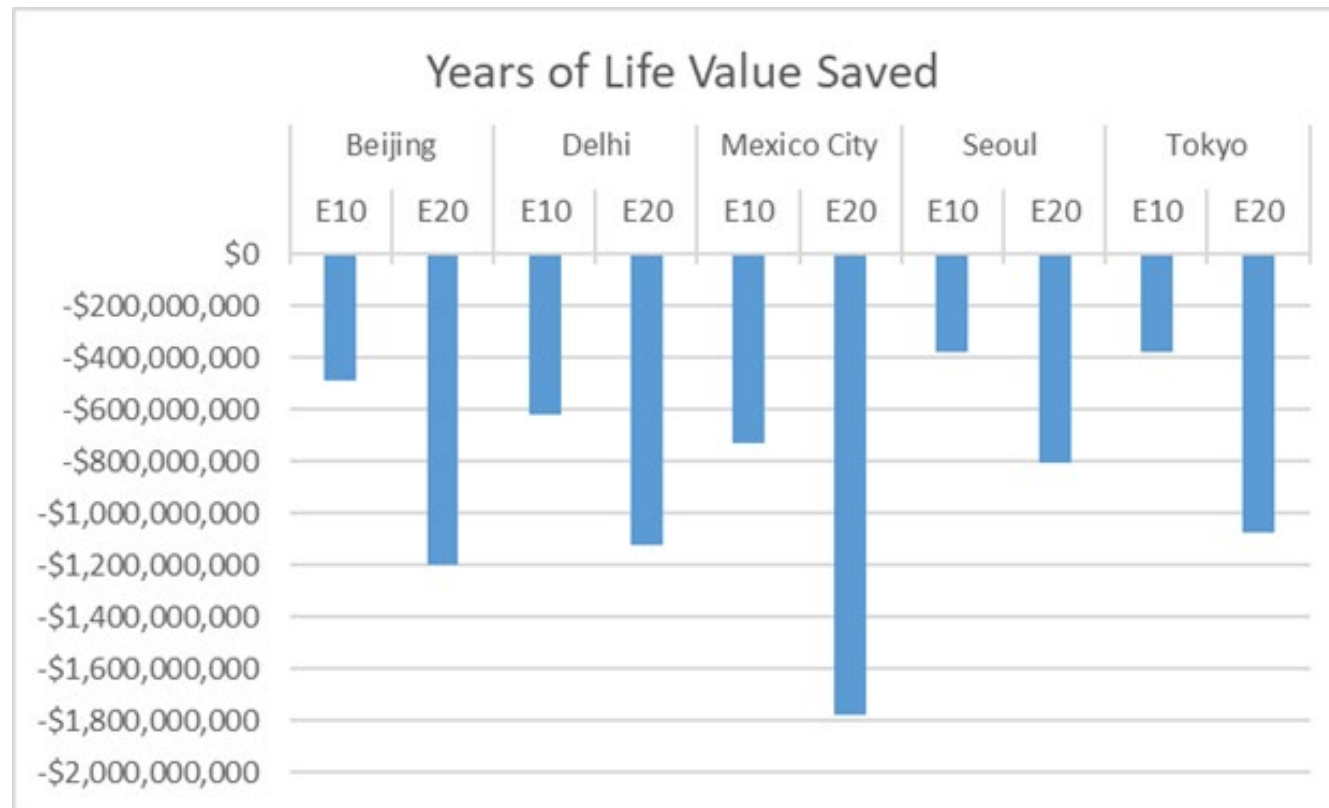


Note: Study performed in collaboration with Dr. Zigang Dong (Executive Director) and Dr. K. S. Reddy, The Hormel Institute for Cancer Research, University of Minnesota. Additional contributions were provided by Dr. Rachel Jones, Associate Professor of Environmental and Occupational Health Sciences, UIC School of Public Health.



Study Results: Reduction in Total Years of Life Lost and Reduction in Cost to Economy with Ethanol Blends

- Air Toxins Cause Years of Life Lost and with that economic damage from lost productivity
- Ethanol Overall Reduces Years of Life Lost and Reduces Economic Damage.



Context

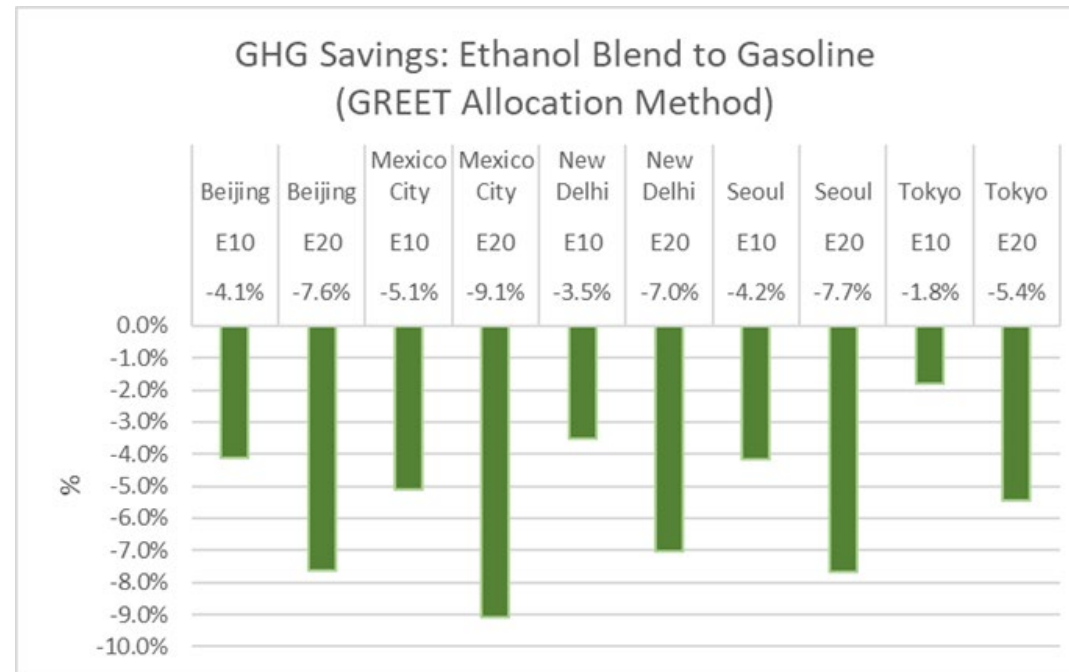


- Ethanol fuel blends were estimated to yield a net reduction of approximately **200-300 cancers** per city, associated with several of the key pollutants varying among cities and between ethanol fuel blends.
 - Save several thousand years of life lost in each city and an additional tens of millions of dollars of direct healthcare costs for cancer treatment.
- For context, other regulatory actions prevent numbers of cancers that seem modest relative to the total burden of disease.
 - Example 1: Permissible Exposure Limit for 1,3-butadiene to 1 ppm was estimated by OSHA to avoid **59 cancers among approximately 9000 exposed workers over a working lifetime of 45 years, or 1.3 cancers per year**. Costs to employers to comply with the new 1,3-butadiene standard was estimated to be \$2.9 million annually, or approximately \$2.3 million per cancer avoided per year.
 - Example 2: The **reduction in the Permissible Exposure Limit for benzene from 10 ppm to 1 ppm was estimated by OSHA to avoid 326 deaths from leukemia and other cancers over 45 years, or 7.2 cancers per year**; a reduction of similar magnitude to the presented ethanol blended gasoline efforts.

Greenhouse Gas Life Cycle Modeling

5 Cities Study GHG Summary

- On a total tonnage and percentage basis the study shows sizable greenhouse gas reductions for all cities and ethanol blends.
 - Cities with high fuel demand and current MTBE use can realize large GHG savings due to the high GHG intensity of the MTBE production pathway.
 - Beijing and Mexico City, for example, can save 10 and 15 million metric tonnes of CO₂ emissions, respectively, from E10 blends through 2027.
- EV Adoption: We looked at projected global EV Vehicle Stock Turnover which projected to be about 6% by 2027.
 - Ethanol adoption into the existing fleet provides about the same benefits **but right now.**



Successful use of this Data: Japan GHG Modeling

- Uses ETBE as oxygenate as opposed to straight ethanol blending
- In past only used sugarcane ethanol to produce ETBE
- With availability of new corn ethanol efficiency data Japanese scientists assessed GHG reductions from corn ethanol completely independently.
- Result: Opened market to include US corn ethanol as feedstock
 - Japan will allow now 44% of the ethanol feedstock going into ETBE production to come from US corn ethanol (96 million gallons of the total estimated ethanol demand of 217 million gallons)
 - Important: Many countries in Asia are following Japanese developments

Summary

- The 5 Cities Study assessed the health impact of key cancer causing compounds in vehicle emissions which are reduced in ethanol blended gasolines.
 - The US **Environmental Protection Agency's Fuel Trend Report shows the link that ethanol reduces aromatics including benzene** in fuels which are carcinogenic.
 - Ethanol also reduces **other carcinogenic subgroups of volatile organic compounds (butadiene)**.
 - **Ethanol also reduces a group of air toxics called PAHs** including benzopyrene which is highly cancerous and
 - Ethanol **reduces carbon monoxide** (linked to premature deaths) and
 - Ethanol **reduces other particulate matter compounds** linked to heart failure.

Note: Small increases from acetaldehyde cases are dwarfed by these reductions

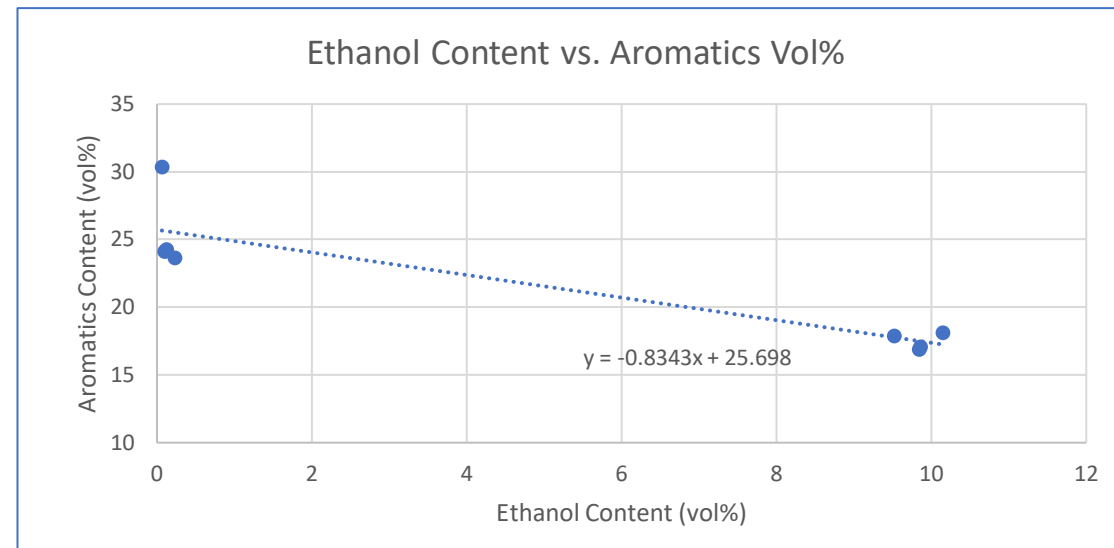
5 Cities Study...

- ... utilized **actual fuel samples** from each city. Used refining model to document reductions in aromatics/benzene in fuels when they include ethanol.
- ... utilized Atmospheric Box Model specific to each city to convert tons of reductions of cancer causing toxins into reductions in atmospheric concentrations from blending ethanol.
- ... utilized inhalation unit risk factors and country specific data (where available) to assess reduction in cancer cases, reduction in years lost and cancer care cost impact from blending ethanol.

Upcoming Study: Domestic Health Impact Study

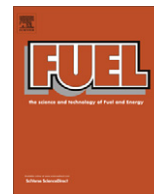
- Will assess the impact of high octane fuels with higher octane numbers (RON 95, RON 98 etc)
- Will quantify cancer reductions from high octane fuels

First Step: Sampled domestic fuels



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Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles

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ABSTRACT

The study investigated the impact of ethanol blends on criteria emissions (THC, NMHC, CO, NO_x), greenhouse gas (CO₂), and a suite of unregulated pollutants in a fleet of gasoline-powered light-duty vehicles. The vehicles ranged in model year from 1984 to 2007 and included one Flexible Fuel Vehicle (FFV). Emission and fuel consumption measurements were performed in duplicate or triplicate over the Federal Test Procedure (FTP) driving cycle using a chassis dynamometer for four fuels in each of seven vehicles. The test fuels included a CARB phase 2 certification fuel with 11% MTBE content, a CARB phase 3 certification fuel with a 5.7% ethanol content, and E10, E20, E50, and E85 fuels. In most cases, THC and NMHC emissions were lower with the ethanol blends, while the use of E85 resulted in increases of THC and NMHC for the FFV. CO emissions were lower with ethanol blends for all vehicles and significantly decreased for earlier model vehicles. Results for NO_x emissions were mixed, with some older vehicles showing increases with increasing ethanol level, while other vehicles showed either no impact or a slight, but not statistically significant, decrease. CO₂ emissions did not show any significant trends. Fuel economy showed decreasing trends with increasing ethanol content in later model vehicles. There was also a consistent trend of increasing acetaldehyde emissions with increasing ethanol level, but other carbonyls did not show strong trends. The use of E85 resulted in significantly higher formaldehyde and acetaldehyde emissions than the specification fuels or other ethanol blends. BTEX and 1,3-butadiene emissions were lower with ethanol blends compared to the CARB 2 fuel, and were almost undetectable from the E85 fuel. The largest contribution to total carbonyls and other toxics was during the cold-start phase of FTP.

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1. Introduction

Currently, a key issue in the transportation sector is expanding the use of alternative and renewable fuels. Interest in alternative fuels has grown as they continue to play an important role not only in meeting the growing global demand for transportation energy but also in reducing greenhouse gas emissions [1]. To help promote the development and expansion of alternative transportation fuels, a number of government initiatives have been implemented at the regional, national, and local levels [2]. Alternative transport fuels such as hydrogen, natural gas, Fischer–Tropsch fuels, and biofuels have also been supported by regulatory organizations and environmental agencies as a viable option to reduce the transport sector contribution to local air pollution [3].

Ethanol is the most widely used renewable fuel for transportation in the United States (US) and is also used extensively in other

parts of world [4,5]. As groundwater and drinking water-related issues precluded the use of methyl *tert*-butyl ether (MTBE) as an oxygenate in gasoline in the US, a transition was made to ethanol to meet nearly all oxygenate requirements [6]. With the push to use increasingly higher levels of renewable fuels, there has been an accompanying push to further increase the ethanol level in gasoline. In fact, ethanol is anticipated to comprise a predominant fraction of the volume needed to meet the US Renewable Fuel Standard (RFS), with ethanol production coming from a combination of conventional starch-based processes and more advanced technologies using cellulosic feedstocks [7].

As the composition of gasoline and other fuels continues to change, it is important to fully understand the impacts of the new fuels on exhaust emissions. While a number of studies have examined the impact of ethanol on exhaust emissions, these studies have mostly focused on ethanol levels of 10% or less [6,8–11], with a few recent studies extending to E20 [12–14]. The limited number of studies focusing on higher ethanol levels may be due to the so-called “blend wall”, as 10% ethanol was previously considered the maximum level that could be used in conventional

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vehicles. Although the ethanol limit was recently raised to 15% for 2007 and newer vehicles, with prospects for increasing the limit to 15% for 2001–2006 vehicles before the end of 2010, there is not sufficient data to support the use of ethanol levels higher than 10% in older vehicles.

Studies of gasolines with ethanol contents of 10% or less have generally shown that emissions of carbon monoxide (CO), unburned hydrocarbons (HC), and non-methane hydrocarbons (NMHC) are reduced with increasing ethanol content [8,10–13,15–17]. A small increase in NO_x emissions is sometimes found with additional ethanol content, but this result is not consistent among studies [6,8,10–13,18–20]. Toxic emissions are also an important consideration. Carbonyls are products from incomplete combustion from the automobile exhaust and certain carbonyls are considered to be toxic or even potential carcinogens [21]. Carbonyls in urban areas are known as key compounds of photochemically generated air pollution, since they are precursors to free radicals (HO_x) and PAN [22]. Other toxic species, such as benzene and 1,3-butadiene, are of particular interest in air pollution research due to their suspected role in the formation of ozone and photochemical oxidants associated with urban smog [23]. Studies have also reported some increases in carbonyl compound emissions with ethanol compared to gasoline fuel [8,20,24,25], and decreases in benzene with increasing ethanol levels [8,10,11,20,26,27]. Yet, in some studies, lower benzene emissions were also associated with lower fuel benzene levels [10,11]. Durbin et al. [6], however, found a trend of increasing benzene emissions with increasing ethanol levels for fuels with similar benzene levels and different volatility levels, indicating a potentially more complex relationship between ethanol and toxics.

The objective of the current research project was to characterize the impacts of ethanol on exhaust emissions with an emphasis on older vehicles, where such information is limited. Criteria and unregulated emissions were measured in a fleet of 7 light-duty gasoline vehicles with model years ranging from 1984 to 2007, representing Tech 3 (1981–1985), Tech 4 (1986–1995), and Tech 5 (1996–2010) technologies. Criteria emissions were NO_x, CO, HC, NMHC, and CO₂. Detailed hydrocarbon speciation was conducted for Tech 5 category vehicles only, and included carbonyl compounds (aldehydes and ketones), 1,3-butadiene, and benzene, toluene, ethylbenzene, and xylenes emissions (BTEX). Emissions and fuel consumption measurements were conducted over the Federal Test Procedure (FTP) driving cycle using a chassis dynamometer.

2. Experimental

2.1. Test fuels and vehicles

A total of six fuels were employed in the study. The fuel test matrix included a CARB phase 2 certification fuel with 11% MTBE (CARB 2) and a CARB phase 3 certification fuel with 5.7% ethanol (CARB 3). CARB 2 served as the base fuel for comparisons, as it is the fuel currently used for certification. CARB 3, with 5.7% ethanol, was used as the base fuel for creating blends with ethanol at proportions of 10 (E10), 20 (E20), 50 (E50), and 85% (E85) by volume. The main physicochemical characteristics of the test fuels are listed in Table 1.

The test matrix included seven vehicles, selected from three categories, based on their technology. Two vehicles (1984 Toyota pickup and 1985 Nissan 720 pickup) were from the Tech 3 category (1981–1985), having early three-way catalysts (TWC) with closed loop fuel control. Two vehicles (1991 Ford Explorer and 1993 Ford Festiva) were from the Tech 4 category (1986–1995), while three vehicles (1996 Honda Accord, 2000 Toyota Camry, and 2007 Chevy Silverado) were from the Tech 5 (1996–2010) category. In the Tech 5 category, one of the vehicles (2007 Chevy Silverado) was a Flex-

ible Fuel Vehicle (FFV), which can be operated on fuels containing 85% ethanol by volume. The vehicles were chosen so that they were representative of the vehicle fleet in the State of California. The Tech 3 and Tech 4 vehicles were tested on a four fuel test matrix including the CARB Phase 2 certification fuel, the CARB Phase 3 certification fuel, E10 and E20. The FFV was tested on a six fuel test matrix including E50 and E85 ethanol blends in addition to CARB 2, CARB 3, E10, and E20. The test vehicles were all in-use vehicles recruited from private owners with an incentive.

2.2. Driving cycles and measurement protocol

Each vehicle was tested on each fuel over duplicate or triplicate Federal Test Procedure (FTP) cycles. The FTP is the primary emission certification cycle for light-duty vehicles in the United States (US) [28]. The FTP cycle consists of three segments or bags representing a cold start phase, a stabilized transient phase, and a hot start phase. The results of these three bags are generally weighted into a single value using a formula provided in the Code of Federal Regulations (CFR).

Prior to testing any particular vehicle, an extensive preconditioning procedure was followed: first, the oil was changed; second, the fuel was changed using a multiple drain and fill procedure with on-road conditioning to minimize carryover effects between different test fuels; third, the vehicle was run through a certification procedure portion of the preconditioning, during which it was drained of fuel and filled again to the 40% level, and then operated over the LA-4 portion of the FTP on the dynamometer; finally, the vehicle was placed into cold soak overnight prior to performing the full FTP test.

After two FTPs were completed, the data were evaluated to determine whether additional testing was required. A third test was performed only if the difference between the two composite FTP emissions test results exceeded the following: HC 33%, NO_x 29%, CO 70% (provided the absolute difference in the measurements was greater than 5 mg/mi).

All tests were conducted in CE-CERT's Vehicle Emissions Research Laboratory (VERL), which is equipped with a Burke E. Porter 48-inch single-roll electric dynamometer. A Pierburg Positive Displacement Pump-Constant Volume Sampling (PDP-CVS) system was used to obtain certification-quality emissions measurements.

2.3. Emission analysis

Regulated bag and second-by-second post-catalyst emissions measurements for NO_x, CO, HC, NMHC, and CO₂ were made with a Pierburg AMA-4000 bench. Emissions of carbonyl compounds, 1,3-butadiene, and BTEX were performed in accordance with protocols developed as part of the Auto/Oil Air Quality Improvement Research Program [29], with enhancements. Samples for BTEX and 1,3-butadiene were collected using Carbotrap adsorption tubes consisting of multi-beds including a molecular sieve, activated charcoal, and carbotrap resin. For BTEX and 1,3-butadiene, the GC sample injection, column, and operating conditions were set up according to the specifications of SAE 930142HP Method-2 for C₄–C₁₂ hydrocarbons. An HP 5890 Series II GC with a flame ionization detector (FID) maintained at 300 °C was used to measure BTEX and 1,3-butadiene. A 2 m × 0.32 mm deactivated fused silica pre-column and a 60 m × 0.32 mm HP-1 column were used. The GC/FID was set up with a dual column and dual detector to allow simultaneous analysis of two GC bag samples. With the thermal desorption tubes, detection limits were improved by several orders of magnitude compared to levels achieved in earlier Auto/Oil programs.

Samples for carbonyl analysis were collected through a heated line onto 2,4-dinitrophenylhydrazine (DNPH) coated silica

Table 1

Main physicochemical characteristics of the test fuels.

Property	CARB 2	CARB 3	E10	E20	E50	E85	Test method
Sulfur content ($\mu\text{g}/\text{kg}$)	30.9	20.7	16.6	15.9	<10	<10	ASTM D 2622
API Gravity, 15 °C	60.1	59.1	58.3	56.8	51	44.2	ASTM D 287
Net heating value (MJ/kg)	42.58	42.27	41.21	39.79	33.34	26.74	ASTM D 240
Distillation							ASTM D 86
IBP	336	100.5	319.5	330.7	328.3		
50	518.9	520	520.5	520.6	521		
90	608.6	611.3	546.4	546.3	547.5		
95	635.1	639	552.6	553.3	554.4		
FBP	661.7	662.4	569.6	564.7	569.1		
Research Octane Number (RON)	97.4	96.2	98.4	101	101.2	101.7	ASTM D 2699
Motor Octane Number (MON)	88.8	87.8	88.8	89.8	91.7	92.5	ASTM D 2700
Reid vapor pressure (psi)	6.65	6.67	7.2	6.92	6.57	5.49	ASTM D 5191
Benzene (wt.%)	1.1	0.86	0.76	0.73	0.43	0.09	ASTM D 5580
Toluene (wt.%)	6.45	11.28	9.97	8.56	5.46	1.21	
Ethylbenzene (wt.%)	5.46	1.54	1.36	1.78	0.85	<0.1	
<i>p/m</i> Xylenes (wt.%)	5.55	5.12	4.53	4.27	2.56	0.74	
<i>o</i> -Xylene (wt.%)	0.58	1.03	0.91	0.78	0.51	<0.1	
$\geq\text{C9}$ Aromatics (wt.%)	9.62	12.08	10.66	9.53	5.87	1.22	
Total aromatics (wt.%)	28.76	31.9	28.2	25.65	15.67	3.25	
Ethanol (wt.%)	<0.1	6.63	11.33	17.19	43.54	74.95	ASTM D 5599
MTBE (wt.%)	11.54	<0.1	<0.1	1.48	0.18	<0.1	
Total oxygen (wt.%)	2.09	2.3	4.16	6.86	17.12	29.56	
Olefins (mass%)	5.5	5	4.8	4.2	2.8	0.5	ASTM D 6550

Note: ASTM method D5599 is specified for use on blends of ethanol up to 20%, so the lower than expected values for the E50 and E85 blends can probably be attributed to issues in measuring ethanol with that method at those levels.

cartridges (Waters Corp., Milford, MA). Sampled cartridges were extracted using 5 mL of acetonitrile and injected into an Agilent 1100 series high performance liquid chromatograph (HPLC) equipped with a diode array detector. A 5 μm Deltabond AK resolution (200 cm \times 4.6 mm ID) with upstream guard column was used and the HPLC sample injection and operating conditions were set up according to the specifications of the SAE 930142HP protocol.

3. Results and discussion

3.1. Criteria emissions and fuel consumption

Weighted average NO_x emissions of the FTP cycle are shown in Fig. 1. Results show that fuel impact on NO_x emissions varied by vehicle. Three vehicles (1984 Toyota pickup truck, 1985 Nissan pickup, and 1993 Ford Festiva) showed increasing NO_x emissions as ethanol content increased. The trend was statistically significant

for two (1984 Toyota and 1993 Ford Festiva) of the three vehicles. Increases in NO_x for the 1984 Toyota were 4.9, 14, and 19.5% for CARB 3, E10, and E20, respectively, compared with CARB 2. For the 1993 Ford Festiva, NO_x increases relative to CARB 2 were 13.2 for E10 and 24.6% for E20. The newer vehicles (1996 Honda Accord, 2000 Toyota Camry, 2007 Chevrolet Silverado) did not show statistically significant trends in NO_x emissions, although ethanol blends generally had lower emissions than CARB 2.

Increasing NO_x emissions with increasing ethanol content in the older vehicles may be due to differences in catalyst technology, aging, or effectiveness. Previous studies with larger vehicle fleets have shown trends of increasing NO_x emissions with increasing ethanol content [6,8,10,12], though other studies have shown no changes, inconsistent changes, or even decreases in NO_x emissions [11,13,30]. Higher fuel oxygen content in the fuel can lean out the air–fuel mixture, which, in turn, can lead to higher NO_x emissions. Older technology vehicles do not have as sophisticated controls of air–fuel ratios at the levels of oxygen investigated in this study, so

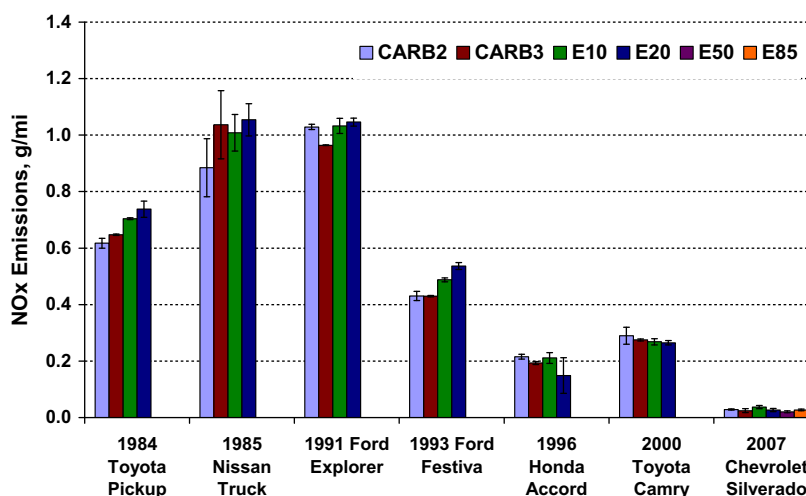


Fig. 1. Average NO_x emissions for all fuel/vehicle combinations over FTP operation.

can be more impacted by increases in ethanol/oxygen in the fuel. A study by NREL showed that vehicles that did not apply long-term fuel trim during wide open throttle operation ran leaner under these conditions as the oxygen content in the fuel increased [13].

Trends in emissions from newer vehicles indicate a more complex set of factors may be at work. For newer vehicles, Durbin et al. [6] found some increases in NO_x with increasing ethanol content, but these trends showed a dependence on fuel volatility. As the fuels in the current study were splash blended, fuel parameters, such as volatility, would have also been varied in conjunction with ethanol content. Thus, for different vehicles, the effects of different fuel properties may have an interaction with the ethanol effects. In recent work with newer vehicles, a consistent increase in NO_x emissions with increasing ethanol content was seen in a study that used a full design approach for fuel properties to compensate for potentially interacting fuel variables [12], while no consistent trends for NO_x were seen in a study where the ethanol content was adjusted by splash blending [13]. Ethanol also has a higher latent heat of vaporization, which can lower flame temperature in the combustion process, thereby contributing to lower NO_x emissions [31].

THC and NMHC emissions over the FTP test cycle are presented in Fig. 2a and b. Total THC/NMHC emissions are an order of magnitude lower for newer vehicles as compared to older vehicles for all fuels tested, as would be expected with the more advanced emission control technologies seen in new vehicles. Four vehicles (1984 Toyota pickup, 1985 Nissan pickup, 1993 Ford Festiva, and

1996 Honda Accord) showed decreasing trends in THC and NMHC emissions as the ethanol content of the fuel increased. Among these four vehicles, the observed trend was statistically significant for the two oldest vehicles (1984 Toyota and 1985 Nissan). Reductions (relative to CARB 2) of -17.4 and -22.7% for E10 and E20, respectively, were seen in the 1984 Toyota pickup. Reductions of -12.2 for CARB 3, -8.1 for E10, and -23% for E20 were seen in the 1985 Nissan pickup. Other vehicles did not show emissions differences for THC and NMHC with varying ethanol levels, with the exception of the 2007 Chevy Silverado, which showed increases in THC and NMHC emissions when the E85 fuel was used.

Trends of decreasing THC/NMHC emissions with increasing ethanol content have generally been seen in studies utilizing larger fleets of older vehicles [8,10–13]. For Tier 1 and newer vehicles, a wider range of results have been seen, with many studies showing decreases in THC/NMHC with increasing ethanol content [12,13,30], and some studies showing no change, or even an increase in THC/NMHC emissions, with increasing ethanol content [6,32]. Reductions in THC emissions may be attributed primarily to the presence of oxygen in the fuel, which leans the air–fuel ratio and promotes oxidation during combustion and over the catalyst. The higher octane number for ethanol blends can also promote more efficient combustion [33]. The more mixed results for Tier 1 vehicles indicate that more complex factors may be at play for THC/NMHC emissions in newer vehicles. Modern vehicles generally tend to have better control of the air–fuel ratio and can adjust the air–fuel ratio to compensate for different levels of ethanol in

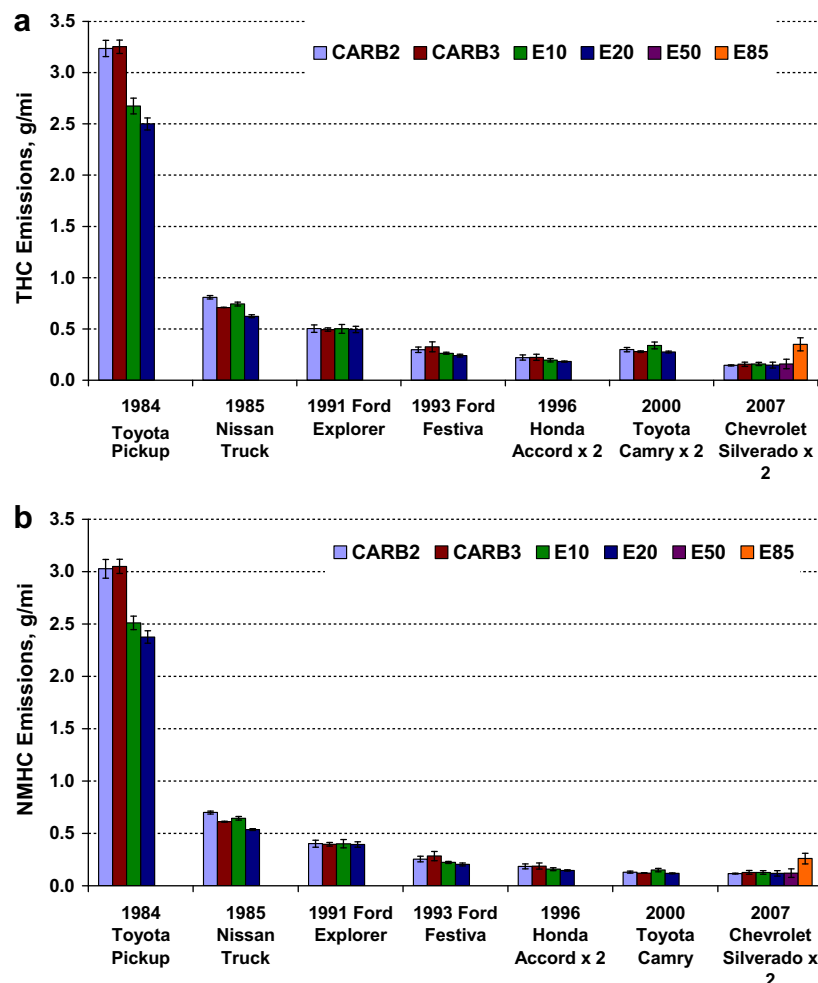


Fig. 2. (a and b) Average emissions of THC (a) and NMHC (b) for the test fuels over FTP.

the fuel, although the ability make these adjustments differs between vehicles under conditions such as wide open throttle (WOT) [13,34]. Durbin et al. [6] also showed that the interaction with fuel volatility may be an important factor. The observed increase in THC/NMHC emissions from the FFV when operated using E85 was mainly due to the lower volatility of the fuel blend, which makes the fuel more difficult to vaporize under cold-start conditions. Increases in THC/NMHC emissions were also observed during the cold-start phase of the FTP (bag 1), where they were on the order of 20–40 times higher than for the bags 2 and 3 for the E85 fuel in the FFV. In general, cold-start THC emissions (bag 1) ranged from 0.267 to 0.740 g/mi, whereas bag 2 and bag 3 emissions ranged from 0.012 to 0.020 g/mi and 0.023 to 0.038 g/mi, respectively. For the E85 fuel, bag 1 emissions were 0.740 g/mi, while bag 2 and bag 3 emissions were 0.020 and 0.038 g/mi, respectively.

Fig. 3 shows CO emissions for all vehicle/fuel combinations. CO emissions displayed an inverse relationship of decreasing emissions with increasing ethanol level for the 1984 Toyota pickup, 1985 Nissan pickup, 1991 Ford Explorer, and 1996 Honda Accord. The relationship was statistically significant for the two oldest vehicles and the 1996 Honda Accord. The largest, statistically significant reductions in CO emissions were for E20 (relative to CARB 2; –72.2% for the 1984 Toyota, –36.4% for the 1985 Nissan, and –32.8% for the 1996 Honda Accord). While the two later model vehicles did not demonstrate a significant impact on CO emissions, a decreasing trend in emissions with higher ethanol levels was observed. The general trend of decreasing CO emissions with increasing ethanol content is consistent with previous studies [6,8,10–13,32], and reductions may be ascribed to the fuel-borne oxygen, which leans the air–fuel ratio and improves oxidation during combustion and over the catalyst [18,35].

Fig. 4a and b shows CO₂ emission and fuel economy results, respectively, for the test vehicles over the FTP. CO₂ emissions did not show any significant trends between the fuels. Fuel economy decreased with increasing levels of ethanol for the five later model vehicles, as shown in Fig. 4b. Fuel economy changes were statistically significant for the 2000 Toyota Camry and 2007 Chevrolet Silverado, but not for the other vehicles. The largest reductions in fuel economy were seen in the 2007 Chevy Silverado with the E50 and E85 ethanol blends, which were –16.2 and –29%, respectively, relative to CARB 2. Reductions in fuel economy with increasing ethanol content can be attributed to the lower energy content of the oxygenated ethanol, as shown in Table 1.

3.2. Unregulated emissions

Carbonyl emissions (aldehydes and ketones) were obtained from two of the seven vehicles. A total of thirteen carbonyls were identified and quantified in the exhaust. Fig. 5a and b shows the carbonyl compounds emitted from the 1996 Honda Accord (a) and the 2007 FFV Chevrolet Silverado (b). Consistent with previous findings [20,21,36,37], formaldehyde, acetaldehyde, and acetone were the most prominent carbonyl compounds for both vehicles. High molecular weight carbonyl compounds were also present, but in significantly lower amounts. For the 1996 Honda Accord, emission levels of acrolein, propionaldehyde, valeraldehyde, tolu-aldehyde, and hexanaldehyde were below the detection limits of the method for all test fuels. For the FFV, in addition to the above compounds, crotonaldehyde, MEK, and methacrolein were almost undetectable. However, only tolu-aldehyde was found in detectable levels for the E85 fuel.

For toxic emissions, acetaldehyde showed the most consistent trend, increasing with ethanol content for both vehicles. For the 1996 Honda Accord, acetaldehyde emissions increased for the E10 blend by 71% and 98%, while E20 increased 202% and 251%, compared with CARB 2 and CARB 3. For the 2007 Chevy Silverado, significant increases in acetaldehyde were only seen with the use of the E85 fuel, with increases on the order of 1097% (compared to CARB 2) and 1430% (compared with CARB3). Acetaldehyde emissions for E10 were –39% and –23% lower than CARB 2 and CARB 3. The changes in acetaldehyde emissions for E20 and E50 were within the experimental variability. Previous studies have generally shown consistent increases in acetaldehyde emissions with increasing ethanol content [6,8,10,11,13,17,32], as ethanol is the main precursor of acetaldehyde in vehicular emissions.

For the 2007 Chevrolet Silverado, the blends of E10, E20, and E50 resulted in reductions in formaldehyde emissions, when compared to CARB 2. The reductions were –44% for E10, –36% for E20, and –27% for E50. Compared to CARB 3, only E10 resulted in limited reductions (–5%) of formaldehyde emissions, while E20 and E50 increased emissions by 8–23%, respectively. The use of E85 resulted in significant increases in formaldehyde emissions – an 88% increase when compared to CARB 2 and a 216% increase when compared with CARB 3. The increased formaldehyde emissions for E85 may be attributed to the presence of ethanol, and the higher oxygen content in the fuel, as well as decreases in fuel aromatics, because these compounds do not participate in formaldehyde formation [38]. For the 1996 Honda Accord, the use of CARB 3 resulted in a 14% decrease in formaldehyde emissions, when compared with

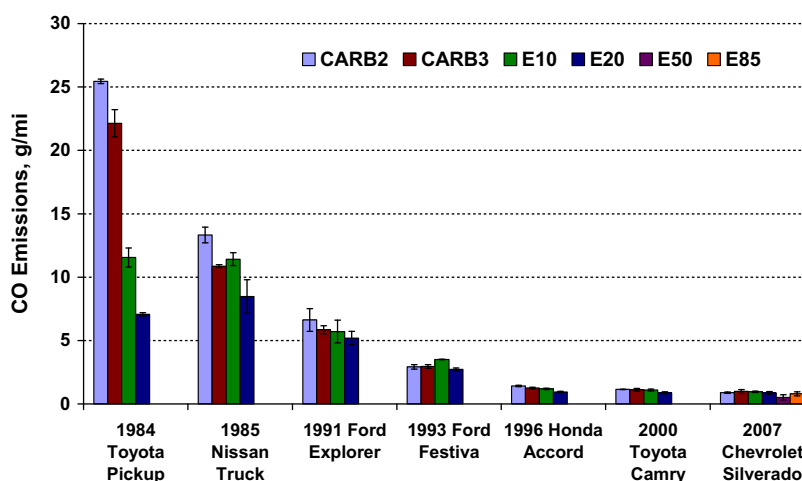


Fig. 3. CO emissions for all fuel/vehicle combinations over FTP operation.

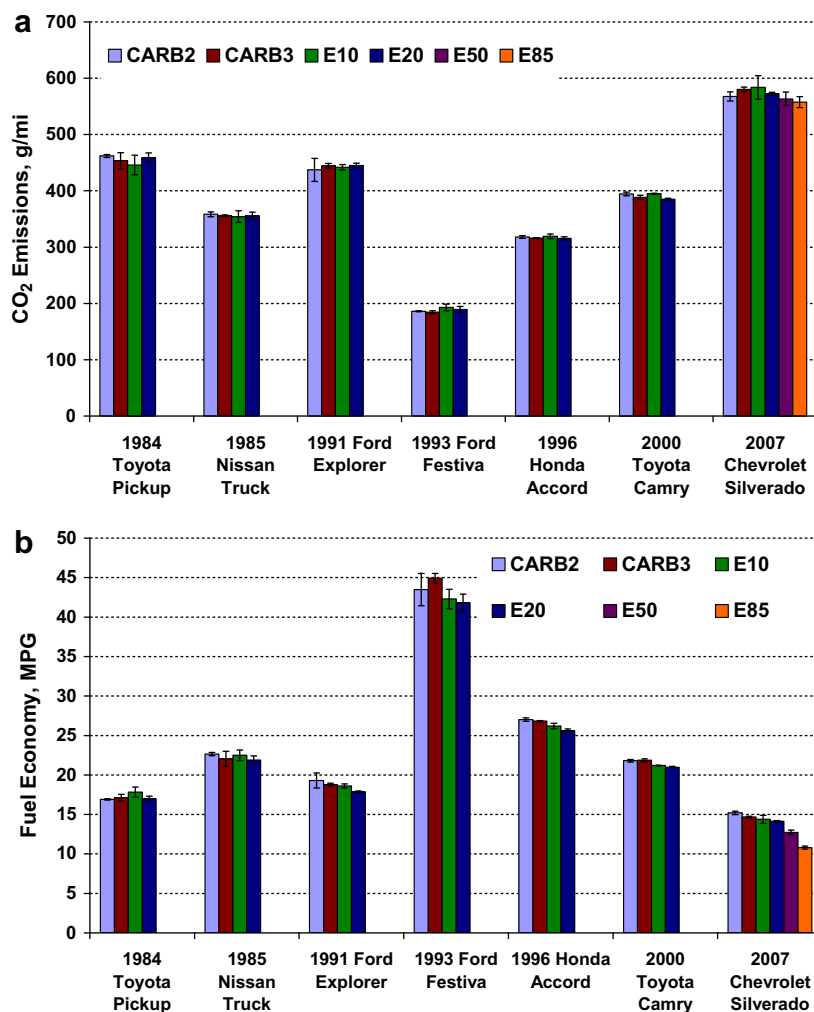


Fig. 4. (a and b) CO₂ emission results (a) and fuel economy (b) for all fuel/vehicle combinations over FTP operation.

CARB 2, with E10 following closely behind showing a 10% reduction, though the reductions were not statistically significant. E20 showed no changes in formaldehyde emissions, which is consistent with previous studies that have shown no or inconsistent changes in formaldehyde emissions as a function of ethanol content [6,8,10,11].

Acetone emission reductions were seen in both the 1996 Honda and the 2007 Chevy Silverado. The 1996 Honda showed reductions in acetone emissions of 39–56%, with higher ethanol levels related to the greater reductions. For the 2007 Chevrolet Silverado, the highest acetone reductions were achieved with E10, with reductions of 63% (compared to CARB 2) and 60% (compared to CARB 3). Higher molecular weight carbonyls were found at fairly low levels for the 1996 Honda Accord and none of the emission changes were statistically significant. Ethanol blended fuels all had higher crotonaldehyde emissions than CARB 2 for the 1996 Honda, as well. In fact, the use of CARB 3, E10, and E20 resulted in increases in crotonaldehyde emissions of 486%, 510%, and 327%, when compared to CARB 2.

Fig. 6 shows the influence of cold-start conditions on total carbonyl emissions for all fuel/vehicle combinations. Total carbonyl emissions were higher for the 1996 Honda Accord when run on E10 and E20; the 2007 Chevy Silverado had higher emissions on the CARB 3 fuel and also had high emissions when run on E85. The impact of the cold-start on emissions was particularly noticeable for both vehicles. Total carbonyl emissions were found at

substantially higher levels during the first phase of the driving cycle, when the engine was cold and the catalyst was below its light-off temperature. On the other hand, exhaust concentrations of most carbonyl compounds were quite low, or below the detection limit during the second and the third phases of the FTP. Increased exhaust temperature and higher performance of the catalytic converter after light-off were the main reasons for the decrease in carbonyls during the second and third phases of the FTP.

The 2007 Chevy Silverado also showed significant increases in total carbonyl emissions when run on E85, compared to the CARB specification fuels and other ethanol blends. Compared to CARB 2, total carbonyl emissions for the E85 blend increased by 1240% during the cold-start FTP and by 138% for the weighted FTP. Compared to CARB 3, total carbonyl emissions for E85 increased by 329% for cold-start FTP and 109% for the weighted FTP. As shown in Fig. 5b, the increase in carbonyl emissions was largely due to increases in acetaldehyde emissions. The increases could be due to the lower volatility of the E85 blend, as compared to the blends with higher gasoline levels, which makes it especially difficult to vaporize, or the vehicle engine control module (ECM) may not be adjusting properly to the higher ethanol content, resulting in higher hydrocarbon emissions.

Fig. 7a and b shows the BTEX and 1,3-butadiene emissions over the FTP for the 1996 Honda Accord (a) and 2007 Chevrolet Silverado (b). It should be noted that ethylbenzene was almost undetectable for all fuels and both vehicles. For the 1996 Honda Accord,

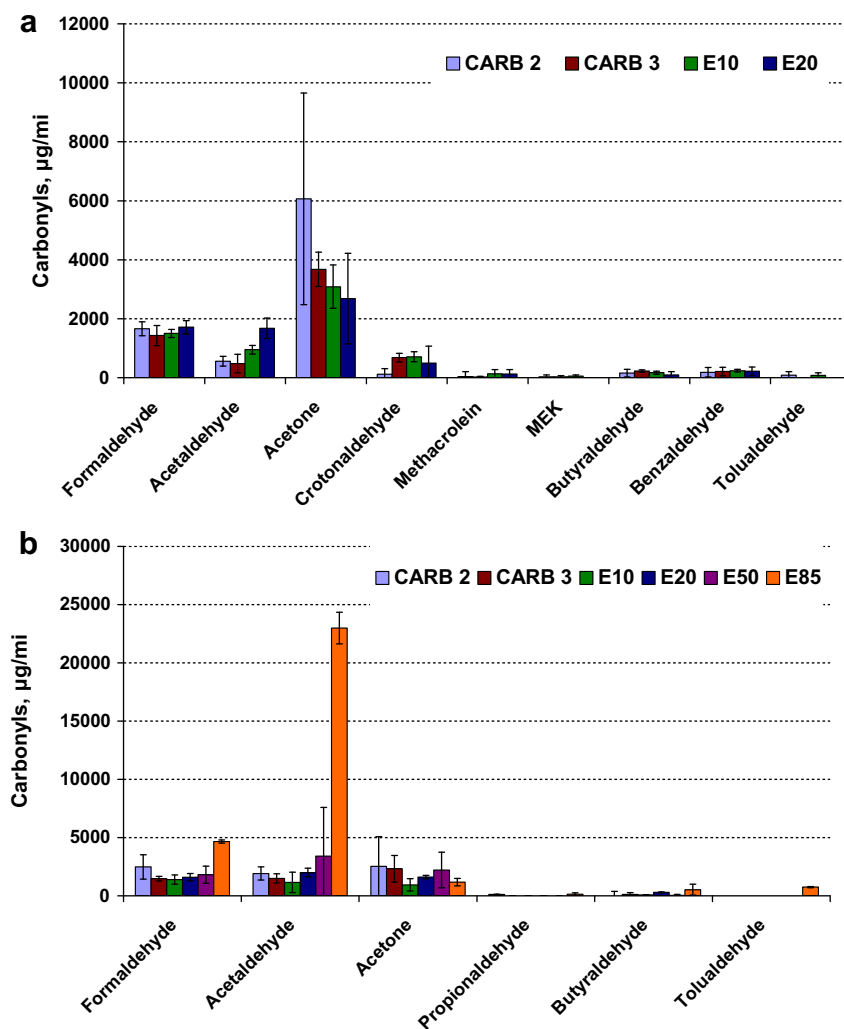


Fig. 5. (a and b) Individual carbonyl compound emissions for the 96 Honda Accord (a) and the 07 FFV Chevrolet Silverado (b) over FTP operation.

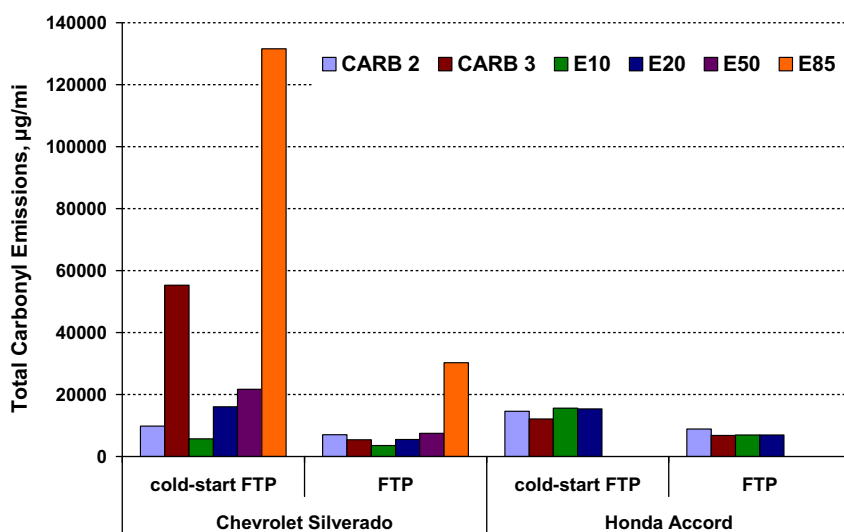


Fig. 6. Total carbonyl emissions for both vehicles over the cold-start FTP (phase 1) and FTP driving cycles.

BTEX and 1,3-butadiene emissions were significantly higher for CARB 2 than the other fuels. As with previous studies, which have

shown that benzene decreases with increasing ethanol levels, the current study showed that E20 had lower benzene, as well as

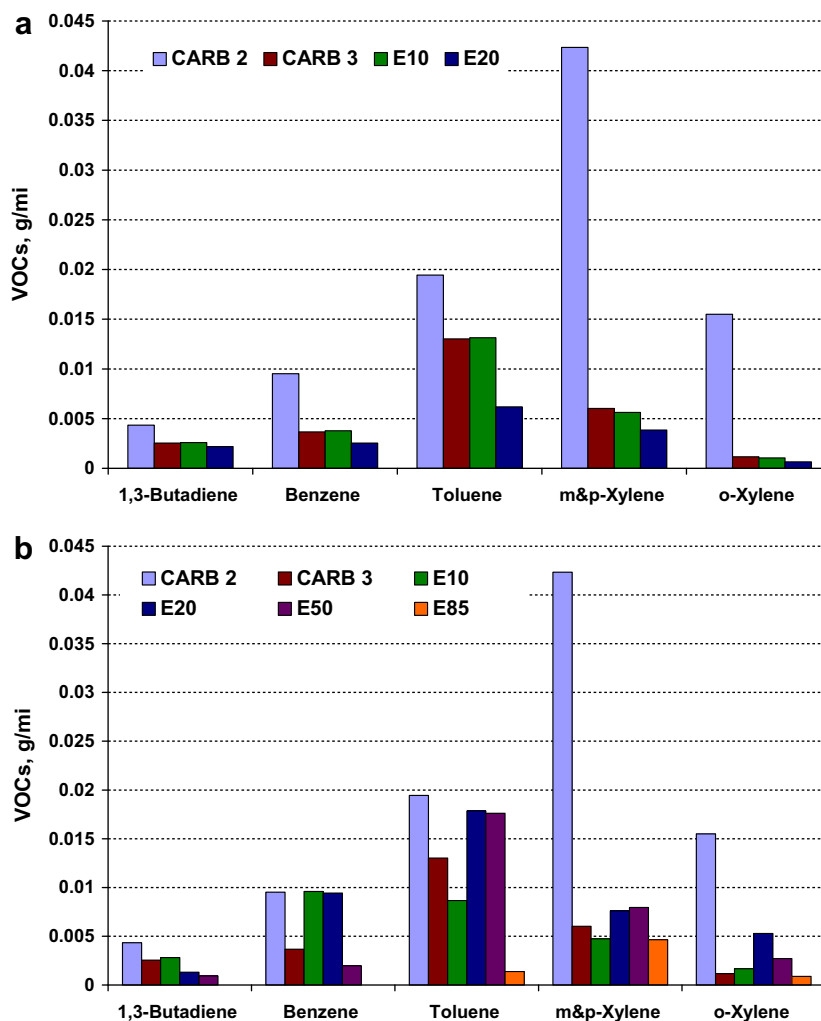


Fig. 7. (a and b) 1,3-Butadiene and BTEX emissions for the 96 Honda Accord (a) and the FFV Chevrolet Silverado (b) over FTP operation.

toluene and xylene emissions than either CARB 3 or E10 [8]. Benzene levels for the 2007 Chevrolet Silverado did not show a consistent trend – benzene levels were undetectable for E85 and were lower for CARB 3 and E50 (compared to CARB 2), while benzene levels for E10 and E20 were similar to those of CARB 2. Table 1 shows that the lower emissions of BTEX species for the E20 blend may be due to lower levels of total aromatics in the fuel. The benzene emissions also follow a trend that is roughly consistent with the benzene level in the fuel. Benzene is formed from either unburned fuel-borne benzene or benzene formed during combustion of other aromatic and non-aromatic compounds found in gasoline [39]. Previous studies have shown that benzene generally decreases with increasing levels of ethanol, with this trend primarily be attributable to benzene levels in the fuel [8]. The higher BTEX emissions for CARB 2 do not appear to be directly attributable to fuel aromatic levels or oxygen content. Although the CARB 2 fuel did have the highest levels of benzene, ethylbenzene, and *m/p* xylenes, the CARB 3 and E10 fuels had either higher or comparable levels of toluene, *o*-xylene, and total aromatics.

Similar conclusions about fuel aromatic levels cannot be drawn about 1,3-butadiene (which is characterized as a human carcinogen and as precursor for secondary formation of formaldehyde and acrolein), because it is a product of fuel fragmentation and is not present originally in the fuel [40,41]. Previous studies have not shown consistent trends for 1,3-butadiene, either

[6,8,11,17]. Yet, in the current study, the 2007 FFV Chevrolet Silverado, showed a consistent decreasing trend in 1,3-butadiene, with emissions decreasing as ethanol level increased. Emissions of 1,3-butadiene were undetectable for E85 and E50 showed a reduction of 78% compared to CARB 2. Benzene levels for the 2007 Chevrolet Silverado did not show consistent trends with increasing ethanol levels. Benzene levels were undetectable for E85 and were lower for CARB 3 and E50 compared to CARB 2, while benzene levels for E10 and E20 were similar to those for CARB 2. The latter phenomenon may be due to the fact that the addition of oxygenated compounds such as ethanol inhibits the oxidation of benzene. It is therefore possible that an increase in soot volume fraction may result in some increases for benzene emissions [42].

For other BTEX compounds, toluene, and *m*-, *p*-, and *o*-xylene, the highest emissions were found for CARB 2, while E20 and E50 showed higher emissions of these species than the other ethanol blends, i.e., CARB 3, E10, and E85. The substantially lower BTEX emissions for E85 relative to the other blends is presumably due to the higher oxygen content and the lower amount of aromatic compounds in the fuel, although the other fuels did not generally follow this trend. For both the 1996 Honda and the 2007 Chevy, emissions of BTEX and 1,3-butadiene were mostly produced during the cold-start of FTP, while their concentration levels during the second and third hot-start phases were negligible.

4. Conclusions

The study of regulated and unregulated emissions profiles of gasoline-powered light-duty vehicles included models ranging in years from 1984 to 2007. The vehicles covered three categories (Tech 3, Tech 4, Tech 5) and represented different engine and exhaust aftertreatment technologies; one Flexible Fuel Vehicle (FFV) was included. Test fuels included a CARB phase 2 certification fuel with an 11% MTBE content, a CARB phase 3 certification fuel with a 5.7% ethanol content, E10, E20, E50, and E85. Regulated and unregulated emission and fuel consumption measurements were performed over the FTP using a chassis dynamometer in at least duplicate for each vehicle/fuel test combination.

The THC and NMHC emission increased for E85, but not the lower ethanol blends for the 2007 FFV Chevrolet Silverado. The CO emissions showed similar trends to those of THC and NMHC emissions, with earlier model vehicles showing a statistically significant decrease as the ethanol level increased. Ethanol did not have a significant impact on CO for the newer vehicles, however. The experimental results showed mixed trends for NO_x, with some older vehicles showing an increase in NO_x emissions as ethanol level increased. The newer vehicles did not show any statistically significant impacts of ethanol on NO_x emissions, although the ethanol blends generally had lower emissions than the CARB 2. CO₂ emissions did not show any significant trends between the fuels. In addition, fuel economy showed a decrease with increasing levels of ethanol for the five latest model vehicles. This is consistent with the lower energy content for the fuels with higher ethanol contents.

In general, carbonyl emissions were lower for the ethanol blends than those of CARB 2 and CARB 3 fuels, with the exception of the E85 fuel. The predominant compounds were formaldehyde, acetaldehyde and acetone, while heavier carbonyls were only detected in very low concentrations for all fuels and both vehicles. Carbonyl emission levels were higher for the 1996 Honda Accord than those of the 2007 FFV Chevrolet Silverado. The most consistent trend for carbonyl emissions was an increase in acetaldehyde emissions with increasing ethanol, which is consistent with ethanol being a precursor for the formation of acetaldehyde. It should be mentioned that the use of E85 resulted in significantly higher formaldehyde and acetaldehyde emissions than for the CARB fuels and the other ethanol blends. The largest contribution to total carbonyl emissions was during the cold-start phase of the FTP, when the engine was cold and the catalyst was below its light-off temperature.

Similar to carbonyl emissions, 1,3-butadiene and BTEX emissions were found in lower levels for the 2007 Chevrolet Silverado than the 1996 Honda Accord. In general, the addition of ethanol resulted in lower toxic emissions for the Honda Accord, compared to the CARB 2 fuel, with E20 having the lowest BTEX emissions. For the Chevrolet Silverado, 1,3-butadiene showed the most consistent trends, with CARB 2 having the highest emissions and emissions decreasing as a function of ethanol level. For toluene, and *m*-, *p*-, and *o*-xylene, for the 2007 Chevrolet Silverado, the highest emissions were found for the CARB 2 fuel, while the E20 and E50 fuels interestingly showed higher emissions of these species than the other ethanol blends, i.e., CARB 3, E10, and E85. Benzene and 1,3-butadiene emissions were undetectable and other aromatics were at low levels for the E85 fuel.

The results show some consistent trends with increasing ethanol content for some vehicles, but for other vehicles it appears that a more complex set of factors are impacting the emissions results. The older vehicles showed the most consistent trends for the regulated emissions, with reductions in THC/MNHC and CO emissions and increasing NO_x emissions with increasing ethanol content. This can be attributed to the leaning of the air–fuel mixture with the

increasing levels of ethanol/oxygen in the fuel, and the inability of the ECM to adjust to this change. For the vehicles that did not show consistent trends for the regulated emissions, these vehicles may be less sensitive to changes in fuel properties or may have ECMs that can readily adjust to the ethanol content in the fuel, or some other factors may be in play, such as interactions with other correlated fuel properties like fuel volatility, or combustion-related effects like changes in the adiabatic flame temperature. The unregulated emissions showed some trends with decreasing BTEX emissions with increasing ethanol for the 1996 Honda Accord and very low levels of toxic aromatics for the E85 fuel for the 2007 Chevrolet Silverado, but the BTEX emissions did not appear to be directly correlated to fuel aromatic levels, although the CARB 2 fuel did have the highest levels of benzene, ethylbenzene, and *p/m* xylenes. Overall, the results indicate that the impact of ethanol on emissions for the in-use gasoline vehicle fleet can depend on a number of factors, including the mix of vehicle technologies and the ability of these vehicles to adjust to the level of ethanol in the fuel, the sensitivities of different vehicles to changes in ethanol content, interactions with other fuel properties, such as volatility, as well as other potential factors.

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Bioethanol Blending Reduces Nanoparticle, PAH, and Alkyl- and Nitro-PAH Emissions and the Genotoxic Potential of Exhaust from a Gasoline Direct Injection Flex-Fuel Vehicle

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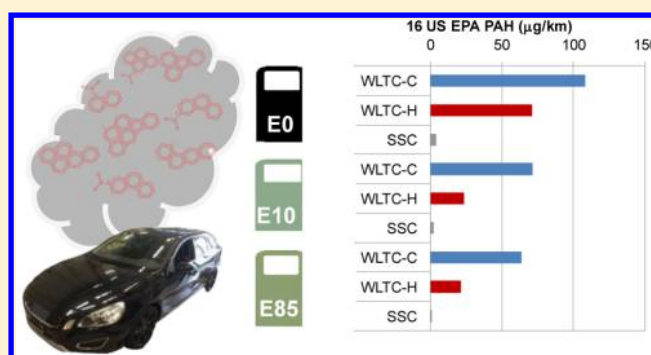
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Supporting Information

ABSTRACT: Bioethanol as an alternative fuel is widely used as a substitute for gasoline and also in gasoline direct injection (GDI) vehicles, which are quickly replacing traditional port-fuel injection (PFI) vehicles. Better fuel efficiency and increased engine power are reported advantages of GDI vehicles. However, increased emissions of soot-like nanoparticles are also associated with GDI technology with yet unknown health impacts. In this study, we compare emissions of a flex-fuel Euro-5 GDI vehicle operated with gasoline (E0) and two ethanol/gasoline blends (E10 and E85) under transient and steady driving conditions and report effects on particle, polycyclic aromatic hydrocarbon (PAH), and alkyl- and nitro-PAH emissions and assess their genotoxic potential.

Particle number emissions when operating the vehicle in the hWLTC (hot started worldwide harmonized light-duty vehicle test cycle) with E10 and E85 were lowered by 97 and 96% compared with that of E0. CO emissions dropped by 81 and 87%, while CO₂ emissions were reduced by 13 and 17%. Emissions of selected PAHs were lowered by 67–96% with E10 and by 82–96% with E85, and the genotoxic potentials dropped by 72 and 83%, respectively. Ethanol blending appears to reduce genotoxic emissions on this specific flex-fuel GDI vehicle; however, other GDI vehicle types should be analyzed.



INTRODUCTION

Bioethanol: A Promising Substitute for Gasoline.

Atmospheric carbon dioxide concentrations increased significantly from preindustrialized levels of 280 ppm up to 400 ppm in 2013.^{1,2} The current annual increase of 1.6 ppm/year corresponds to an uptake of 3.4 Gt carbon or 12.5 Gt CO₂ in the atmosphere. Petroleum-based fuels account for 82% of the global total primary energy supply,² and substitution of petroleum-based with renewable fuels to lower fossil CO₂ emission appeals as an urgent and important step. Alcohol-based fuels exhibit high potential in this respect. Therefore, bioethanol from renewable sources is increasingly blended with gasoline. New ways of ethanol production from biomass or other feedstocks allow a further increase in these shares. The production of bioethanol is strongly promoted in the United States of America, Brazil, and the European Union (EU). According to the U.S. Department of Energy, 95% of gasoline typically contains 10% ethanol (E10). The EU also forced the application of ethanol/gasoline blends, currently at a level of 10%.

Most fuel properties do not change much, and current vehicle technologies can operate with E10 without further adaptations.

Most significant is the higher oxygen content of ethanol/gasoline blends, which affects the combustion chemistry. It has been reported^{3,4} that the concentration of CO, HC, and NO_x decreases with the use of ethanol. These findings are from port-fuel injection vehicles, and effects on GDI vehicles might differ due to higher injection pressures and different forms of mixing the fuel with air, where a less homogeneous mixture can contribute to particle formation.

Impact of Bioethanol Blending on Genotoxic Polycyclic Aromatic Hydrocarbon (PAH) Emissions. Even less certain and sometimes contradictory is the impact of ethanol blending on emissions of nonregulated pollutants such as PAHs. Genotoxic PAHs, commonly present in combustion exhausts,^{5,6} have a substantial health impact, especially when coreleased with soot-like nanoparticles. Figure 1 displays structures of those PAHs, alkyl-PAHs, and nitro-PAHs that were found in exhausts in this study.

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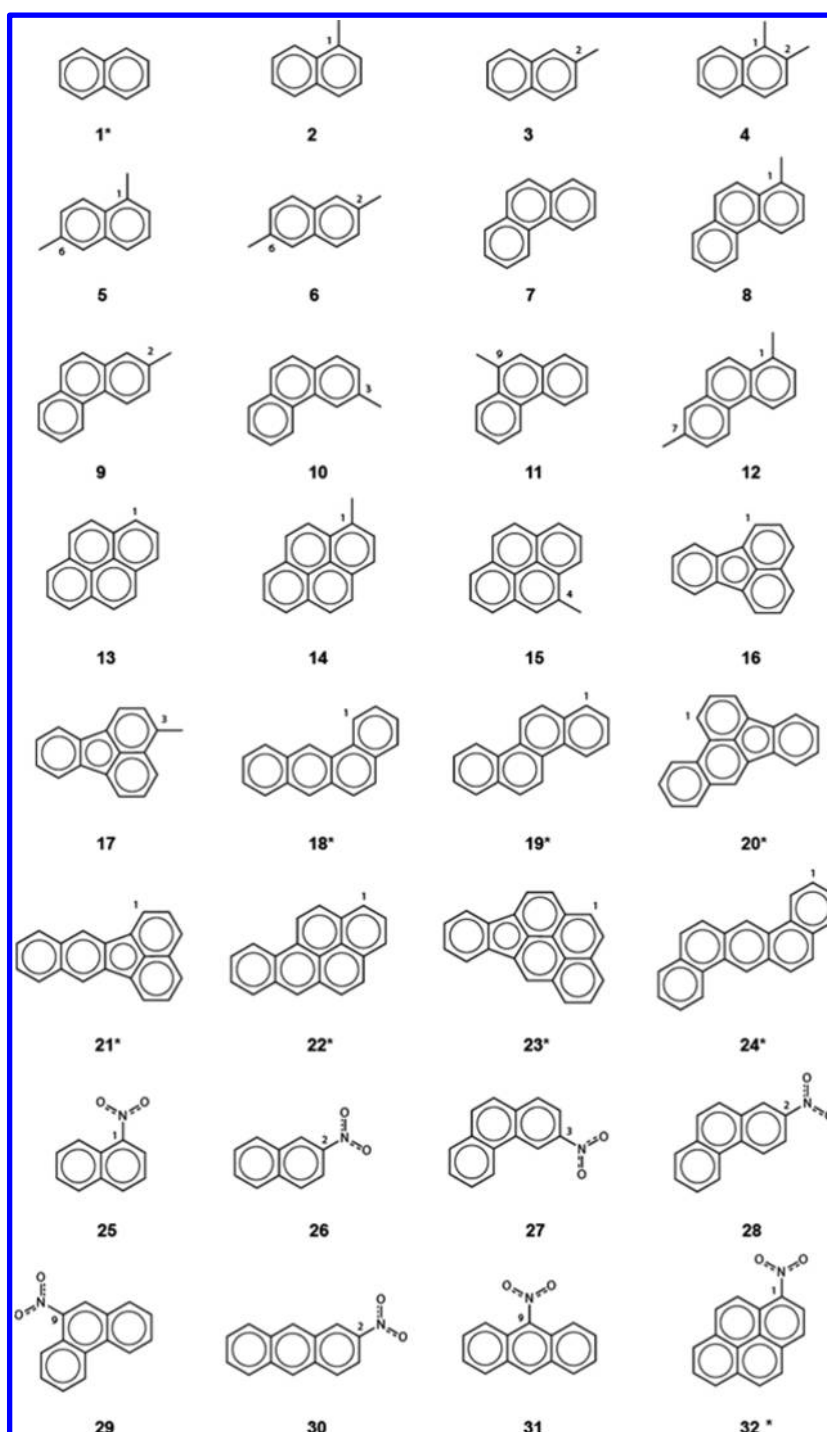


Figure 1. Chemical structures and numbering of PAHs and alkyl- and nitro-PAHs. Genotoxic compounds are labeled with asterisks; respective names, numbers, and abbreviations are given below. Naphthalene (1*, NAP), 1-methylnaphthalene (2, 1MeNAP), 2-methylnaphthalene (3, 2MeNAP), 1,2-dimethylnaphthalene (4, 1,2diMeNAP), 1,6-dimethylnaphthalene (5, 1,6diMeNAP), 2,6-dimethylnaphthalene (6, 2,6diMeNAP), phenanthrene (7, PHEN), 1-methylphenanthrene (8, 1MePHEN), 2-methylphenanthrene (9, 2MePHEN), 3-methylphenanthrene (10, 3MePHEN), 9-methylphenanthrene (11, 9MePHEN), 1,7-dimethylphenanthrene (12, 1,7diMePHEN), pyrene (13, PYR), 1-methylpyrene (14, 1MePYR), 4-methylpyrene (15, 4MePYR), fluoranthene (16, FLT), 3-methylfluoranthene (17, 3MeFLT), benzo(a)anthracene (18*, BaA), chrysene (19*, CHR), benzo(b)fluoranthene (20*, BbF), benzo(k)fluoranthene (21*, BkF), benzo(a)pyrene (22*, BaP), indeno(1,2,3-cd)pyrene (23*, IndP), dibenz(ah)anthracene (24*, DBaA), 1-nitronaphthalene (25, 1NitroNAP), 2-nitronaphthalene (26, 2NitroNAP), 3-nitrophenanthrene (27, 3NitroPHEN), 2-nitrophenanthrene (28, 2NitroPHEN), 9-nitrophenanthrene (29, 9NitroPHEN), 2-nitroanthracene (30, 2NitroANT), 9-nitroanthracene (31, 9NitroANT), 1-nitropyrene (32*, 1NitroPYR).

In general, PAHs are products of incomplete combustion of carbon-containing fuels and organic matter. Conesa et al.⁷ showed the importance of the chemical composition of the feed stock and the impact of the oxygen level on the formation of

PAHs. PAH emissions from internal combustion engines^{8,9} depend on parameters such as fuel type, vehicle technology, and whether the engine has been warmed or not and if it is operated in steady or transient conditions.

Several PAHs and nitro-PAHs are genotoxic compounds or act as precursors for genotoxic nitro-PAHs. Genotoxicity describes the property of chemical agents to damage the genetic information within cells, causing mutations which may lead to cancer. After uptake, PAHs are transformed in cells into active metabolites which can interact with DNA, causing mutations which eventually lead to cancer. The World Health Organization (WHO) classifies carcinogenic substances in five groups (<http://monographs.iarc.fr/ENG/Classification>). Benzo(a)pyrene (**22**) is classified as a group 1 carcinogen, being carcinogenic to humans. PAHs **1**, **18**, **19**, **20**, **21**, and **23** represent group 2A carcinogens, probably carcinogenic to humans, and PAHs **24** and **32** are group 2B carcinogens, possibly carcinogenic to humans (Figure 1, asterisk). Other PAHs appear in group 3 (not classifiable as to its carcinogenicity to humans) and group 4 (probably not carcinogenic to humans). Increased attention is given to certain nitro-PAHs due to higher mutagenic (up to 200 000 \times) and carcinogenic (10 \times) properties compared to those of their respective parent PAHs.¹⁰ Nitro-PAHs can be a significant fraction of the direct-acting mutagenic compounds present in diesel vehicle exhausts^{11,12} and ambient air particles.¹³ Although negligible concentrations have been found in traditional gasoline vehicles,^{14,15} it is important to consider its formation in GDI vehicles, as it has been shown that these vehicles emit more particles than traditional gasoline and diesel vehicles.¹⁶ They form from parent PAHs and NO₃ and OH radicals present in air.^{17,18} Nitro-PAHs formed are rapidly adsorbed on the airborne particles. Moreover, they can be formed by reaction of PAHs adsorbed in particles with N₂O₅ or HNO₃.¹⁰

GDI Vehicles Quickly Replace PFI Technologies. Traditional port-fuel injection vehicles are quickly being replaced by the GDI technology in many markets. It is expected that GDI vehicles will represent around 50% of the vehicle fleet in 2020.¹⁹ These vehicles have been introduced promising enhanced engine power and fuel efficiency and hence lower CO₂ emissions in comparison with PFI vehicles.

However, an important drawback of the GDI technology is the release of nanoparticles of unknown toxicity. GDI vehicles can release up to 10¹² particles/km, exceeding those of current diesel vehicles, which are now equipped with filters, by orders of magnitude.¹⁶ In other words, most GDI vehicles cannot fulfill the Euro-5 particle number limit of 6 \times 10¹¹ particles/km applied to diesel vehicles, which is valid for all new type approvals since September 2011 and for all new cars since January 2013.^{20,21}

GDI particles resemble those of diesel vehicles without after-treatment. They are agglomerates of soot-like nanoparticles formed in the engine under high pressure. In 2012, the WHO classified untreated diesel exhaust as a group 1 carcinogen inducing lung cancer in humans. Due to the striking similarities, concerns on GDI exhausts are on the rise because these exhausts might also be carcinogenic to humans. Therefore, detailed studies on the genotoxic potential of GDI vehicle exhausts are urgently needed to assess these new risks.

Blending of gasoline with ethanol affects particle emissions of spark ignition engines of PFI vehicles and possibly of GDI vehicles.^{22,23} In this paper, we report particle, PAH, and alkyl- and nitro-PAH emissions of a flex-fuel GDI vehicle operated with gasoline (E0) and two ethanol/gasoline blends (E10 and E85) and establish a relationship between PN and PAH emissions under transient and steady driving under hot- and cold-start conditions. The findings indicate that the release of particles and PAHs, including the genotoxic ones, are well-correlated, and

blending with ethanol reduces particle and PAH formation in the engine.

EXPERIMENTAL SECTION

Vehicle, Test Cycles, and Fuels. A Euro-5 flex-fuel GDI vehicle (Volvo V60) with a 1.6 L engine was used. Tests were performed at the chassis dynamometer of the University of Applied Science Bern (Nidau, Switzerland). Two driving cycles simulating transient and steady driving were applied. The worldwide harmonized light-duty vehicle test cycle (WLTC) was used, which includes urban, extra-urban, highway, and motorway driving (Figure 2). The cycle was investigated under cold- (cWLTC) and hot-start conditions (hWLTC). Furthermore, a steady-state cycle (SSC) representing mean velocities of the WLTC and idle was applied (Supporting Information, Figure S1 and Table S1). Two batches of commercial gasoline, one without (E0, RON 95, Class D/D1) and one with 85% ethanol (E85) were used as such and blended to obtain fuel with 10% ethanol (E10). Respective fuel properties are given in Tables S2–S5 (Supporting Information).

Exhaust Sampling, Workup, and Analysis. Carbon monoxide (CO) and carbon dioxide (CO₂) were investigated by IR spectrometry (Horiba MEXA-9400H, Japan). Total hydrocarbons (THC) were analyzed with flame ionization detection, and nitrogen oxides (NO_x) were analyzed with chemiluminescence detectors (Horiba). PN emissions were determined from dilute exhaust with a condensation particle counter (TSI 3790, Minnesota, United States) following the PMP protocol.²⁴ Diluted exhausts were sampled from a constant volume sampling (CVS) tunnel. Aliquots were collected in all-glass sampling devices including filter, condenser, and adsorber units (XAD2) according to the filter/condenser method described in the European standard EN-1948-1.²⁵ This allows quantitative sampling of semivolatile compounds in combined samples, including particle-bound, liquid, and gaseous fractions. An approximated scheme of the setup is explained elsewhere.^{12,26}

All solvents were analytical grade. Prior to sampling, the glass apparatus was cleaned and heated to 450 °C overnight. Aliquots of ¹³C-labeled **1**, **7**, and **13** were placed on a quartz swab and given to the condensate separator prior to each sampling. These compounds were used to calculate the losses during sampling and workup. The complete analytical procedure is described in the Supporting Information.

Quality Assurance, Recoveries, and Nitration Artifacts. Nitration of PAHs can occur during sampling and cleanup, which is considered as an unwanted artifact. To test the extent of nitration during sampling and cleanup, ¹³C-labeled **1**, **7**, and **13** were spiked to the device prior to sampling, and recoveries for these compounds and the extent of ¹³C-labeled nitro-PAH formation during sampling and cleanup were determined. Different measures can reduce these risks. Rapid dilution of the exhaust in a dilution tunnel is one option; however, dilution with air represents an additional contamination source. CVS blank samples ($n = 3$) were collected during the campaign to determine detection limits for the employed methodology. Compounds detected at average blank levels are reported as not detected.

RESULTS AND DISCUSSION

Ethanol Effects on PN, CO, and CO₂ Emissions during Transient and Steady Driving. Injection of gasoline at high pressures allows charging the engine with dispersed fuel, enhancing the combustion performance and lowering fuel

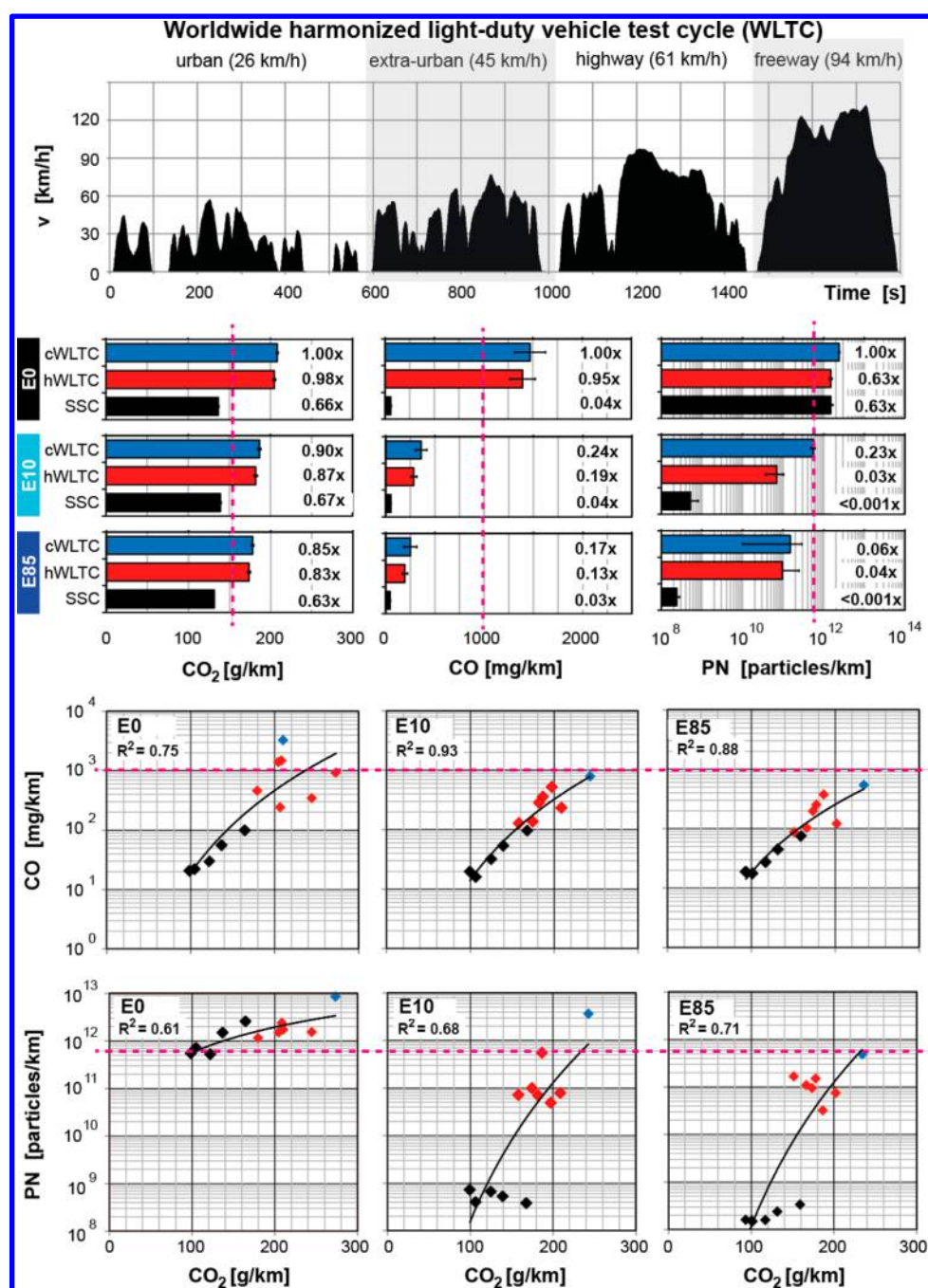


Figure 2. CO₂, CO, and PN emission factors of a flex-fuel GDI vehicle (Volvo V60, 1.6 L, 132 kW). The vehicle was operated with gasoline (E0) and blends with 10% (E10) and 85% (E85) ethanol in the cold- (blue) and hot-start (red) WLTC and SSC (black). Reductions relative to respective reference values (E0, cWLTC, 1.00x) are indicated. The velocity–time diagram of the WLTC is also given, and the four cycle phases are distinguished. Correlations of CO₂ (g/km), CO (mg/km), and PN (particles/km) data at different phases of the WLTC (red and blue) and SSC (black) for E0 (left), E10 (middle), and E85 (right) and respective trend lines are also shown. The red dashed line is the emission limit value.

consumption.²⁷ In other words, a comparable performance can be achieved with a down-sized engine. The Euro-5 flex-fuel vehicle (Volvo V60 T4F) has a 1.6 L engine with a specified performance of 132 kW and fuel consumption (FC) of 6.6 L/100 km in the homologation cycle, currently the European driving cycle (EDC). This corresponds to CO₂ emissions of 153 g/km. Figure 2 displays the time–velocity diagram of the WLTC, which will replace the EDC in 2017, as the new legislative type-approval cycle. Four phases with urban, extra-urban, highway, and freeway driving are included with average velocities of 26, 45, 61, and 94 km/h, respectively. The WLTC is expected to represent real-

world driving in a much better way than the currently applied EDC. Fuel consumption of this vehicle in cold and hot start WLTCs reached 9.1 ± 0.1 and 8.9 ± 0.1 L/100 km, corresponding to CO₂ emissions of 208 ± 1 and 205 ± 2 g/km and exceeding the specified EDC-value by 34–37%. The vehicle had the lowest fuel consumption of 5.9 ± 0.1 L/100 km and CO₂ emissions of 137 ± 1 g/km when smoothly operated in the steady state cycle (SSC) consisting of four phases of constant vehicle operation at 95, 61, 45, and 26 km/h and idling (Figure S1, Supporting Information). Thus, transient engine operation in the WLTC with fast and frequent load changes

induced a 51–54% increase in the FC compared to that of steady vehicle operation in the SSC. Cold start effects were small with an increased FC of 2–3%. Blending with ethanol had a significant effect on CO₂ emissions, which dropped by 10% (E10) and 15% (E85) to levels of 187 ± 2 and 178 ± 2 g/km in the cWLTC, respectively (Figure 2 and Table S6).

It has been reported elsewhere^{28,29} that fuel consumption and CO₂ emissions for each driving cycle depend on the starting temperature and exhaust system. Thus, higher fuel consumption and CO₂ emission are obtained with lower starting temperatures. According to the mentioned study, vehicle tested under WLTC produces CO₂ emissions higher than those under EDC. This would explain the higher values obtained here which exceed the limit for EDC.

Figure 2 also displays mean ($n = 4$) CO and PN emission factors (middle) of the GDI vehicle operated with E0, E10, and E85 and CO, PN, and CO₂ correlation diagrams for different cycle phases (bottom). Table S6 (Supporting Information) reports respective values. CO emissions were 25-fold higher at transient (1470 ± 160 g/km) rather than steady vehicle operation (56 ± 7 g/km) with E0 exceeding the CO emission limit of 1000 mg/km (Figure 2, dashed line) for Euro-5 vehicles under homologation conditions. The vehicle was originally calibrated in the EDC cycle by the manufacturers as it is usually done, and tests were performed with the WLTC. The EDC cycle is a poor dynamic cycle, and the acceleration of this cycle can be driven without an enrichment of the air-fuel mixture. The WLTC cycle is more dynamic than the EDC cycle. Moreover, the vehicle tested in this research is very sensitive to the dynamic driving and often, by the WLTC cycle, the air-fuel mixture is enriched by the acceleration, explaining why the CO value is so high.

PN emissions of $2.4 \pm 0.1 \times 10^{12}$ particles/km were obtained in the cWLTC with E0 exceeding the PN limit of 6.0×10^{11} particles/km (dashed line) valid for Euro-5 diesel vehicles but were within the limit of 6.0×10^{12} particles/km valid for Euro-6 gasoline vehicles. Ethanol blending lowered CO emissions by 76 and 83% in the cWLTC when comparing E10 and E85 with E0 data. PN emissions dropped likewise by 77 and 94% in the cold and by 97 and 96% in the hWLTC (Figure 2 and Supporting Information, Table S2). Note that, for most comparisons throughout the text, E0 emission data of the cWLTC are taken as the reference (1.00×).

In terms of other concerning emissions, it was found that negligible HCHO, very low NO₂ emissions (below 1.8 ppm), and no N₂O were observed with E85 in the WLTC and SSC. Very similar results regarding these emissions were obtained for E10. According to literature, there are usually no measurable concentrations of NO₂, N₂O, and HCHO with a correctly working three-way catalyst (below 1 ppm).³⁰

In summary, blending with ethanol induced a moderate decrease in CO₂ (10–15%) and overproportional reductions of CO (76–87%) and PN (77–97%) emissions. Transient versus steady driving has a large impact on PN and CO emissions, indicating that the vehicle, when operated with gasoline (E0), often is in fuel-rich and oxygen-deficient conditions. Upon blending with ethanol, combustion efficiency improved, and CO and PN emissions were lowered substantially.

It is important to mention that contradictory results can be found in literature, where ethanol addition increases PM (particulate matter).^{31–33} This could be due to the higher heat of evaporation of ethanol compared to gasoline, which causes cooling in the combustion chamber, thereby reducing vaporization of the least volatile hydrocarbon fuel species and

resulting in residual liquid fuel that promotes PM formation by diffusion burning.

Ethanol Effects on PAH and Nitro-PAH Emissions during Transient and Steady Driving. From a chemical point of view, soot-like nanoparticles and PAHs are similar and might form under the same conditions in those transients where oxygen is deficient in the combustion chamber and increased CO and PN emission are observed (Figure 2). Figure 3 includes a selection of 2- to 6-ring PAHs from **1**, the most volatile PAH, with a boiling point (BP) of 218 °C to **22**, a class 1 carcinogen with a BP of 495 °C. Emission factors (μg/km) of 11 PAHs and 13 alkyl- and 6 nitro-PAHs during cold- (blue) and hot-started (red) WLTC and SSC (black) driving with E0 (gray), E10 (blue), and E85 (violet) are shown. EFs of other PAHs not displayed are given in Table S7 (Supporting Information). All PAHs shown in Figure 1 were found in E0 samples, whereas some of the less-volatile PAHs were not detected in E10 and E85 samples. Nondetected compounds are reported as equal to blank levels, which correspond to those levels found in CVS dilution air (Figure 3, light color).

PAH emission factors varied up to 5 orders of magnitude from 0.0002 to 80 μg/km. In most cases, E10 and E85 emissions are lower than those of E0 samples with few exceptions such as **16**. **1**, the most abundant PAH, was released 3 orders of magnitude higher than most genotoxic PAHs, e.g., **22**, in agreement with literature data.³⁴ **1** emissions of 79, 60, and 44 μg/km were found in the cWLTC with E0, E10, and E85, respectively; respective EFs in the hWLTC were 44, 15, and 17 μg/km. This corresponds to reductions of 24 and 80% (cWLTC and hWLTC) and 45 and 79% when comparing E10 and E85 with E0 data, respectively. As another example, **22** emissions of 0.08, 0.02, and 0.01 μg/km were observed for E0, E10, and E85, respectively, in the hWLTC, corresponding to 68 and 85% reductions.

In conclusion, blending of gasoline with ethanol induced substantial PAH reductions, most pronounced in WLTC. PAH emissions in the SSC were one to three orders of magnitude lower than those in the WLTC, indicating that PAHs are mainly formed during transient vehicle operation.

As shown in Figure 4 (top), mean emissions of 2-, 3-, 4-, 5-, and 6-ring PAHs were lowered in the cWLTC by 35, 73, 77, 52, and 66% and by 60, 38, 66, 84, and 97% when comparing E10 and E85 with E0 data, respectively. Slightly larger effects were observed in the hWLTC with 2-, 3-, 4-, 5-, and 6-ring PAH emissions reduced by 67, 77, 74, 88, and 96% and 85, 82, 85, 91, and 97% with E10 and E85, respectively. Thus, ethanol blending has a comparable impact on PN and PAH emissions, most pronounced at transient driving.

A moderate cold-start effect ranging from 34 to 80% was also found for the 16 US EPA PAHs under cold-start conditions. This is in accordance with the literature.^{35,36}

Figure 4 (middle) displays correlation diagrams of the observed emission reduction (%) of individual PAHs and their boiling point (°C) when comparing E10 (left) and E85 (right) with E0 data. Despite considerable scatter, it seems that the percentage of PAH reduction obtained increases with ring number (size) and boiling point.

Higher ethanol proportions (E85) further reduced PAH emissions, but effects are already substantial with relatively low proportions, e.g. E10, indicating that combustion chemistry is already affected.^{4,37} The most-known genotoxic PAHs are 5- and 6-ring compounds with the exception of **1**, and also, their respective genotoxic potentials are lowered when ethanol blends are used, as will be discussed later.

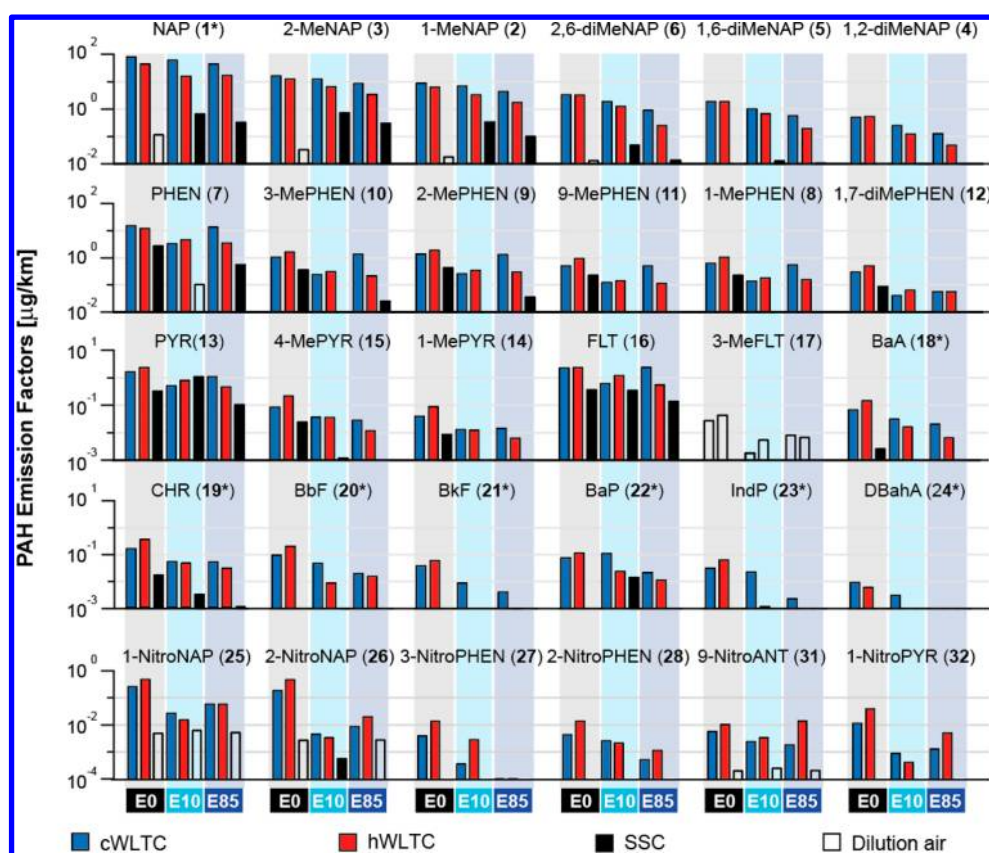


Figure 3. Effects of ethanol blending on selected PAH and nitro-PAH emissions. Values are reported as emission factors in $\mu\text{g}/\text{km}$. The genotoxic compounds NAP (1), BaA (18), CHR (19), BbF (20), BkF (21), BaP (22), IndP (23), and DBaH (24) are labeled (*). PYR (13) and FLT (16) are precursors of respective genotoxic alkyl- and nitro-PAHs. Emission factors for gasoline (E0, gray) and two ethanol/gasoline blends (E10, blue; E85, violet) were determined under cold- (blue) and hot-start conditions (red) in the WLTC and SSC (black). Emissions at the blank level (CVS dilution air) are given as white bars.

Figure 3 and Table S8 (Supporting Information) also report on nitro-PAH EFs ($\mu\text{g}/\text{km}$), which were about three orders of magnitude lower than those of the respective parent PAHs. For example, 79 and 44 $\mu\text{g}/\text{km}$ of 1 was released in the cold- and hot-started WLTC with gasoline (E0), but only 0.25 and 0.48 $\mu\text{g}/\text{km}$ of 25 and 0.18 and 0.46 $\mu\text{g}/\text{km}$ of 26 were found in these exhausts. Another example is 32, which was released at 0.11 and 0.39 $\mu\text{g}/\text{km}$, while 1.6 and 2.3 $\mu\text{g}/\text{km}$ of pyrene was emitted under the same conditions (c and hWLTC with E0). Note that nitro-PAH emissions in the hWLTC are often higher than those in the cWLTC. In general, nitro-PAH emissions were lowered by 31–96 and 38–95% when E10 and E85 were used, respectively, compared to E0.

Nitro-PAHs are also critical constituents of nonfiltered and filtered diesel exhausts¹² (such as some nitro-naphthalenes, nitro-phenanthrenes, and nitro-pyrenes). Concentrations of 25 of 170–560 ng/m^3 for engine-out diesel exhaust and 4–12 ng/m^3 after diesel particle filters were reported.¹¹ Values of 38–663 ng/m^3 were obtained in this study. Comparable results are also found for other nitro-PAHs. In other words, nitro-PAH emissions of the GDI vehicle were at levels of nonfiltered diesel exhausts and one or two orders of magnitude above those of filtered diesel exhausts.

In conclusion, nitro-PAHs respond like PAHs and are reduced with ethanol blending. Furthermore, nitro-PAH levels were up to 4 orders of magnitude lower than those of respective parent PAHs indicating that nitration chemistry in the GDI exhaust is less important than in diesel vehicle exhausts.^{11,12}

It should be pointed out that, with some PAHs and nitro-PAHs (Figures 3 and 4 and Tables S7 and S8 in the Supporting Information), the concentrations obtained using E85 are higher than those obtained with E10 and even higher than those of E0. A reason for that could be explained as previously commented for the regulated pollutants and as reported in literature, where ethanol addition increases PM (particulate matter).^{31–33} In this situation, the higher heat of evaporation of ethanol compared to that of gasoline causes cooling in the combustion chamber, thereby reducing vaporization of the least volatile hydrocarbon fuel species and resulting in residual liquid fuel that promotes PM formation by diffusion burning.

Ethanol Effects on Genotoxic Potential. Toxicity equivalency factors (TEFs) can be used to compare the cumulated toxicity of multicomponent mixtures with similar mode of action. Several authors reported different PAH TEFs, often applied are those proposed by Nisbeth and LaGoy³⁸ which we and others used.^{39–41} Table S4 (Supporting Information) reports these TEF. The genotoxic potential of a single PAH is calculated from its emission factor (ng/km) multiplied by the respective TEF. Figure 1 displays structures of PAHs 1, 18–24 and 32 which are genotoxic (*) according to the WHO. Their absolute ($\text{ng}\text{-TEQ}/\text{km}$) and relative contributions to the overall genotoxic potential and respective patterns are shown in Figure 4 (bottom). Blending with ethanol reduced the genotoxic potential of the GDI exhaust which accounted for 190 $\text{ng TEQ}/\text{km}$ in the cWLTC with gasoline (E0) but was lowered to 180 and 70 $\text{ng TEQ}/\text{km}$ with E10 and E85, corresponding to reductions of

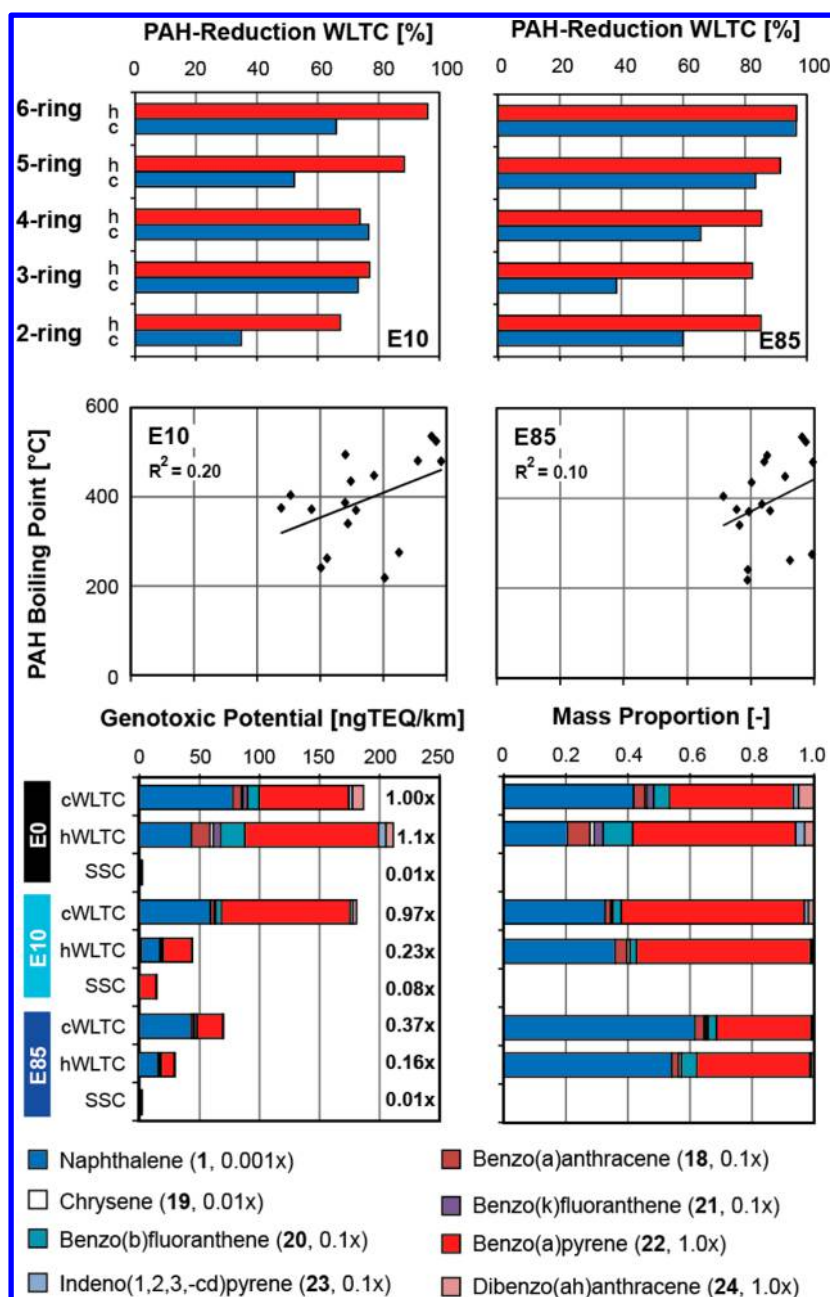


Figure 4. Percentage PAH reduction and genotoxic potential. Upper diagrams compare PAH reductions (%) from E10 (left) and E85 (right) blends relative to gasoline (E0). The influence of ring number in hot- (red) and cold-started (blue) WLTC (first row) and boiling point (°C) of individual PAHs (second row) in the hot WLTC is given. Cumulated genotoxic potentials (ng TEQ/km) of genotoxic PAHs and respective patterns are shown in lower diagrams. Name, color code, toxicity equivalence factor of genotoxic PAHs, and fold-reduction relative to E0 data in the cWLTC are also included.

3 and 63%. Even larger effects were observed in the hWLTC with reductions of 77 and 84% for E10 and E85. Figure 4 also reports genotoxic potentials in the SSC which in all cases account only for 1–8% of those in transient operation.

The respective patterns are clearly dominated by 22 (red) with the highest TEF (1.0) and 1 (blue) with the lowest TEF (0.001) but with emissions 3 orders of magnitude higher. The proportion of 1 increased from E0 to E85 in respective patterns (Figure 4). This is due to larger reductions of 5- and 6-ring versus 2-ring PAHs.

Environmental Impact. PAHs and nitro-PAHs are ubiquitous air pollutants and as such are also found in dilution air. However, concentrations in examined GDI exhausts exceeded those of the dilution air by orders of magnitude in most cases. Therefore, it is evident that the GDI vehicle released relevant

amounts of PAHs and nitro-PAHs together with large numbers of soot-like nanoparticles. In other words, such vehicles will substantially contribute to ambient PN, PAH, and nitro-PAH burdens in traffic-affected areas.

Blending gasoline with ethanol induced substantial reductions of nanoparticle, CO, PAH, and nitro-PAH emissions and with it the genotoxic potential of the GDI exhausts. Effects are strongest in transient driving conditions. Using only 10% ethanol is sufficient to reduce PN by 95% and PAH and nitro-PAHs in a range of 67–96%. These are promising results that should be confirmed with further vehicles and other oxygenated fuels.

One can conclude that particles and PAHs form simultaneously in the engine in fuel-rich and oxygen-deficient zones where incomplete combustion is prevailing. CO data, which is

correlated well with particle emissions, supports this hypothesis. Furthermore, we conclude that ethanol with a high oxygen content of 35% inherently increases oxygen levels in fuel-rich zones, lowering soot particle, PAH, and CO emissions, which are typical markers for incomplete combustion. Blending gasoline with ethanol leads to a more complete combustion, which is most obvious under transient vehicle operation where optimal fuel-air stoichiometry is not reached. Ethanol not only improved the combustion efficiency but also lowered the genotoxic potential of these exhausts up to 77 and 84% with E10 and E85.

As reported in literature,^{4,42,43} GDI vehicles emit more particles and certain pollutants than traditional PFI; therefore, we conclude that the fast replacement of PFI vehicles with this technology will be associated with increased emissions of particles and genotoxic PAHs. This can partly be compensated with ethanol blending, which improves the combustion efficiency and suppresses particle, PAH, and nitro-PAH formation in the engine and with it lowers the genotoxic potential of GDI vehicle exhausts.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02606.

Additional figures, tables, and descriptions: Figure 1 and Tables S1–S5 provide additional information about the driving cycle, the fuels used, and the analytical procedure for the analysis of the PAHs; quantitative results are reported in Tables S6–S9 and represent the specific emission factors obtained for regulated pollutants, PAHs, nitro-PAHs, and the TEF values used (Table S8) (PDF)

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■ Notes

The authors declare no competing financial interest.

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An Overview of the Effects of Ethanol-Gasoline Blends on SI Engine Performance, Fuel Efficiency, and Emissions

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ABSTRACT

This paper provides an overview of the effects of blending ethanol with gasoline for use in spark ignition engines. The overview is written from the perspective of considering a future ethanol-gasoline blend for use in vehicles that have been designed to accommodate such a fuel. Therefore discussion of the effects of ethanol-gasoline blends on older legacy vehicles is not included.

As background, highlights of future emissions regulations are discussed. The effects on fuel properties of blending ethanol and gasoline are described. The substantial increase in knock resistance and full load performance associated with the addition of ethanol to gasoline is illustrated with example data. Aspects of fuel efficiency enabled by increased ethanol content are reviewed, including downsizing and downspeeding opportunities, increased compression ratio, fundamental effects associated with ethanol combustion, and reduced enrichment requirement at high speed/high load conditions. The effects of ethanol content on emissions are also reviewed, including NMOG/CO/NO_x, particulate matter, toxic compounds, and off-cycle and evaporative emissions.

Considering the engine and vehicle-related factors reviewed in this paper, a mid-level ethanol-gasoline blend (greater than E20 and less than E40) appears to be attractive as a future fuel. To provide high knock resistance, this fuel should be formulated using a blendstock that retains the octane of the current blendstock used for regular-grade E10 gasoline. Further work is needed to recommend a specific ethanol blend level, including analysis of fuel efficiency and CO₂ benefits for representative powertrain/vehicle applications, and of fuel production and supply considerations.

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INTRODUCTION

In recent years there has been intense interest in the use of bio-ethanol as a fuel for internal combustion engines. Drivers for this interest are the desire for energy security and independence, concern for reducing greenhouse gas (GHG) emissions, and economic value to domestic agriculture and related industries. In recognition of the potential benefits of renewable fuel, the U.S. Congress passed the Energy Independence and Security Act of 2007 [1], which mandates the use of 36 billion gallons of ethanol-equivalent renewable fuel by 2022.

The intense interest in ethanol has resulted in a vast amount of information in the technical literature. The purpose of this paper is to provide an overview of the effects of ethanol-gasoline blends on full load performance, fuel

efficiency, and emissions of modern spark ignition internal combustion engines.

The effects of ethanol content on engine component durability and on material compatibility requirements are beyond the scope of this review. However, these aspects have been addressed in flexible fuel vehicles (FFVs) operating on E85 and thus solutions for intermediate blends are expected to be practicable.

FUTURE REGULATIONS

A brief overview of highlights of future U.S. GHG, criteria, and toxic emissions regulations is provided in this section to provide background for the potential impact of ethanol-gasoline blends in meeting these requirements. Regulations in the U.S. are complicated by the fact that the California Air Resources Board (CARB) and the U.S.

Environmental Protection Agency (EPA) have separate requirements. Historically, CARB levels have been more stringent than those of the EPA, and to date fourteen “Green States” have adopted the California requirements for light duty and medium duty vehicles.

In January 2012, CARB adopted new emission rules for cars and light trucks through the 2025 model year (MY), including Low Emission Vehicle III (LEV III) requirements. LEV III includes standards for greenhouse gases, gaseous tailpipe air pollutants, particulate matter (PM), and evaporative emissions. The CARB LEV III standards are more stringent than the current EPA Tier 2 standards; therefore the following sections are a discussion of CARB LEV III rules.

Greenhouse Gases

The GHG standards are expressed as grams of carbon dioxide equivalent per mile ($\text{gCO}_2\text{e}/\text{mi}$). The amount of each greenhouse gas emitted is multiplied by a factor that accounts for its global warming potential relative to that of CO_2 over a 100-year time horizon: 1 for CO_2 , 25 for methane (CH_4) and 298 for nitrous oxide (N_2O).

Current CARB and EPA regulations covering vehicles through the 2016 MY are intended to provide a 30% reduction in GHG emissions compared to 2010 levels. LEV III includes regulations applicable for the 2017 MY to 2025 MY, with average reductions of 4.5% per year. The GHG standards are indexed based on vehicle footprint (wheelbase x average track width), and the target $\text{gCO}_2\text{e}/\text{mi}$ curves are different for passenger cars and light trucks. Compliance is determined for a manufacturer by comparing the sales-weighted target with the sales-weighted performance for all of the models manufactured in a given year. By 2025, GHG emissions are intended to be reduced by 34% compared to 2016 levels.

Air Pollutants

Vehicle emissions that are regulated due to their adverse impact on air quality are non-methane organic gases (NMOG), carbon monoxide (CO), oxides of nitrogen (NO_x), and PM. For LEV III, fleet average standards for the first three pollutants are reduced to super ultra-low emission vehicle (SULEV) levels by 2025, which represents a reduction of approximately 75% compared to 2014 MY and greater than 99% compared to 1975. The regulation creates new emission bins (intermediate emission level categories) between current SULEV levels and the Zero Emission Vehicle (ZEV) levels. Separate NMOG and NO_x fleet standards are replaced with a combined NMOG + NO_x standard, as shown in Figure 1.

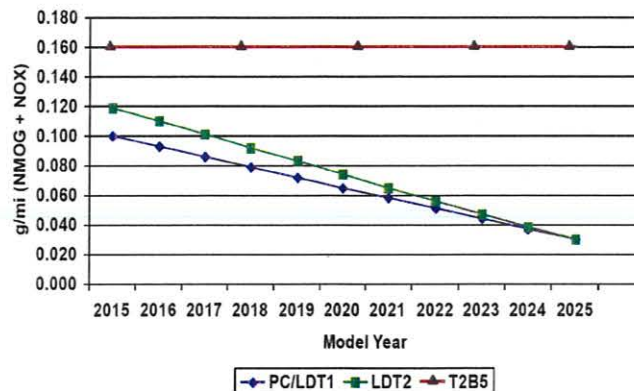


Figure 1. Combined NMOG + NO_x standards of LEV III for passenger car/light duty 1 and light duty 2 category vehicles; EPA Tier 2 Bin 5 shown for reference.

LEV III standards for particulate mass are tightened from the current 10 mg/mile to 3 mg/mile, with a gradual phase-in from 2017 to 2021. The particulate mass standard will be further reduced to 1 mg/mile beginning with 2025 and phasing in through 2028.

Toxic Emissions

A provision of LEV III applies to substitute fuels and new clean fuels in 2015 and subsequent years. This provision requires that the tailpipe emissions of four specific toxic compounds (1,3-butadiene, benzene, formaldehyde, and acetaldehyde) are measured along with CO, NO_x , and the ozone forming potential of the NMOG emissions. CARB requires that the potency-weighted sum of these four toxics be below a limit that is based on the corresponding value for the certification fuel [2].

PROPERTIES OF ETHANOL-GASOLINE BLENDS

Prior to discussing the effects of ethanol-gasoline blends in SI engines, it is instructive to review the fuel property effects of blending ethanol with gasoline. Properties of typical E0 regular grade U.S. gasoline and ethanol are shown in Table 1. Some of the properties blend in a linear manner; for example, the heat of vaporization (HoV) is the mass-weighted average of the values for ethanol and the gasoline blendstock (minus the heat of mixing which is comparatively small [5]). The Research Octane Number (RON) [6] and Motor Octane Number (MON) [7] values blend approximately as the molar concentration weighted average [8]. However, volatility parameters such as vapor pressure and distillation curves exhibit non-linear behavior with ethanol content [9, 10, 11, 12, 13, 14, 15, 16]. Each of these properties is discussed in detail in the sections below.

Table 1. - Properties of typical regular grade E0 U.S. gasoline and pure ethanol [3,4].

	Gasoline	Ethanol
RON	91-92	109
MON	82-84	90
Sensitivity	7-9	19
AKI	87-88	99
NHV ^a (MJ/kg fuel)	42-44	26.9
(MJ/L fuel)	31-32	21.1
(MJ/kg air at stoich)	2.9-3.0	3.0
HoV ^b (kJ/kg fuel)	~350	920
(kJ/kg stoich mixture)	~22	92
Stoichiometric A/F	14.5-14.9	9.0
Density ^b (kg/L)	0.72-0.76	0.785
Molecular Weight (g/mole)	95-115	46

^a ASTM D240 or D4809

^b at 25 °C

Energy Content

It is well known that the energy content of ethanol as measured by the net heating value (NHV) is approximately 33% less than that of gasoline on a volumetric basis (Table 1). NHV is equivalent to lower heating value and net heat of combustion. The NHV per volume of an ethanol-gasoline blend is the volume-weighted average of the values for ethanol and the gasoline blendstock (Figure 2). Hence as the ethanol content of the fuel is increased, the fuel economy in miles per gallon (mpg) and driving range for a given fuel tank size are reduced. This penalty can be partially offset by improved thermal efficiency, as discussed later in this paper.

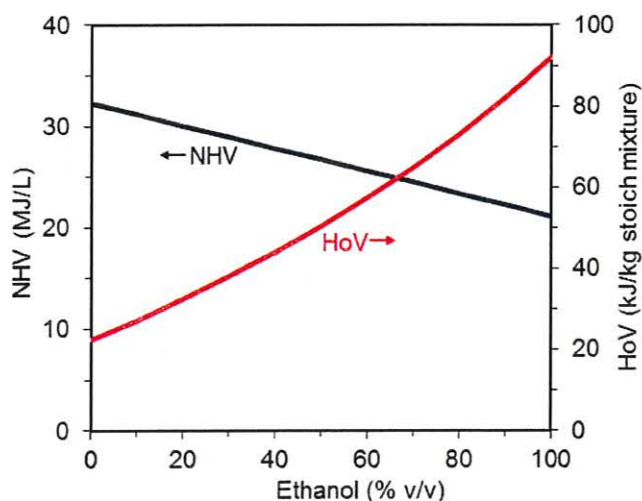


Figure 2. NHV and estimated HoV of ethanol-gasoline blends for a typical gasoline blendstock.

The heat released per engine cycle and thus the full load torque of an engine is directly proportional to the mass of trapped fresh air per engine cycle and to the heating value of the fuel per unit mass of fresh air. As shown in Table 1, typical gasoline and pure ethanol have nearly equal NHV per unit mass of air at stoichiometry, and therefore engine torque per unit mass of air would be equivalent at equal thermal efficiency.

Heat of Vaporization

The heat (or enthalpy) of vaporization represents the amount of energy required to evaporate a liquid fuel. In a direct injection (DI) engine, the amount of cooling of the fresh charge and consequent knock relief provided by evaporation of the fuel is proportional to the fuel flow per unit mass of air. The stoichiometric air-fuel ratio (A/F) of ethanol is 9.0 and that of gasoline is about 14.6 (the exact value depends on the composition of the gasoline), and hence more mass of ethanol than gasoline is required at stoichiometry for a given mass of air. The HoV of ethanol is about 2.6 times that of gasoline per unit mass of fuel, and about 4.2 times that of gasoline per unit mass of a stoichiometric mixture (Table 1). In Figure 2, the HoV per unit mass of stoichiometric mixture for ethanol-gasoline blends for a typical gasoline blendstock is plotted vs. percent ethanol volume.

Octane Number

The RON and MON of an ethanol-gasoline blend can be conservatively estimated by a molar concentration-weighted average of the respective values for ethanol and the gasoline blendstock [8,17]. This behavior results because the molecular fraction and partial pressure of each compound in the fully vaporized fuel during combustion is equal to its molar fraction in the liquid fuel. Because the molecular weight of ethanol (46 g/mole) is much less than that of typical gasoline hydrocarbons (95 - 115 g/mole), the mole fraction of ethanol in a blend is higher than its liquid volume fraction, as shown in Figure 3. The relative difference is particularly evident in low- and mid-level ethanol-gasoline blends. Note in Figure 3 that 10% and 30% ethanol blends by volume correspond to approximately 20% and 50%, respectively, in molar concentration.

The molar-weighted estimate of RON and MON values for ethanol-gasoline blends can be improved by the addition of a non-linear term [17]. In the study of [17], measured RON values were up to 3 RON greater than values estimated by linear molar weighting. The additional term enabled a greatly improved model fit as seen in Figure 4 and can be interpreted as accounting for positive interactions between ethanol and certain hydrocarbons.

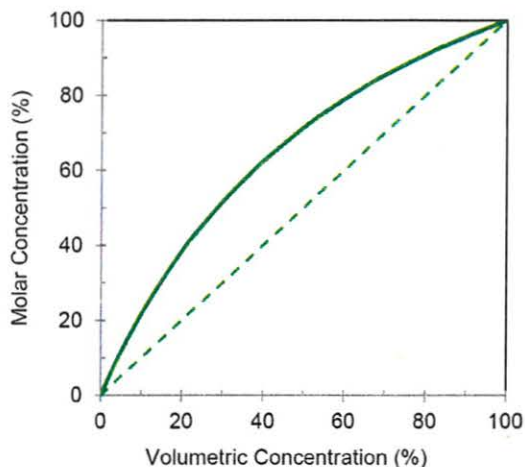


Figure 3. Molar vs. volumetric concentration for ethanol-gasoline blends (solid) and 1:1 reference line (dashed) [8].

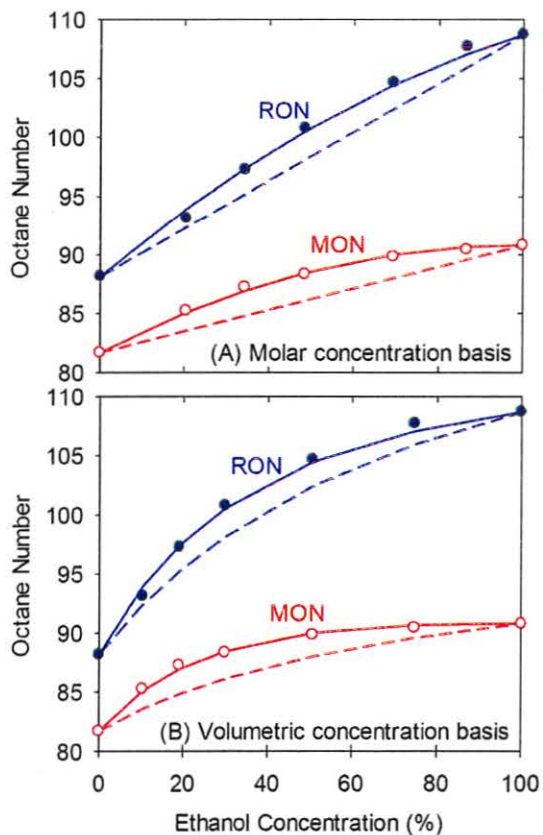


Figure 4. RON and MON values for an ethanol-gasoline blend series versus molar (A) and volumetric (B) ethanol concentration; symbols are measured data, dashed lines show linear molar blending model, solid lines show non-linear molar blending model [17].

The autoignition kinetics of a fuel are dependent on the temperature of the unburned end gas. A measure of this dependency which has been commonly used is the difference between the RON and MON values, defined as the sensitivity (S) of the fuel: $S = \text{RON} - \text{MON}$. As will be discussed in a later section, the sensitivity of a fuel has a profound effect on its knock behavior as test conditions are varied. Because RON and MON values of an ethanol-gasoline blend can be estimated by molar weighting, it follows that the sensitivity can also be estimated by molar weighting.

Vapor Pressure

The most commonly used measure of vapor pressure is the Reid vapor pressure (RVP), defined as the vapor pressure measured at 37.8°C (100°F) in a chamber with a vapor-to-liquid volume ratio of 4:1. RVPs for blends of ethanol in a certification gasoline blendstock are shown in Figure 5 [12]. (EEE gasoline from Haltermann Solutions was used for this study. This is equivalent to fuel with the trade name “Indolene”. Both of these fuels are used for vehicle certification and serve as a standard reference gasoline without additives and having consistent, well-defined properties.)

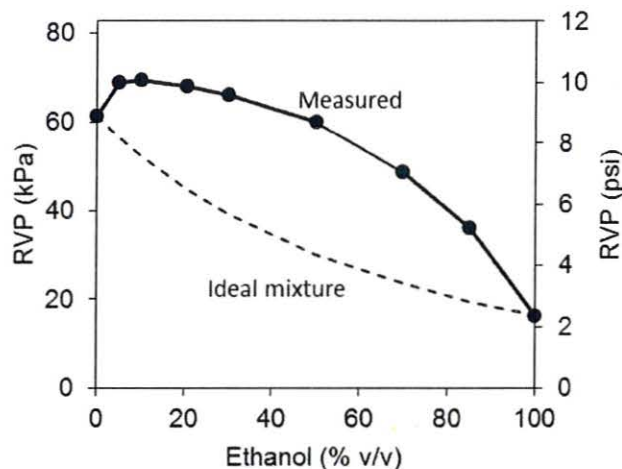


Figure 5. Reid vapor pressures (predicted Dry Vapor Pressure Equivalent) for ethanol-gasoline blends and values for an ideal mixture [12].

As shown in Figure 5, when ethanol is added to gasoline, the blend exhibits a vapor pressure that is higher than that of both the gasoline and ethanol portions of the blend. Note that the highest RVP was observed when 10% v/v ethanol is added. Further increasing ethanol content reduces the RVP, such that RVPs match that of the base gasoline at ethanol concentrations of 30% to 55% v/v, with higher concentrations needed for base gasolines with lower RVP [11, 12, 13].

This non-intuitive behavior is a consequence of molecular interactions between the gasoline components and ethanol. For an ideal mixture of components, vapor pressure would follow a molar concentration weighting (dashed line in Figure

5). In ethanol-gasoline blends, the nonpolar (even distribution of electron charge) hydrocarbon molecules in gasoline interfere with the intermolecular hydrogen bonding between the polar (uneven distribution of electron charge, creating positive and negative poles) ethanol molecules, and the ethanol interferes with molecular interactions between the gasoline hydrocarbons [9,10,15]. These interferences with intermolecular bonding allow the respective molecules to more readily escape the liquid as vapor, increasing vapor pressure, and result in formation of near-azeotropes of ethanol and gasoline components. For a true azeotrope, the relative concentrations of the components in the vapor are the same as those in the liquid mixture. In other words, a true azeotropic mixture vaporizes as if it were a single component. While ethanol-gasoline blends are not true azeotropes, the volatility characteristics are affected in a near-azeotropic manner.

An extensive set of data illustrating vapor pressure behavior for ethanol blends with market gasolines and blendstocks of varying volatility is provided in a study by the American Petroleum Institute (API) [11]. The RVP increase with ethanol addition to gasoline was shown to be dependent on the composition of the gasoline, with greater RVP increase observed for gasoline with lower RVP or greater saturated hydrocarbon content. In that study, the RVPs of E10 blends was nearly always greater than or equal to the RVP of E12.5, E15, E20, and E30 with the same blendstock.

The fuel components that contribute most to the vapor pressure are the most volatile gasoline components, primarily isomers of butane and pentane, plus ethanol when present. Vapor pressure increases with temperature, and the vapor pressure of ethanol-gasoline blends shows a greater change with temperature than gasoline containing no ethanol [12]. Thus, for E0 and E10 fuels with the same RVP, the E10 will have an increasingly higher vapor pressure than the E0 as temperature is increased above the RVP temperature (37.8°C). Likewise, the E10 will have a lower vapor pressure than the E0 at lower temperatures.

Distillation Curve

The normal boiling point of ethanol is 78°C, and it might be expected that the ethanol in an ethanol-gasoline blend would distill at this temperature. However, distillation in this test method does not occur as discrete segments of compounds being distilled; rather it represents vaporization of mixtures with gradually varying composition and with decreasing volatility. As with the vapor pressure, the near-azeotropic behavior of an ethanol-gasoline blend affects the distillation characteristics for portions of the distillation curve [12,16]. An extensive set of data illustrating distillation curve behavior for ethanol-gasoline blends with gasoline blendstocks of varying volatility (ASTM D4814 Class AA to Class E) is provided in the study by API [11]. As an illustration of this behavior, the typical response of the distillation curve as ethanol content is varied is shown in Figure 6 for a certification gasoline blendstock [16].

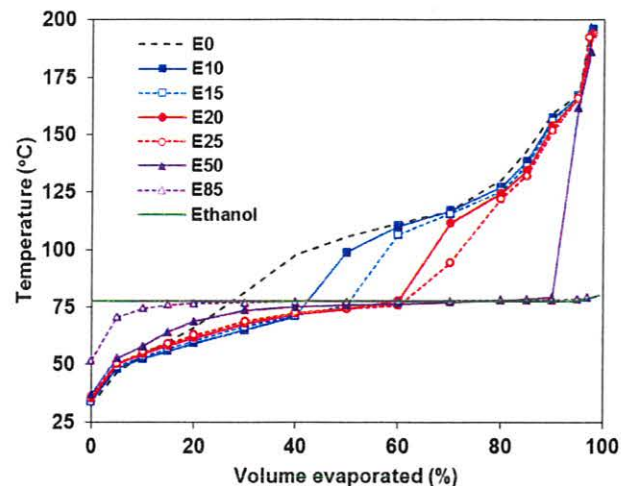


Figure 6. Distillation curves for ethanol-gasoline blends [16].

In Figure 6, the near-azeotropic behavior of the ethanol-gasoline blends is visible as a more slowly rising curve with higher volatility than that of the base gasoline (i.e., a greater volume distilled at a given temperature). For increasing ethanol content, this slowly rising curve expands to cover a larger portion of the distillation curve. Note in Figure 6 that T10 and T90 values (the temperature at which 10% and 90% of the fuel volume has distilled, respectively) are only slightly affected for ethanol-gasoline blends up to E25, whereas T50 decreases significantly from E0 to E15. Note also that the fraction of fuel evaporated at 100 °C increases substantially as ethanol content is increased.

ASTM D4814, the Standard Specification for Automotive Spark-Ignition Engine Fuel [18], specifies limits on T10, T50, and T90 which depend on the volatility class of the fuel. ASTM D4814 also specifies limits on the driveability index, which is defined by equation 1:

$$\text{Driveability Index} = 1.5 T_{10} + 3.0 T_{50} + 1.0 T_{90} + 1.33 \times \%v \text{ ethanol} \quad (1)$$

This equation was based on a study of vehicle driveability conducted at ambient temperatures of -1°C to 4°C (30° to 40° F) for ethanol blends of 3%, 6%, and 10% by volume ethanol using 2002 and 2003 MY vehicles [19]. This temperature range was chosen because it corresponded to the temperature below which enrichment was used to improve driveability for production vehicle calibrations at that time. Note that this equation was developed for ethanol blends up to E10, and therefore may not be relevant for higher ethanol blends or for later model year vehicles with more sophisticated engine control strategies.

KNOCK LIMIT

It is well known that blending ethanol in gasoline provides a large improvement in knock resistance. This is a

consequence of three knock-related properties of ethanol: RON, sensitivity, and HoV [20]. Ethanol's RON value of 109 provides high inherent or chemical knock resistance; the high sensitivity of ethanol results in longer autoignition delay time and greater knock resistance as combustion phasing is retarded due to reduced unburned gas temperature; and the high HoV of ethanol results in substantial cooling of the charge, especially with DI. Further, the effect of charge cooling on reducing the rate of autoignition kinetics is amplified by the high sensitivity of ethanol [20,21]. (Lower temperature provides a greater benefit in knock resistance with a high sensitivity fuel).

Vehicle calibrations of production gasoline engines retard spark timing from the thermodynamic optimum timing (Minimum spark advance for the Best Torque, or MBT) at high load to avoid knock, resulting in retarded combustion phasing. This is especially pronounced for turbocharged gasoline engines, which run with very retarded combustion phasing at low speed-high load. Therefore, the improvement in knock resistance at retarded combustion phasing with ethanol has a large impact on the full load torque for a turbocharged gasoline engine.

Example data are shown in Figure 7 for a boosted single cylinder direct injection engine [20]. For these data, inlet pressure was swept at constant engine speed, and spark timing was set to borderline knocking at each inlet pressure. The resulting combustion phasing, as measured by the location of 50% mass fraction burned in degrees aTDC (CA50), is plotted as a function of the 720°CA-based Net Mean Effective Pressure (NMEP). As shown in this figure, the improvement in knock-limited NMEP as ethanol content is increased is much greater at retarded combustion phasing than at the thermodynamic optimum MBT combustion phasing [20].

The increase in knock-limited torque with increasing ethanol content can be limited by the available boost pressure of the turbocharger system and the peak pressure capability of the engine structure, especially at high ethanol content. An example of multi-cylinder data for a gasoline turbocharged direct injection (GTDI) engine is shown in Figure 8, which is a comparison of knock-limited brake mean effective pressure (BMEP) and brake thermal efficiency (BTE) vs. engine speed for 91 RON E0 gasoline and E85 [22,23]. For this engine, the BMEP with E85 below 2250 rpm is limited by the available boost provided by the turbochargers, and above 2250 rpm by the turbine inlet temperature constraint of 950°C and the peak cylinder pressure (mean plus three sigma) constraint of 150 bar. The BMEP with 91 RON E0 gasoline is limited by knock at all engine speeds and by the turbine inlet temperature constraint above 2250 rpm at stoichiometry ($\lambda = 1$) and above 3000 rpm with enrichment ($\lambda = 0.8$).

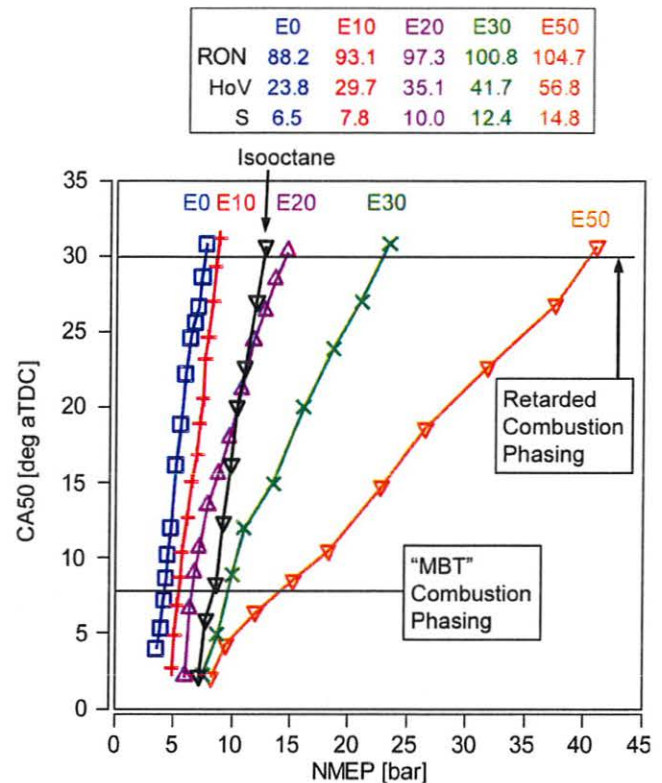


Figure 7. CA50 vs. NMEP for 88 RON blendstock at 1500 rpm and stoichiometry in a single-cylinder engine at 10:1 CR with DI [20].

For the data set of Figure 8, peak BMEP with 91 RON E0 gasoline is 18 bar at stoichiometry and 23 bar with enrichment compared to 32 bar with E85 at stoichiometry. BTE is higher for E85 than for gasoline at stoichiometry due primarily to combustion phasing which is closer to optimum. BTE is significantly degraded when the E0 gasoline is run with enrichment to improve full load BMEP. Improved efficiency at high load with increasing ethanol content of the fuel is discussed in more detail in a later section of this paper.

The increased knock resistance of ethanol blends is best utilized in boosted engines as described above; however, it is also advantageous in naturally aspirated engines. In a study by GM [24] on a naturally aspirated DI engine, knock-limited BMEP at full load was increased by 13-15% with E85 compared to a customer intent 87 AKI E0 gasoline. These performance gains were enabled by the increased knock resistance of E85 which allowed optimum combustion phasing, by increased volumetric efficiency due to the higher HoV and consequent charge cooling of E85, and by improved indicated efficiency due to lower burned gas temperatures (discussed in more detail later in this paper).

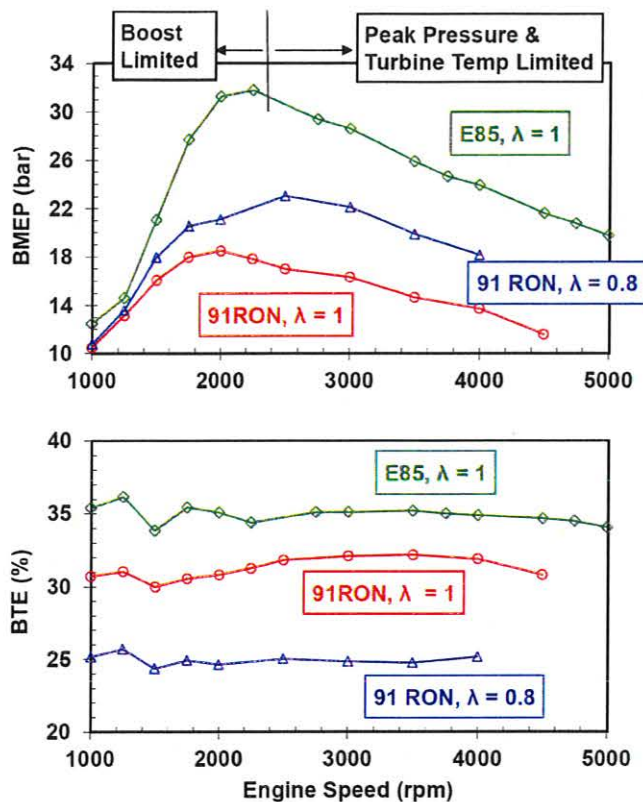


Figure 8. BMEP and BTE vs. engine speed for E85 and 91 RON E0 gasoline in a V8 GTDI engine at 9.5:1 CR [22].

FUEL EFFICIENCY

Downsizing/Downspeeding

As shown in the above examples, the increase in knock resistance with increasing ethanol content enables a substantial increase in full load BMEP for a GTDI engine. This increase in BMEP may be translated into improved vehicle fuel economy through downsizing of the engine displacement and/or running lower engine rpm (downspeeding) through revised gear ratios, final drive ratio, or shift scheduling. Both downsizing and downspeeding move the operating regime of the engine in the vehicle to a more efficient part of the engine speed-load map, providing improved vehicle fuel efficiency.

The extent of downsizing/downspeeding with GTDI engines can be limited in practice by vehicle performance attributes which are affected by the characteristics of the boost system, including transient response and the capability to provide sufficient boost at low speed as well as at high speed, where the latter can become limited by the turbocharger shaft speed at high altitude. The trade-offs and limits of single stage boosting can be significantly extended by two stage boosting [25], but with an associated increase in cost and complexity. The vehicle fuel efficiency benefits of

downsizing and downspeeding are also highly dependent on the displacement and gearing of the baseline engine. Thus, quantifying the benefit of increased ethanol content on vehicle fuel efficiency through incremental downsizing and downspeeding requires a detailed analysis of the specific application. Nevertheless, improved knock resistance and lower exhaust temperatures (discussed later in this paper) with increasing ethanol content enable opportunity for further gains in this area.

Increased Compression Ratio

The increase in knock resistance with increasing ethanol content can also enable an increase in compression ratio (CR), which at constant combustion phasing provides a direct increase in thermal efficiency [3,26]. The increase in thermal efficiency is non-linear with increasing CR, where the CR for maximum efficiency is a function of the engine displacement-per-cylinder [3] and the bore-stroke ratio. Optimum CR occurs where the trade-off is balanced between increased expansion ratio vs. increased heat transfer and crevice volume losses and mechanical friction. Increased displacement-per-cylinder and lower bore-stroke ratio provide reduced surface-to-volume ratio and lower ratio of crevice volume to clearance volume, and hence the optimum CR is higher. Thus, the benefit of increased CR enabled by increasing ethanol content is engine design specific.

A study by Ford evaluated splash blended 91 RON E10, 96 RON E20 and 101 RON E30 fuels in a 3.5L GTDI "EcoBoost" engine at 10:1 and 11.9:1 CR [27]. In this engine, E20 at 11.9:1 CR exhibited knock-limited performance equivalent to that of E10 at 10.0 CR. Similarly, E30 at 11.9:1 CR resulted in knock-limited performance equivalent to E20 at 10.0:1 CR, indicating that E30 could have been run at even higher CR with acceptable knock behavior. The engine data was then used in a vehicle simulation program to estimate volumetric fuel economy (mpg) and CO₂ emissions (tank-to-wheels) on the combined EPA metro and highway drive cycles (EPA M/H) and on the high speed-high load US06 drive cycle. The results indicated that 96 RON E20 at 11.9:1 CR provides comparable fuel economy and about 5% improvement in CO₂ emissions on EPA M/H and US06, compared to the baseline 91 RON E10 fuel at 10:1 CR. The results also indicated that 101 RON E30 at 11.9:1 CR provides improvements in CO₂ emissions of 5% on EPA M/H and 7.5% on US06, while fuel economy was 3% lower on EPA M/H and approximately equal on US06, compared to the baseline E10 fuel at 10:1 CR. Results were more favorable on the high speed-high load US06 cycle than on EPA M/H because the baseline E10 fuel at 10:1 CR was more knock-limited than E30 at 11.9:1 CR.

Although increased CR and engine downsizing/downspeeding provide improved thermal efficiency and CO₂ emissions in the vehicle, they will cause degraded vehicle performance if the engine is not supplied with fuel having at least the intended ethanol content and RON. An example for

the effect of 91 RON E0 gasoline on full load BMEP for an engine with increased CR is shown in Figure 9 [23]. As shown, the loss in full load BMEP is substantial across the entire engine speed range. With engine downsizing, the reduction in full load torque with regular grade 91 RON fuel will be proportional to the amount of downsizing, and can result in unacceptable vehicle performance attributes for aggressive levels of downsizing. Therefore, optimization of the CR and/or engine displacement for an ethanol-gasoline blend will be dependent upon availability of the intended blend on a widespread basis.

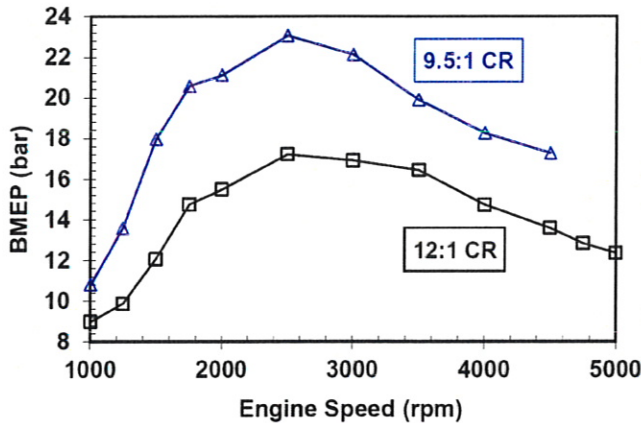


Figure 9. Full load performance for a GTDI engine with 91 RON E0 gasoline at $\lambda = 0.8$ for 12:1 and 9.5:1 CR [23].

Reduced Enrichment

Currently, enrichment is used at high speed-high load engine conditions to reduce exhaust temperature to avoid thermal damage of engine or emissions aftertreatment system components. When enrichment is used, thermal efficiency rapidly degrades due to wasted fuel energy. As shown in Figure 8, E85 allows a large increase in full load performance while maintaining stoichiometry compared to E0 gasoline with enrichment. As shown, BTE is $\sim 35\%$ with E85 at stoichiometry compared to $\sim 25\%$ with 91 RON gasoline with enrichment of 0.8 lambda. Thus, increased ethanol content enables improved efficiency by reducing or eliminating the need for fuel enrichment at high speed-high load.

Another example of reduced enrichment with increasing ethanol content is shown in Figure 10 [20]. Isooctane (100 RON by definition), 93 RON E10, and 105 RON E50 were run at an engine speed of 3500 rpm at 12:1 CR. Exhaust (turbine inlet) temperature increases as inlet pressure and NMEP are increased due to reduced heat transfer per unit mass and due to more retarded combustion phasing. For this study, enrichment was used (lambda was decreased) as needed so that the exhaust temperature did not exceed an 850°C limit. As shown, E50 enabled 21 bar NMEP operation before enrichment was required, compared to 13 bar NMEP

for isooctane and 11 bar NMEP for E10. The corresponding net thermal efficiency (NTE) is shown in the bottom plot of Figure 10. The NTE for E50 was about 38% at 21 bar NMEP at stoichiometry vs. about 26% at 17 bar NMEP for E10 with enrichment.

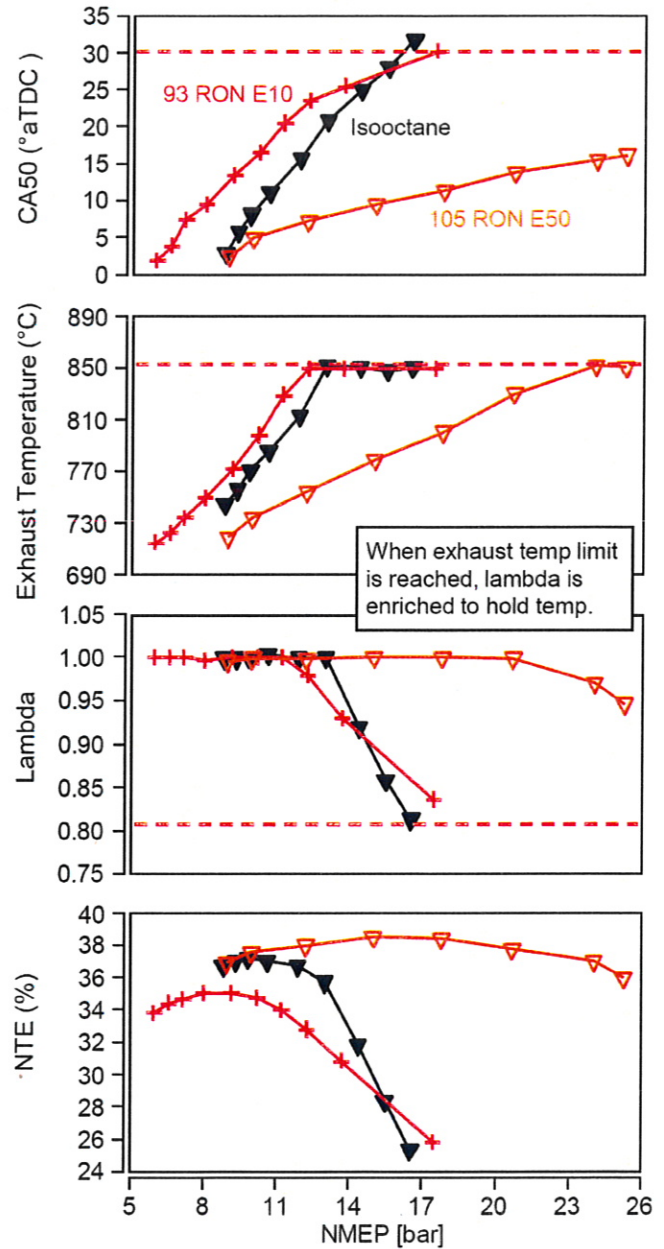


Figure 10. Comparison of enrichment for isooctane, E10, and E50 at 12:1 CR and 3500 rpm with DI [20].

In modern engines, enrichment is avoided as much as possible to maintain three-way catalyst (TWC) function, and therefore enrichment does not typically affect test cycle or label fuel economy. However, under high speed-high load conditions it can have an effect on energy consumption and CO_2 emissions. The magnitude of this effect depends on

customer driving cycles and patterns, and is thus difficult to quantify.

Improved Efficiency at Part Load

Several studies have reported improved efficiency with increasing ethanol content at part load and MBT spark timing [24,28,29]. GM researchers reported efficiency improvements of 3-6% with E85 compared to an optimized DI gasoline baseline at specific BMEP and engine speed operating conditions [24]. These gains were attributed to a reduction in heat transfer losses and increased dilution tolerance, which was available with variable valve timing. Similarly, a Toyota study documented efficiency improvements of 3% by increasing ethanol content from zero to 100 percent at equal dilution level and combustion phasing with a port fuel injected (PFI) engine, and attributed this improvement to reduced heat transfer losses [28]. Lower heat transfer losses are due to lower burned gas temperature, which is a consequence of two factors: 1) charge cooling due to ethanol's high HoV results in lower charge temperature at the start of combustion (this effect is greater for DI than for PFI); and 2) combustion of ethanol results in a greater number of moles in the exhaust gas per unit of heating value input, resulting in higher heat capacity of the combustion products and lower adiabatic flame temperature.

CO₂ emissions at part load for ethanol are reduced compared to gasoline due to improved efficiency as discussed above, and also due to the comparatively high hydrogen-to-carbon ratio (H/C) of ethanol. Ethanol has an H/C ratio of 3, compared to about 1.9 for gasoline. Thus, complete combustion of ethanol results in a ratio of H₂O to CO₂ molecules of 1.5 in the combustion products, whereas for gasoline this ratio is about 0.95. This effect equates to CO₂ emissions per unit of heating value which are about 3% lower for ethanol than for gasoline, with the exact value dependent on the H/C ratio of the gasoline. The cumulative effect of improved efficiency and lower H/C ratio is an improvement in CO₂ emissions of about 6-9% for ethanol compared to gasoline at equal BMEP and engine speed at MBT spark timing. For ethanol-gasoline blends, it is expected that this benefit in CO₂ emissions will scale approximately linearly with the molar fraction of ethanol in the blend, since both the adiabatic flame temperature rise and the ratio of CO₂ to H₂O in the combustion products are a function of the molar fraction.

EMISSIONS

As discussed earlier, vehicle manufacturers must meet specific emissions limits for each model year and associated regulatory target (see [Figure 1](#)) using the appropriate certification fuels. Emissions from SI engines include gaseous emissions such as volatile organic compounds (VOCs), CO, and NO_x, as well as PM emissions. The effects

of ethanol blends on these emissions are discussed in the sections below.

NMOG, CO, and NO_x Emissions

Non-methane organic gases (NMOG) are defined as total VOCs minus methane. VOCs are defined by the EPA as "any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions" [30]. EPA also excludes compounds such as methane and ethane which have been determined to have negligible photochemical reactivity. However, as mentioned earlier, methane will be included in GHG standards with a weighting factor of 25 relative to CO₂.

In CARB and EPA regulations, measured NMOG emissions from vehicles powered by fuels other than conventional gasoline are multiplied by a reactivity adjustment factor (RAF) to calculate a gasoline-equivalent NMOG emission value. The RAF is defined as the ozone-forming potential of the exhaust divided by the ozone-forming potential of conventional gasoline vehicle exhaust. The Maximum Incremental Reactivity (MIR) scale is used to estimate the equivalent ozone that would be produced by the various exhaust species which are measured.

An investigation into the emissions of ethanol-gasoline blends from one 2006 MY and six 2007 MY FFVs was conducted by the Coordinating Research Council (CRC) [31]. All of these vehicles had PFI engines. The testing included E6, E85, and intermediate blends of E32 and E59 obtained by splash blending the E6 and E85 fuels in 2:1 and 1:2 ratios, respectively. Analysis of the E85 indicated that the remaining 15% consisted of typical gasoline and extra iso-pentane to obtain 48 kPa (7 psi) RVP to match the E6 fuel. Benzene content decreased from 0.54% by mass for E6 to 0.11% for E85 due to dilution with ethanol. The drive cycles evaluated included the cold start Federal Test Procedure (FTP), the hot start high speed-high load driving cycle (US06), and the cold start unified driving cycle (LA92 or UC). Only one test was conducted per vehicle/fuel/test cycle condition in this study, nevertheless, the overall results over the seven vehicles provide a useful indication of the effects of increasing ethanol content.

In this CRC study, the average non-methane hydrocarbons (NMHC), NMOG, CO, and NO_x emissions for the seven vehicles tested did not exhibit an emission trend with increasing ethanol level, with the exception of NMHC and NMOG for US06. The results for the US06 drive cycle showed a statistically significant trend of decreasing NMHC and NMOG with increasing ethanol content. The average MIR of the exhaust decreased with increasing ethanol content on the cold start FTP. There were mixed results for average MIR for the US06 and UC tests.

Overall, the data of the CRC study indicate neutral or favorable emission changes with increasing ethanol content over the cycles tested. However, starting engines at very low

ambient temperatures has historically been problematic with high ethanol content fuel (E85 and hydrous E100) with PFI engines, resulting in excessive cranking and high unburned HC emissions [24,28,32]. Several papers have reported significant potential to improve starting emissions at low ambient temperatures with ethanol by utilizing DI. An AVL study demonstrated that multiple injections at 40 bar injection pressure can improve starting with E100, due to significantly reduced wall films which were visualized on a single cylinder engine with optical access [33]. Similarly, a GM study found that utilizing a 40 bar injection pressure stratified start significantly reduced the amount of fuel required for starting and improved startability at cold ambient temperatures with Class III E85 fuel [24]. Thus, the use of DI provides injection strategy flexibility which can be utilized to improve startability and emissions associated with high ethanol blends at low ambient temperatures compared to the starting behavior possible with PFI.

Toxic Emissions

According to the U.S. EPA, "alcohol fuels are inherently cleaner than conventional gasoline because they do not contain toxics such as benzene. In addition, they are made of simpler chemical compounds which yield lower levels of complex combustion by-products such as 1,3-butadiene" [34]. 1,3-butadiene is a known human carcinogen, and benzene and 1,3-butadiene are classified by CARB as "toxic compounds", as are formaldehyde and acetaldehyde. The latter two compounds are emitted as products of incomplete combustion of ethanol, especially during cold starts. According to CARB [2], the relative toxicity values of these compounds compared to a value of 1.0 for 1,3-butadiene are 0.17 for benzene, 0.035 for formaldehyde, and 0.016 for acetaldehyde. As mentioned previously, CARB requires that the potency-weighted sum of emissions of these four toxic compounds for substitute fuels and new clean fuels in 2015 and subsequent years is below a value determined from tests using certification fuel [2].

The molecular composition of the fuel is of critical importance in determining the composition of the engine-out emissions [35,36]. Unburned fuel is the largest single component of engine-out hydrocarbon emissions. For hydrocarbon fuels such as gasoline, olefin products of partially combusted fuel-air mixture flowing out of crevices are also important emissions [36]. Olefins such as 1,3-butadiene are produced from decomposition of alkyl radicals formed from the unburned fuel, particularly from terminal straight-chain olefins and/or cyclic paraffins [35,37]. Benzene can be formed from dealkylation reactions of aromatic hydrocarbons or from cycloalkanes present in the fuel [35].

From consideration of combustion chemistry (oxidation of ethanol does not give 1,3-butadiene or benzene precursors), it is expected that higher levels of ethanol in gasoline will reduce the engine-out emissions of benzene and 1,3-butadiene and increase the emissions of acetaldehyde and formaldehyde. Exhaust catalysts in modern vehicles convert a

very high percentage of the engine-out emissions, but are not expected to alter these emission trends.

There have been several studies of the effect of ethanol on emissions of the four compounds defined by CARB as toxic emissions. The results from studies of the impact of a change in ethanol blend from E0 to E85 are in agreement and are consistent with the expected trends of decreased benzene and 1,3-butadiene and increased acetaldehyde and formaldehyde emissions [31,38,39,40]. When weighted by the CARB relative toxicity factors, the sum of these toxics is lower for E85 as compared to E0. This is a consequence of the much higher toxicity weighting for 1,3-butadiene compared to the other toxics (e.g., a factor of 62.5 relative to acetaldehyde).

In contrast, mixed results have been reported from studies of the impact of relatively modest changes in blends such as E0 to E10 [39, 40, 41, 42, 43] and E6 to E32 [31]. In four of these studies [31,39,41,42], the expected trends of decreased benzene and 1,3-butadiene with increased ethanol blends were observed. However, in two of these studies [40,43], increased emissions of benzene and 1,3-butadiene were reported for E10 compared to E0. There are two probable explanations for the anomalous trend reported in references [40,43]. First, there may be confounding effects associated with changes in the gasoline blendstock composition. Second, it is experimentally difficult to measure small differences in concentrations of individual hydrocarbon components such as 1,3-butadiene (typically emitted at levels of 1 to 2 mg/mile [31]) with sufficient precision to discern trends.

The increased emissions of acetaldehyde and formaldehyde with increasing ethanol content can be compared to those of benzene and 1,3-butadiene by utilizing the CARB relative toxicity factors. Of the available studies, the CRC study [31] included the most recent (2006-2007 MY) vehicles and used FFVs designed for higher ethanol content fuel, and is thus the most relevant regarding consideration of a future fuel with higher ethanol content. Figure 11 shows the toxicity-weighted emissions from this study for Phase 1 of the FTP. The bars show the average of results from the seven vehicles tested, and the error bars represent one standard deviation.

As shown in Figure 11, benzene emissions decrease significantly with increasing ethanol content (due mainly to reduced aromatic hydrocarbon content of the fuel), while acetaldehyde increases significantly and formaldehyde increases slightly. Emissions data for 1,3-butadiene had a significant degree of scatter as shown by the error bars, reflecting the experimental difficulties associated with these measurements and the inherent variability of cold start emissions. As shown, the weighted sum of these four toxic compounds in this study was dominated by 1,3-butadiene, and did not show a clear trend with increasing ethanol content due to the comparatively high 1,3-butadiene value for E59. Excluding 1,3-butadiene, the weighted sum decreases with increasing ethanol content.

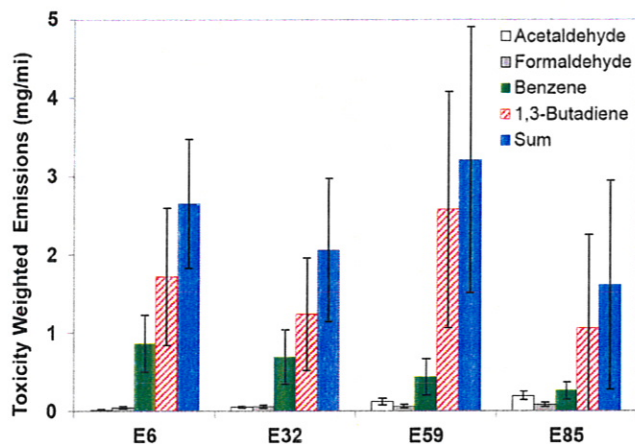


Figure 11. Toxicity-weighted emissions for FTP Phase 1 for CRC study of [31], error bars are standard deviations.

In summary, based on consideration of fundamental combustion chemistry, increased ethanol content in the fuel is expected to decrease emissions of benzene and 1,3-butadiene and increase emissions of acetaldehyde and formaldehyde. This behavior is consistently observed in studies of E85 compared to E0. Studies of lower ethanol content are not consistent, possibly due to changes in the gasoline blendstock and the difficulty of measuring low concentrations of these compounds. Because the toxicity weighting factors are much higher for 1,3-butadiene and benzene, these two compounds dominate the weighted sum of the four toxics regulated by CARB for future fuels.

Particulate Matter Emissions

The chemistry of particulate formation is complex and beyond the scope of this review. However, in simple terms, particulates are formed during diffusion-controlled combustion within localized areas of insufficient oxygen [44]. Historically, diesel engines have been recognized as a source of significant PM emissions due to their use of diffusion-controlled combustion. Recently, ultrafine particulates from gasoline combustion have become a subject of research and regulatory interest [45].

DI gasoline engines can produce significantly higher levels of particulates than port fuel injection (PFI) engines [46,47]. In a PFI engine at throttled part load conditions, the backflow of hot combusted gases into the intake port during valve overlap greatly assists fuel vaporization and air-fuel mixing. In a DI engine, the fuel is sprayed directly into the cylinder and, depending on the engine conditions and the details of the in-cylinder charge motion, fuel spray, and fuel injection parameters, liquid fuel can impact the cylinder walls, valves, or piston. Late evaporation of this fuel or the persistence of liquid fuel through the intake and compression strokes can result in localized poor air-fuel mixing or diffusion flames during combustion with high levels of PM

production [48]. This is particularly an issue during cold starting when the metal surfaces of the combustion chamber and piston are below normal operating temperatures.

In a study by Honda, a predictive model for PM was proposed that defined the “PM Index” of the fuel based on the weight fraction, vapor pressure, and double bond equivalent (DBE) value of each component in the fuel [49]. Lower vapor pressure corresponds to higher boiling point and increased tendency for the fuel component to remain in the liquid state. The DBE value is a measure of the number of double bonds and rings in the fuel molecule, such as found in olefins, aromatics, and cycloalkanes and is defined as the number of hydrogen atoms which would be required to fully saturate the molecule. Components of fuel with high DBE values were observed to more readily form particulate emissions in a vehicle with a 2.3L turbocharged engine. The DBE value for ethanol and paraffins such as isooctane is zero, whereas for aromatics it is in the range of four to seven. Thus, aromatic hydrocarbons (which tend to have high DBE values and low vapor pressure) disproportionately contribute to PM formation, and increasing paraffin or ethanol content of the fuel tends to decrease PM.

In addition to its DBE value of zero, ethanol may reduce PM formation for two additional reasons. First, ethanol has a relatively high vapor pressure and low boiling point (78 °C), and as discussed earlier, also tends to increase gasoline volatility through formation of a near-azeotropic mixture. In contrast, gasoline has heavy end components with boiling points as high as 225 °C [18]. Second, ethanol is an oxygenated molecule and oxygenates have been shown to reduce soot formation in flame studies by limiting the formation of aromatic precursors to soot [50].

The effect of ethanol on PM formation has been assessed using flame imaging in engines with optical access. A comparison of flame images for gasoline and E85 is shown in Figure 12 [51]. These images were acquired under typical cold-start catalyst heating mode conditions, with direct injection of fuel late in the compression stroke being used to provide a rich mixture near the spark plug to extend spark retard capability and thereby increase exhaust temperature for rapid catalyst light-off. Statistical average flame images at 30° aTDC and 90° aTDC are shown. With gasoline, soot producing flames (denoted by red color) were observed, especially in the region close to the piston where fuel impingement would have created a fuel film. When the engine was operated on E85 at the same conditions, only non-sooting combustion flames were observed. It should be noted that further optimization of injection parameters (timing, pressure, spray pattern, etc.) may allow reduction of particulates formation for the E0 gasoline [47], but nevertheless these data taken under identical engine operating conditions illustrate a fundamental advantage of ethanol for reducing particulate formation.

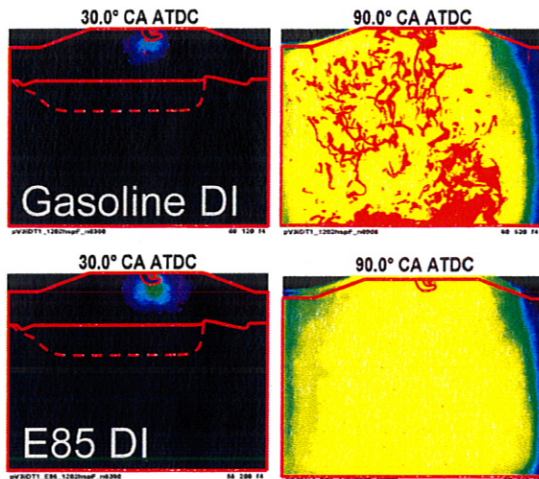


Figure 12. Flame images in catalyst heating mode comparing E85 operation with gasoline [51].

Numerous studies have shown reduced PM emissions with increasing ethanol content in blends with gasoline [24,44,49,52,53,54]. In a study by Oak Ridge National Laboratory (ORNL), particulate mass and particulate number distributions were obtained for E0, E10, and E20 fuels using certification fuel as the blendstock [52]. A 2007 MY vehicle with a 2.0L GTDI engine was operated over several transient drive cycles and steady state driving conditions including FTP 75, US06, and gradual and full load accelerations. The ethanol blends yielded reduced PM mass and number concentration emissions for both the transient cycles and steady-state conditions. As the ethanol blend level increased from E0 to E20, the average particulate mass emissions decreased by 30% and 42% over the FTP and US06 cycles, respectively. Likewise, emissions of particulate number were also lower using E20 during hot cycle transient operation. While particulates in internal combustion engine exhaust contain both organic carbon (OC) and elemental carbon (EC), in this study the OC fraction was effectively removed by the TWC.

In a study by Ford, particulate mass and number were measured in a light-duty truck with a 3.5L GDTI engine and TWC aftertreatment system over the FTP 75 test cycle [44]. A range of ethanol-gasoline blends were tested including E0 certification gasoline and splash-blended E17, E32, and E45. As the ethanol content was increased from 0% to 17% v/v, a small (< 20%) benefit in particulate mass and number emissions was observed, but this reduction was within test variability. The reduction in PM mass and number (30-45%) became statistically significant when the ethanol content was increased to 32% and 45%. The PM composition for these tailpipe emissions was determined to be primarily EC, consistent with the findings of the ORNL study [52].

A few studies have reported increased PM with higher ethanol content [5,46], but it is likely that these results are a consequence of differences in the gasoline components of the

fuels or of not having optimized the fuel injection system for the higher ethanol content. A study by Southwest Research Institute and Honda [46] reported an increase in PM emissions for E10 compared to E0 for commercially available fuels. As is the case for the toxic emissions discussed earlier, the PM emissions of ethanol blends are dependent on the composition of the gasoline blendstock. Typically, the gasoline composition is changed by refiners when producing a blendstock to which ethanol is to be added. Because ethanol addition can increase volatility and vapor pressure, gasoline blendstocks for commercial E10 are modified such that the vapor pressure and driveability index of the blended fuel are within ASTM 4814 specifications [18]. If the amount of blendstock components with low vapor pressure and high DBE values is increased, then the PM emissions could increase due to these components. In [46], the increase in PM emissions with E10 was consistent with the empirical PM index model [49].

In a study on a naturally aspirated DI engine, University of Oxford researchers observed increased PM emissions with increasing ethanol content. They hypothesized that the higher HoV of ethanol impeded fuel vaporization and thus caused a less homogeneous mixture, resulting in increased PM emissions [5]. Typically, CO emissions data at stoichiometry can be used to infer the degree of air-fuel mixture inhomogeneity because CO is formed in rich regions. Although CO data is not available in [5], CO emissions results are presented in a study by GM [24] comparing gasoline to E85 in a naturally aspirated DI engine at a part load condition similar to that of the University of Oxford study. The GM results show comparable CO levels, indicating similar levels of air-fuel homogeneity for gasoline and E85. The GM study also shows lower smoke emissions as ethanol content is progressively increased from E0 to E85. Thus, it is difficult to reconcile the results of the Oxford study with this study from GM and the studies discussed previously. A possible explanation is that the in-cylinder charge motion and the interaction of the charge motion with the fuel spray were significantly different between the engine of [5] and that of [24], thereby affecting the influence of the charge cooling due to fuel vaporization on subsequent air-fuel mixing. Another factor which could potentially cause increased PM emissions with increasing ethanol content is increased injection duration (due to ethanol's lower volumetric energy content). This could result in increased fuel impingement on combustion chamber surfaces and greater production of PM from the least volatile fraction of the gasoline (aromatics with high boiling point and high DBE value). In general, these increases are avoidable if the injection system and injection calibration parameters are optimized [47].

Depending on the details of the injector design, deposits on the injector tip of a DI engine can affect the quality and targeting of the fuel spray, and can also result in a diffusion flame on the injector tip [55]. As a consequence of these effects, direct injector deposits can have a significant impact

on PM emissions. In a Toyota study [56], it was observed that increasing ethanol content reduced injector deposits in a DI engine, and that ethanol content as low as E20 was effective in this regard. This reduction of deposits was attributed to lower injector temperature and lower aromatic and sulfur content as the ethanol content of the splash-blended fuel was increased. Thus, increasing ethanol content can be expected to improve injector robustness to deposits and thereby reduce the sensitivity of PM emissions to injector design and to gasoline hydrocarbon composition as vehicle mileage accumulates.

As described above, ethanol appears to present significant fundamental advantages with respect to PM emissions compared to gasoline. However, it should also be noted that significant reductions in PM mass and number emissions in gasoline DI engines can be accomplished by careful optimization of the injector design, spray targeting, and charge air motion, and through the use of multiple injections [47]. These actions decrease or eliminate impingement of the fuel on metal surfaces and improve fuel vaporization, and thereby reduce PM emissions. Reduced PM emissions may also be achieved by using a combination of PFI and DI [57]. Therefore, the magnitude of PM reduction associated with increasing ethanol content in blends with gasoline will depend strongly on the degree to which the engine and injection parameters have been optimized for the fuel (baseline gasoline and/or the ethanol-gasoline blend).

Off-Cycle Emissions

As discussed previously, enrichment is used to reduce exhaust temperature to avoid thermal damage of emissions aftertreatment system or engine components. However, enrichment results in large increases in engine-out CO and HC emissions due to insufficient oxygen for complete combustion. For example, the net specific HC (NSHC) and net specific CO (NSCO) emissions data corresponding to the data of Figure 10 are shown in Figure 13. Since a TWC cannot oxidize CO and HC when lambda is rich of stoichiometric, these high levels of CO and HC are also emitted from the vehicle tailpipe.

Enrichment is avoided as much as possible to maintain TWC function, and therefore it does not typically affect test cycle emissions. However, under high speed-high load conditions, enrichment can impact tailpipe emissions of HC and CO. As seen in Figure 13, the use of ethanol can extend the range of stoichiometric operation and thereby reduce this emission source.

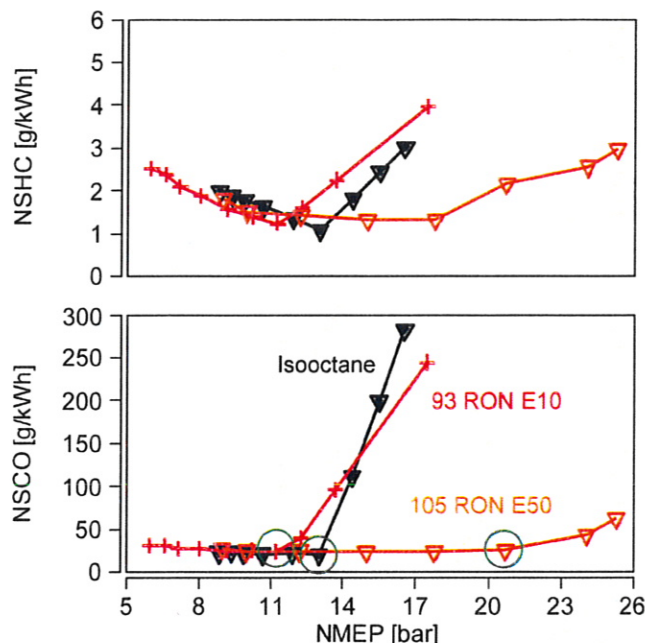


Figure 13. NSHC and NSCO emissions for the data of Figure 10 at 12:1 CR and 3500 rpm in a single cylinder engine with DI (last stoich points denoted by circles) [20].

Evaporative Emissions

Evaporative emissions result from refueling, diurnal temperature change, running loss, hot-soak, and permeation. Most evaporative emissions derive from fuel vapors generated in the fuel tank and thus their magnitude is generally a function of fuel RVP. Ethanol added to gasoline at low to moderate concentrations (E5-E30) increases fuel RVP and thus vapor generation. However, blendstocks for ethanol-gasoline blends are modified as needed to meet seasonal and regional fuel RVP limits [13], including a federal waiver allowing an additional 7 kPa (1 psi) for most E10 fuel in the U.S. While gasoline is regulated based on vapor pressure measured at 37.8 °C (100 °F), the fuel in the vehicle is exposed to both higher and lower temperatures. Vapor pressures of ethanol-gasoline blends exhibit a greater change with temperature than gasoline containing no ethanol [13].

Refueling emissions result from displacement of fuel vapors in the fuel tank headspace and thus depend on the fuel RVP as well as refueling system design [14]. Refueling evaporative emissions tests are generally conducted at temperatures less than 37.8 °C, thus for E0 and E10 fuels with equal RVP, E10 yields lower refueling emissions than E0 [14]. Ethanol blends from E10 to E85 exhibit similar emissions if their RVPs are equal [12], but emissions would be reduced if RVP is reduced with the higher ethanol content, though this may be offset by a greater frequency of refueling events because of lower volumetric energy content.

Diurnal emissions (from vapors generated by daily ambient temperature cycling), running loss (from fuel heating during engine operation), and hot-soak emissions (fuel heating after engine operation stops) are primarily caused by increases in fuel vapor pressure and vapor generation as the fuel tank is heated. Ethanol could affect these emissions because of the greater vapor pressure change with temperature for ethanol-gasoline blends than gasoline without ethanol, but this may be partially offset by the fact that ethanol has a greater HoV than gasoline.

The aforementioned evaporative emissions are controlled by capture using activated carbon canisters and then later purging them into intake air and combusting them in the engine. Ethanol has little to no effect on the capture on activated carbon and regeneration. "Running loss" vapors are immediately combusted with engine intake air, but this and hot-soak emissions can become uncontrolled if fuel boiling occurs (i.e., when fuel is heated to the temperature where its vapor pressure equals the fuel tank pressure). Ethanol decreases gasoline boiling temperature and thus could reduce the design margin preventing this occurrence, but again the higher HoV may partially offset this.

Permeation emissions are caused by fuel compounds leaching through the materials of the fuel tank and distribution system. These emissions increase with temperature, fuel RVP, aromatic hydrocarbon content, and solubility in the fuel system materials [58]. In modern plastic multi-layer coextruded fuel tanks, ethanol can negatively interact with the ethylene vinyl alcohol barrier layer designed to control hydrocarbon permeation and increase hydrocarbon permeation. However, more stringent evaporative emissions limits such as PZEV have resulted in continually improved materials and designs that reduce permeation.

Published studies [31,40,59] suggest that ethanol content has some effect on permeation emissions but little effect on diurnal, running loss, and hot-soak emissions. In a Canadian government study [40], diurnal and hot-soak emissions were unaffected by ethanol content using E0, E10, and E20 fuels with equal vapor pressure and an E10 splash blend with higher RVP. A CRC study [59] investigated the effect of ethanol content on both diurnal and steady-state permeation emissions using E0, E6, E10, E20, and E85 with similar RVP. Five MY 2000-2004 vehicle fuel system rigs were used, including two relatively advanced emissions control systems (LEV II and PZEV) and one FFV. The presence of ethanol (E6, E10 and E20) significantly increased permeation emissions as compared to the E0 fuel. The more advanced evaporative emissions control technologies yielded much lower permeation emissions for all blends. Diurnal permeation increased with ethanol content up to E20, but steady-state permeation rates did not. Although the mass of emissions increased when ethanol was present, the overall reactivity (ozone formation potential) of the emissions decreased.

A subsequent CRC study [31] examined evaporative emissions from four MY2006-2007 FFVs with E6, E32, E59,

and E85 with matched RVP. Running loss and hot-soak emissions did not show a trend with ethanol content. Diurnal emissions for E6 and E32 were similar, but an increase for the E59 and E85 fuels was indicated. The result was only statistically significant for the first day of the two-day test and was primarily due to permeation. The reactivity of these emissions showed no clear trends with ethanol content.

To summarize, relative to E10, mid-level ethanol blends (e.g., E20 or E30) with equal RVP are expected to have little impact on refueling, diurnal, running loss, and hot-soak emissions, however some impacts on permeation were observed for high-level ethanol blends (e.g., E51-E85). Any reduction in RVP from blends above E10 should tend to reduce the magnitude of these emissions. The overall reactivity of the emissions also tends to decrease with increasing ethanol content.

CONSIDERATIONS FOR AN "OPTIMAL" ETHANOL-GASOLINE BLEND

The preceding sections of this paper attempt to provide an overview of the effects of increasing ethanol content on spark ignition engine operation. Determining an "optimal" ethanol-gasoline blend as a future fuel to enable increased vehicle fuel efficiency/GHG reduction and facilitate meeting future emission standards requires consideration of all of these factors. Other factors which are outside the scope of this paper must also be considered, such as the available ethanol supply [4,60], and the infrastructure required to produce and supply such a fuel including implications and alternatives for the octane rating of the blendstock and finished fuel [4]. It is envisioned by the authors that such a future fuel would be offered as a high octane fuel competitively priced with regular grade E10 fuel, but not as an immediate replacement for regular grade E10 fuel. Therefore this future fuel would not be subject to constraints imposed by the requirements of the legacy fleet of vehicles or of small off-road engines, such as those used in boats, lawn mowers, chain saws, etc.

From an engine standpoint, the primary motivation for increasing ethanol content is improved knock resistance. By adding ethanol to a blendstock having a fixed octane rating, knock resistance improves continuously as the ethanol content is increased from E0 to E100 [17,20]. Based on this criterion, E20 is suggested as a lower bound to gain a significant improvement in knock resistance relative to E10. (The E20 should have correspondingly higher octane ratings than today's regular-grade E10, e.g., approximately 96 RON and 91 AKI). As shown in Figure 7, knock resistance is further improved above E20, especially for late combustion phasing which is typical at full load for GTDI engines. However, above a certain ethanol content the improved knock resistance becomes unusable at high load for a given engine structural peak pressure limit; in other words, the engine becomes limited at high load by peak pressure and not by knock. Additionally, improvements in thermal efficiency

enabled by improved knock resistance, such as increasing compression ratio and downsizing/downspeeding, become subject to diminishing returns.

Higher ethanol content has generally neutral effects on gaseous emissions, including tailpipe air pollutants and evaporative emissions, and beneficial effects on emissions of PM and toxic compounds, and on off-cycle emissions due to enrichment. These generally positive impacts could be beneficial to automakers by assisting them in meeting increasingly stringent emissions limits, assuming the future fuel is sufficiently prevalent in the marketplace and is used as an emissions certification fuel.

A few factors degrade with increasing ethanol content. Energy content per volume is reduced, and although this can be partially or perhaps completely offset by improved thermal efficiency as ethanol content is initially increased, volumetric fuel economy (mpg) is expected to decrease at higher ethanol content which in turn will reduce driving range before refueling is required (both are important factors for customer satisfaction). At very high ethanol content, startability and emissions at low ambient temperatures may also be an issue, although DI provides an opportunity for improvement in this area.

Based on the above factors, and in particular the criterion of consumer acceptance of reduced volumetric fuel economy and driving range, an upper bound of E40 is suggested as it has approximately 11% lower energy content per volume compared to E10. Furthermore, most projections of future ethanol supply in the next two decades indicate very low likelihood of supporting a higher level than E40 across the U.S. gasoline pool [4].

Thus, a mid-level ethanol-gasoline blend (greater than E20 and less than E40) appears to be attractive as a long-term future fuel for automotive engines in the U.S. As an example, E30 has approximately 7% lower energy content per volume compared to E10. This can be partially or perhaps completely offset by improved thermal efficiency enabled by the higher octane rating of E30, which allows increased CR [27] and greater amounts of engine downsizing. Using current regular-grade E10 blendstocks, E30 would have correspondingly higher octane ratings, approximately 100 RON and 94 AKI. For engines realizing the potential benefit of higher octane-rating E30, the peak pressure requirement will be moderately higher than for E10, but still within the range of conventional SI engine design practice [27]. PM emissions for E30 should be less than for E10, and startability and cold start emissions at very low temperatures will be better than for high ethanol blends such as E85.

An additional comment pertains to the range of ethanol content allowed in a future fuel. Currently, vehicle OEMs are required to calibrate FFVs using both E0 gasoline and E85 with 85%v ethanol content. Recent modifications to the ASTM D5798 specification, however, allow E85 to contain as little as 51%v ethanol and as much as 83%v ethanol. Also, D5798 specifies no minimum octane rating for E85, and as a result, both the ethanol content and the gasoline fraction

determine the knock resistance of E85. To ensure adequate performance for all E85 fuel that could be encountered in the market, E85 vehicles could at best be optimized for E85 with the minimum 51%v ethanol and the lowest possible octane rating. This issue highlights the need for reasonably tight limits for future fuel specifications (e.g., E25-E30 rather than E15-E30).

SUMMARY

Based on this review of relevant literature, the following observations can be made regarding blends of ethanol in gasoline:

- Knock resistance: Increasing the ethanol content in an ethanol-gasoline blend results in a large increase in knock resistance, due to ethanol's high values of RON, sensitivity, and HoV. Improved knock resistance enables increased knock-limited BMEP, particularly with boosted, direct injection engines, and/or increased compression ratio. The increase in knock-limited BMEP can be limited by the peak pressure capability of the engine structure or the boost capability of the boosting system.
- Fuel efficiency:
 - Downsizing/downspeeding: Increased knock-limited BMEP enables improved thermal efficiency in the vehicle, either by downsizing the engine displacement or downsizing the engine rpm.
 - Compression ratio: Increased CR enabled by increased ethanol content provides a direct improvement in fuel efficiency.
 - Enrichment: Increasing ethanol content results in lower burned gas and exhaust temperatures due to the high HoV of ethanol and due to higher heat capacity of the combustion products. Combined with more favorable combustion phasing, this results in reduced enrichment and consequent improvement in fuel efficiency and tailpipe emissions at high speed, high load conditions.
 - Part load CO₂: Ethanol has fundamentally lower CO₂ emissions at part load than gasoline (by approximately 7% at equal BMEP and engine speed) due to lower burned gas temperature, which results in reduced heat transfer losses and improved thermal efficiency, and due to higher hydrogen-to-carbon ratio, which results in a reduced proportion of CO₂ to H₂O in the combustion products.
 - Volumetric fuel economy: Due to the lower energy content of ethanol compared to gasoline, volumetric fuel economy (mpg) decreases with increasing ethanol content of the fuel as does the driving range for a given fuel tank size. This degradation can be partially offset (or perhaps completely offset for E20 - E30) by the improved fuel efficiency effects described above.

• Emissions:

◦ Air pollutant gaseous emissions: Tailpipe NMHC, NMOG, CO, and NO_x emissions do not indicate significant trends with increasing ethanol content on late model FFVs on FTP75, while NMHC and NMOG decrease somewhat on the US06 drive cycle. Cold starting with PFI using high ethanol blends at very low ambient temperatures has been problematic, resulting in poor starting and high unburned HC emissions, but direct injection has been shown to improve startability and emissions under such conditions.

◦ Toxic emissions: Increased ethanol content in gasoline should decrease emissions of 1,3-butadiene and benzene and increase emissions of acetaldehyde and formaldehyde. Due to much higher toxicity weighting factors, 1,3-butadiene and benzene dominate the weighted sum of these four toxics even at high ethanol content.

◦ PM emissions: Increasing ethanol content results in lower PM emissions because 1) oxygenated fuels inhibit formation of soot precursors; 2) ethanol replaces soot-prone gasoline hydrocarbons in the fuel; and 3) ethanol reduces the boiling temperature for low- and mid-level blends. Increasing ethanol content has also been shown to reduce direct injector deposits, which can affect PM emissions.

◦ Evaporative emissions: Relative to E10, mid-level ethanol blends are expected to have little impact on evaporative emissions in modern vehicles. Reduction in RVP from blends above E10 should reduce these emissions. Also, the overall reactivity of the emissions tends to decrease with increasing ethanol content.

CONCLUSION

Increased ethanol content in an ethanol-gasoline blend provides a substantial increase in knock resistance due to ethanol's high values of RON, HoV, and sensitivity. This enables improved vehicle fuel efficiency and CO₂ emissions through downsizing, downspeeding, and/or increased compression ratio. Effects of higher ethanol content on gaseous emissions, including tailpipe air pollutants and evaporative emissions, are generally neutral for modern vehicles. PM emissions, emissions of toxic compounds, and off-cycle emissions due to enrichment are expected to decrease significantly.

As ethanol content is increased, volumetric fuel economy (mpg) and fuel tank range decrease and vehicle fuel efficiency/CO₂ improvements become subject to diminishing returns. At high ethanol content, startability and emissions at very low ambient temperatures is a potential issue. Also, typical SI engines are limited by peak cylinder pressure at high loads and thus cannot fully utilize the knock resistance of the fuel at these conditions.

Based on the above considerations, a mid-level ethanol blend (greater than E20 and less than E40) appears to be

attractive as a long-term future fuel for the U.S., especially if used in vehicles optimized for such a fuel. To provide high knock resistance, this fuel should be formulated using a blendstock that retains the octane rating of the current blendstock used for regular-grade E10 gasoline.

Further work is needed to recommend a specific ethanol blend level and corresponding octane rating, including analysis of fuel efficiency and CO₂ benefits for representative powertrain/vehicle applications, and assessment of the potential ethanol supply and required infrastructure.

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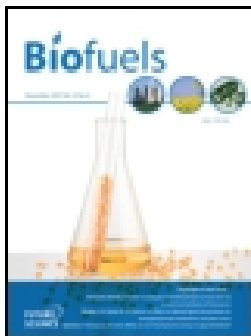
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DEFINITIONS/ABBREVIATIONS

%v/v - percent by volume	MY - model year
A/F - air to fuel ratio	N₂O - nitrous oxide
AKI - anti-knock index	NHTSA - National Highway And Traffic Safety Administration
API - American Petroleum Institute	NHV - net heating value
ASTM - American Society for Testing and Materials	NMEP - net mean effective pressure based on the 720° integral of p-dV
aTDC - after top dead center	NMHC - non-methane hydrocarbons
BMEP - brake mean effective pressure	NMOG - non-methane organic gases
bTDC - before top dead center	NO_x - nitrogen oxides
BTE - brake thermal efficiency	NSCO - net specific carbon monoxide emissions
CA50 - crank angle of 50% mass fraction burned	NSFC - net specific fuel consumption based on the 720° integral of p-dV
CAFE - corporate average fuel economy	NSHC - net specific unburned hydrocarbon emissions
CARB - California Air Resources Board	NTE - net thermal efficiency based on the NHV of the fuel and the NMEP
CH₄ - methane	OC - organic carbon
CO - carbon monoxide	OEM - original equipment manufacturer
CO₂ - carbon dioxide	ORNL - Oak Ridge National Laboratory
CR - compression ratio	OVI - open valve injection with PFI
CRC - Coordinating Research Council	PFI - port fuel injection
DBE - double bond equivalent	PM - particulate matter
DI - direct fuel injection into the cylinder	PP - peak cylinder pressure
E10, etc. - ethanol content of 10%, etc. by volume	PRF - primary reference fuel blend of isooctane and n-heptane
EC - elemental carbon	RAF - reactivity adjustment factor
EPA - Environmental Protection Agency	RON - research octane number
FFV - flexible fuel vehicle	RVP - Reid vapor pressure
FTP75 - federal test procedure 75	S - sensitivity (RON minus MON)
g - gram	SI - spark ignition
gCO_{2e} - grams CO ₂ equivalent	Sigma - standard deviation
GHG - greenhouse gas	SULEV - super ultra-low emissions vehicle
GTDI - gasoline turbocharged direct injection	TiT - turbine inlet temperature
H/C - hydrogen-to-carbon ratio of the fuel	TWC - three way catalyst
HC - unburned hydrocarbons	UC - unified cycle (LA 92)
HoV - heat of vaporization	US06 - high speed-high load driving cycle
kg - kilogram	VOC - volatile organic compound
kJ - kilojoule	ZEV - zero emission vehicle
L - liter	
Lambda (λ) - air-fuel ratio divided by the stoichiometric air-fuel ratio	
LEV - low emissions vehicle	
MBT - minimum spark advance for the best torque	
M/H - combined EPA metro (city) and highway cycles	
MIR - maximum incremental reactivity	
MJ - megajoule	
MON - motor octane number	
mpg - miles per gallon	



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The greenhouse gas benefits of corn ethanol – assessing recent evidence

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ABSTRACT

In 2010, the U.S. Environmental Protection Agency (EPA) released a life-cycle analysis of the greenhouse gas (GHG) emissions associated with the production and combustion of corn ethanol. EPA projected that by 2022, the emissions profile of corn ethanol from a new refinery would be 21% lower than that of an energy equivalent quantity of gasoline. Since 2010, the 21% value has dominated policy discussions and federal regulations related to corn ethanol as a renewable fuel and a GHG mitigation option. It is now 2018 and new data, scientific studies, technical reports, and other information allow us to examine the emissions pathway corn-ethanol has actually followed since 2010. Using this information, we assess corn ethanol's current GHG profile at 39–43% lower than gasoline. We also develop two projected emissions scenarios for corn ethanol in 2022. These scenarios highlight opportunities to produce ethanol with emissions that are 47.0–70.0% lower than gasoline. Many countries are now developing or revising renewable energy policies. Typically, bio-fuel substitutes for gasoline are required to reduce GHG emissions by more than 21%. Our results could help position U.S. corn ethanol to compete in these new and growing markets.

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Introduction

Between 2004 and 2014, US ethanol production, virtually all from cornstarch, increased from 12.87 to 54.13 billion liters per year. This increase was driven by two pieces of legislation that mandated the nation's supply of transportation fuel, in aggregate, must contain specific amounts of biofuels. The Energy Policy Act of 2005 established the Renewable Fuel Standard (RFS), which included a schedule of required biofuel use that started at 15.14 billion liters in 2006 and rose to 28.39 billion liters by 2012. The Energy Independence and Security Act of 2007 replaced the RFS with the Revised Renewable Fuel Standard (RFS2). The RFS2 included a new schedule of required biofuel use that began at 34.07 billion liters in 2008 and ramps up to 136.26 billion liters by 2022. Corn ethanol's mandate started at 34.07 billion liters in 2008, increased to 56.78 billion liters in 2015, and remains at that level through 2022.

A key objective of the RFS2 is to reduce greenhouse gas (GHG) emissions associated with transportation fuels. Currently, the only cost-effective biofuel substitute for gasoline is ethanol. Under the RFS2, ethanol can qualify as a conventional, advanced, or cellulosic biofuel. Conventional biofuel is defined as ethanol made from cornstarch. To be a renewable fuel, corn ethanol produced in refineries that began construction on or after 19 December 2007 must have life-cycle GHG emissions at least 20% lower than an

energy-equivalent quantity of average gasoline in 2005.¹ Corn ethanol produced in refineries in place or under construction on that date is grandfathered in as conventional biofuel regardless of its GHG profile. Ethanol made from cellulose, hemi-cellulose, lignin, sugar, starch (not from corn), and various types of waste biomass that has life-cycle GHG emissions at least 50% lower than those of gasoline qualify as 'advanced biofuels'. Additionally, ethanol made from cellulose, hemi-cellulose, or lignin that has a GHG profile at least 60% lower than that of gasoline qualifies as 'cellulosic biofuel'. Over time, advanced and cellulosic biofuels receive increasing shares of the annual renewable fuel mandate.

Quantifying the GHG profile of corn ethanol has been contentious since Searchinger et al. [2] concluded that the emissions associated with its production and combustion exceeded the emissions associated with producing and combusting an energy-equivalent quantity of gasoline. The authors argued that using billions of kilograms of US corn to produce ethanol reduces supplies of, and increases prices for, corn and other commodities in domestic and world food and feed markets. Farmers in the United States and elsewhere respond by bringing new land into production. These land-use changes (LUC) are related to ethanol production because the new land is used to grow more corn and to replace some of the decreased production of other commodities that occurs when US farmers allocate more existing cropland to corn.

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Searchinger et al. [2] argued that including emissions related to LUC, particularly international LUC (iLUC), results in corn ethanol having a higher GHG profile than gasoline.

The RFS2 directed the US Environmental Protection Agency (EPA) to do a full GHG life-cycle analysis (LCA) for corn ethanol and to include both direct and significant indirect sources of emissions. EPA designated iLUC, international livestock, international rice methane, and international farm inputs as significant indirect sources. The LCA was released in the 2010 Regulatory Impact Analysis (RIA) of the RFS2 [1]. It included projections through 2022 of the GHG emissions associated with 11 source categories that, collectively, capture the full range of direct and indirect GHG emissions associated with the production and combustion of corn ethanol. The EPA concluded that in 2022, the emissions profile of a unit of corn ethanol from a new natural gas-powered refinery would be 21% lower than the emissions profile of an energy-equivalent quantity of 'average' gasoline in 2005.

Since 2010, the RIA LCA for corn ethanol has dominated policy discussions and federal regulations related to ethanol as a renewable fuel and a GHG mitigation option. During this time, a large body of new data, scientific studies, technical reports, and other information has become available collectively showing that the emissions pathway corn ethanol has followed since 2010 is much lower than that projected in the RIA. Our objective is to assess corn ethanol's current GHG profile in light of this new information. This work is timely as many countries (e.g. Colombia, Japan, Brazil, Canada and the European Union) are developing renewable energy policies that require biofuel substitutes for gasoline to reduce GHG emissions by more than 21%. Our results could help position US corn ethanol to compete in these new and growing markets.

We also develop two projected emissions profiles for corn ethanol in 2022. A business-as-usual (BAU) scenario assumes a continuation through 2022 of several trends that have been reducing corn ethanol's GHG profile over time (e.g. refineries switching from coal to natural gas as a process fuel). A high efficiency-high conservation (HEHC) scenario assumes a proactive approach by refineries to lower the GHG profile of ethanol. In addition to the BAU trends, this scenario assumes refineries adopt specific GHG emissions-reducing technologies and practices. The results of this scenario could apply to a refinery, a set of refineries, or the industry as a whole.

Methods

In 2010, the RIA LCA was the most comprehensive assessment of corn ethanol's GHG profile. EPA developed three scenarios to assess the impacts of the RFS2's ethanol mandate. A 'reference case' considered the situation with no RFS2. Projected volumes in 2022 of corn ethanol, soybean biodiesel, and cellulosic ethanol (46.56, 0.38, and 0.0 billion liters, respectively) were taken from the Energy Information Agency's (EIA) Annual Energy Outlook for 2007 [3]. A 'control case' included the renewable fuel volumes mandated by the RFS2 by 2022. For corn ethanol, soybean biodiesel, and cellulosic ethanol these are, respectively, 56.78, 2.27, and 48.45 billion liters. A 'corn ethanol only case' set

corn ethanol at its reference case volume and soybean diesel and cellulosic ethanol at their 2022 RFS2 levels. Comparing the control and corn ethanol only cases isolated the impacts of the corn ethanol mandate.

The RIA LCA is the starting point for our analysis. For each of the 11 emissions categories we: (1) review the RIA projection; (2) describe relevant new information that has become available since 2010; and (3) quantify a new emissions value based on the new information.² For some categories, no substantive new information has appeared since 2010. In these cases, we apply, as appropriate, new emissions coefficients and global warming potentials (GWPs) to the RIA values. For source categories where new information indicates that emissions have not developed as projected in the RIA, we use a variety of methods to derive new emissions values. In some cases, our methods differ from those used in the RIA. This is particularly true for categories where emissions reflect changes in domestic and international land use.

Most of the new data, emission factors (EFs), and global warming potentials we use in this analysis have become available from 2010 to 2015. Most of the studies we draw on have publication dates between 2013 and 2015. This means our current GHG profile does not reflect a specific year but rather a composite year representative of the mid-2010s. Finally, in developing updated emissions values we use a variety of metrics. To aggregate emissions across categories and facilitate comparisons with RIA emissions values, we convert the total emissions for each category to the RIA metric, grams of CO₂ equivalent per million Btu (g CO₂e/MMBtu).³

Results

Domestic farm inputs and fertilizer N₂O

This category includes emissions related to the on-farm use of fertilizers, other chemicals, fossil fuels, and purchased electricity. We also include here an emissions credit that accounts for emissions reductions associated with substituting ethanol co-products for grains in livestock diets.

EPA used the Forestry and Agricultural Sector Optimization Model (FASOM) to assess the US farm sector impacts of the RFS2 on production, land use, and input use. FASOM is a dynamic partial equilibrium economic model that disaggregates US agriculture into 11 market regions and 63 sub-regions [4]. The model includes over 2000 crop, livestock, and biofuel production systems. In FASOM simulations, lands shift between commodities in response to new policy or market conditions and the model tracks changes, by commodity, in acres, production and input use (including nitrogen, phosphorus, potash, herbicides, pesticides, diesel, gasoline, natural gas, and electricity). Life-cycle EFs for fuels and fertilizers are from Argonne National Laboratory (ANL)'s GREET 2009 model. EFs for fertilizer-related N₂O are from Colorado State University's DAYCENT model. Comparing simulation results for the 'control' and 'corn only' cases, the RIA emissions value for this category was 10,313 g CO₂e/MMBtu [1].

The RIA projected 19.66 million additional tonnes of corn would be needed by 2015 to produce the 9.84 billion liters of ethanol required to meet the RFS2's 56.78 billion liter cap. Since the overall mandate was 55.98 billion liters

Table 1. Ethanol production market breakdown and animal feed displacement by ethanol plant type.

Ethanol plant type	Ethanol market share (%)	Total displaced animal feed (g/L of ethanol)				Co-product credit	
		Corn	Soybean meal	Urea	Soy oil	g CO ₂ e/L ethanol	g CO ₂ e/MMBtu
Dry mill w/o corn oil extraction	17.7	527	207	15.3	–	–262	–12,981
Dry mill w/corn oil extraction	70.9	504	198	14.6	–	–250	–12,417
Wet mill	11.4	857	–	13.1	117	–291	–14,449
Weighted average	–	–	–	–	–	–257	–12,749

in 2014 and 56.78 billion liters thereafter, we use the RIA corn projection as the basis for assessing the current emissions for this source category. Dividing 19.66 by the average US per-hectare corn yield in 2015 of 10.57 tonnes, we estimate the RFS2 corn ethanol mandate would require US farms to increase corn area by 1.86 million hectares.⁴ We allocate these acres regionally based on corn acreage data in the United States Department of Agriculture's (USDA) 2010 Agricultural Resource Management Survey (ARMS) [6].

For inputs, we consider changes in farm sector use of nitrogen (N), phosphorus (P), and potassium (K); composites for herbicides, insecticides, and fungicides; and diesel fuel. We get chemical application rates for corn, nationally and by region, from the 2010 ARMS [6].⁵ For fungicide, ARMS data identify application rates for the Corn Belt and the nation. For non-Corn Belt regions, we use the national rate. Based on University of Tennessee farm budgets for 2015 [7], we set diesel fuel use at 72.36 L/ha under conventional tillage. To account for hectares on which a given chemical is not applied, we calculate an effective application rate by multiplying the ARMS regional application rate by the percentage of hectares in each region that apply that chemical [6].⁶ Our region-weighted national average effective application rates for nitrogen, phosphorus, potassium, herbicides insecticides, and fungicides are 155.27, 53.55, 54.34, 2.36, 0.02, and 0.01 kg/ha, respectively. Regional effective application rates are available in Rosenfeld et al. [5].

From the regional acreage changes and effective application rates, we obtain changes in chemical and fuel use by US agriculture in response to the RFS2 corn ethanol mandate. Multiplying these changes by EFs from several sources, we get corresponding emissions estimates. Energy-related emissions also occur in the manufacture and transport of chemicals and fuel inputs. EFs reflecting these 'upstream' activities for nitrogen, phosphorus, potassium, and insecticides are obtained from the GREET 2015 model [8]. From GREET 2015 we also obtain EFs for diesel fuel covering both upstream activities and on-site combustion. EFs covering upstream activities for herbicides and fungicides come from theecoinvent v2 database [9]. For nitrogen fertilizer applications, N₂O is emitted directly to the atmosphere from cultivated soils, and indirectly at other locations when N is transported off-site through volatilization, leaching, and runoff. EFs for these direct and indirect N₂O emissions follow IPCC guidance per kilogram of N fertilizer applied [10].

We assess emissions related to fertilizers, herbicides and pesticides and fuel at 10,815, 8382, and 2617 g CO₂e/MMBtu, respectively. Summing these values, we estimate the total emissions-related domestic use of farm chemicals and fuel at 21,814 g CO₂e/MMBtu. Our approach differs from the RIA's, which simultaneously accounts for the substitution of ethanol co-products for grain in animal feed markets, resulting in a reduction in additional corn production (and therefore hectares) required to meet the RFS2

ethanol mandate. Our use of regional effective application rates means our emissions estimates apply to 'representative' incremental regional acres.⁷ Hence, we still need to account for the co-product emissions credit.

Animal feed co-products from ethanol production include distiller grains and solubles (DGS) from dry milling and corn gluten meal and corn gluten feed (CGM and CGF) from wet milling. We use the 'displacement method' to assess the co-product credit. In this approach, all energy and emissions associated with separating solids from the ethanol stream, drying the solids, and transporting the finished feeds to the point of final sale are allocated to the ethanol pathway. The pathway then receives a credit equal to the emissions that would have occurred if the displaced feed grain had been produced. GREET 2015 includes values for displaced animal feed per unit of ethanol by milling process. Table 1 shows these values and the co-product emissions credits per liter of ethanol and per MMBtu.

Summing the farm inputs emissions (+21,814 g CO₂e/MMBtu) and the weighted average co-product credit (–12,749 g CO₂e/MMBtu) gives a total emissions value of 9065 g CO₂e/MMBtu. This is slightly lower than the RIA value and largely reflects the lower GWP for N₂O from the Intergovernmental Panel on Climate Change's (IPCC) Fourth Assessment Report (AR4). EPA used GWPs from the IPCC's Second Assessment Report (AR2).

Domestic land-use change

Domestic LUC includes: (1) direct land-related emissions associated with shifting cropland and land from other uses into corn production; and (2) indirect emissions related to bringing new lands into production to replace some of the decreases in output of non-corn commodities that occur when farmers allocate more existing cropland to corn. For the RIA, EPA used FASOM to estimate domestic LUC and the associated emissions. FASOM tracks carbon stored in trees, understory, and litter within forests and plantations of woody energy crops but excludes carbon stored in cultivated crops. For agricultural lands, FASOM CO₂ and N₂O EFs are from the DAYCENT/CENTURY model.

EPA compared FASOM LUC results from the control and corn only scenarios. For each scenario, the model summed LUC emissions over the period 2000–2022. To these values were added cumulative land-related emissions that occur in the 30 years following 2022 (reflecting continuing emissions from agricultural soils, decaying biomass, and wood products). For total cropland and total corn area the net changes were 0.581 and 1.477 million hectares, respectively. The difference in annualized emissions between the two scenarios was –4000 g CO₂e/MMBtu, which was the RIA emissions value for this category [1].

We estimate domestic LUC emissions using results of a 2013 simulation of the Global Trade Analysis Project-Biofuels (GTAP-Bio) model and LUC emissions coefficients available in ANL's Carbon Calculator for Land Use Change from Biofuels Production (CCLUB) tool [11]. The GTAP-Bio 2013 results, developed in Taheripour and Tyner [12], include domestic and international land-use changes related to US corn ethanol production increasing from its 2004 level (GTAP-Bio's base period) to the RFS2 cap of 56.78 billion liters per year. Globally, the GTAP-Bio model estimates regional area changes for 18 agro-ecological zones (AEZs), and within each AEZ, changes in four land types (forests, grassland, cropland-pasture, and young forest shrub). Only AEZs 7–16 apply to US agriculture. For the United States, summing area changes across AEZs shows increasing US ethanol production resulted in conversions to cropland of 13,999 hectares of young forest shrub, 64,773 hectares of forest, 92,617 hectares of grassland and 1,788,462 hectares of cropland pasture (conversions by AEZ and land type are in Rosenfeld et al. [5, table 2-12]).

The CCLUB tool also includes LUC results for a similar analysis by Taheripour, Tyner, and Wang using a 2011 GTAP model [13]. Comparing the 2011 and 2013 GTAP results highlights how much new information has improved our understanding of the links between, and impacts related to, changes in corn ethanol markets and LUC relative to 2010. GTAP-Bio expands the set of land transformation elasticities from a single value to a set of region-specific values. GTAP-Bio also incorporates an improved cost structure that reflects the higher cost of converting forest to cropland versus converting pasture to cropland. Comparing the LUC results, conversions of young forest shrub, forest, and grasslands in the 2013 GTAP-Bio simulation are 79%, 80%, and 86% less, respectively, than in the 2011 simulation. There is also a 53% increase in conversions of cropland pasture to cropland. Overall, the GTAP-Bio analysis shows the large increase in US corn ethanol production since 2004 resulted in a large increase in land in corn production, a relatively small increase in aggregate agricultural land, and increases in cropland coming predominantly (over 90%) from cropland pasture.

We pair the GTAP-Bio AEZ-land type area changes with LUC emissions coefficients from the Century/COLE model. Relative to the RIA, which uses 2010 Century coefficients for agricultural land emissions, the coefficients used in our analysis better reflect irrigation effects and N₂O emissions from cropland and pasture.

The CCLUB tool also includes LUC emissions coefficients from Woods Hole (WH), and Winrock International (WI). We chose the Century/COLE coefficients because they align with the GTAP-Bio's AEZ-land-use type structure. The WH and WI coefficients apply to regions and have fewer land types. The WH coefficient set includes forest and grasslands; the WI set includes forest, grassland, and cropland-pasture. Hence, using the WH or WI coefficients with the AEZ-land type requires some aggregation across AEZs and land types. Additionally, distinct Century/COLE EFs are available for conventional and reduced tillage systems and soil depths of 30 and 100 cm. We assume the 100 cm soil-depth coefficients present a more complete picture of soil carbon changes than the 30 cm coefficients. We also note the conventional tillage scenarios are slightly less in

absolute value (i.e. more conservative) than the reduced tillage coefficients. Based on these considerations, we use Century/COLE 100 cm conventional tillage coefficients to estimate the GHG emissions related to agricultural lands. The Century/COLE EFs by AEZ and land type for conventional and reduced tillage systems and soil depths of 30 cm and 100 cm are in Rosenfeld et al. [5, tables 2-14 and 2-15].

We aggregate emissions across all AEZ-land type combinations and then annualize the total using the CCLUB default value of 30 years. We divide these emissions by 43.87 (i.e. the increase in annual ethanol production, in billion liters, from 2004 to the RFS2 cap of 56.78 billion liters) to get emissions per billion liters of increased annual ethanol production. We convert these emissions to the common metric g CO₂e/MMBtu using a heating value of 20,166 Btu/L.

As shown in Table 2, our emissions value for the domestic LUC category is −2038 g CO₂e/MMBtu. The negative value indicates net sequestration associated with all ethanol-related LUC. This sequestration is due to: (1) over 90% of all new lands shifting into cropland coming from the cropland pasture category; and (2) the Century/COLE emissions coefficients for such conversions being negative across all AEZs. The net sequestration associated with conversion of cropland pasture to cropland reflects root growth deeper in the soil profile that more than offsets CO₂ emissions due to oxidation of carbon near the surface. Net emissions associated with conversions of forest, grassland, and young forest shrub are all positive. For completeness, Table 2 also shows domestic LUC emissions for our land use changes using the WH and WI EFs and the Century/COLE emissions factor for reduced tillage and 30 cm soil depth.

Finally, several recent studies examine changes in US agricultural land use between 2006 and 2012 using USDA's Cropland Data Layer (CDL) series. These studies conclude that over this period, increases in US corn ethanol production helped shift millions of acres from grassland uses (and some forest and wetland uses) to cropland, and produced a large increase in cropland acres planted to corn and corn/soybean systems. Wright and Wimberly [14], Lark et al. [15], and Wright et al. [16] extend the grassland conversion results to significant losses of native prairie and other long-term grasslands, and to previously unaccounted-for GHG emissions attributable to corn ethanol. Lark et al. [15] put the GHG emissions from recently converted lands used to grow corn or soybeans at 94–186 MMTCO₂e. For reasons developed below, we do not incorporate the results of these studies in our analysis.

The CDL is a land cover data product developed annually by USDA's National Agricultural Statistics Service (NASS) to provide detailed maps of commodity production over the growing season. NASS starts with a series of satellite images covering the contiguous 48 states. Each image consists of pixels with a resolution of 30 square meters. Each pixel is photographed multiple times between April and October, which gives a dynamic visualization of the pixel. A small set of cropland pixels are ground truthed to match with specific crops. Using this information, a software package assigns non-sampled cropland pixels to specific crops.

Extending conversions of grassland to cropland using CDLs to decreases in native prairie, or other long-term grassland, is not straightforward. CDLs do not distinguish

Table 2. Domestic land-use change emissions for GTAP 2013 simulation using emission factors from Century/COLE, Woods Hole, and Winrock International.

	Total direct emissions (Mg CO ₂ e)	Annualized emissions (Mg CO ₂ e/year)	Direct emissions (g CO ₂ e/L)	Direct emissions (g CO ₂ e/MMBtu)
Century/COLE – 30 cm – Reduced till	–52,191,279	–1,739,709	–39.65	–1965
Century/COLE – 100 cm – Reduced till	–62,656,429	–2,088,548	–47.60	–2359
Century/COLE – 30 cm – Conventional till	–45,625,214	–1,520,840.5	–34.66	–1718
Century/COLE – 100 cm – Conventional till	–54,120,694	–1,804,023.1	–41.13	–2038
Woods Hole	48,163,909	1,605,464	36.59	1813
Winrock International	280,879,558	9,362,652	213.4	10,577

Table 3. Methane emission factors from irrigated rice by region (in kg CO₂e/ha).

Study	Corn belt	Pacific Southwest	South central	Southeast	Southwest	United States
EPA RIA ^a	4512	4406	5557	N/A	10,811	N/A
Present ^b	5928	5310	7500	9222	11,421	7324

Sources: ^a [1, Table 2.4-9]; ^b [21]; N/A = not applicable; kg CO₂e/ha = kilograms of carbon dioxide equivalent per hectare.

Table 4. Changes in population, emission factors, and total emissions by livestock type.

Livestock type	Change in population (in 1000 head)	Enteric emissions		Manure management emissions		Total g CO ₂ e/MMBtu
		per head (g CO ₂ e/head)	Total emissions (g CO ₂ e/MMBtu)	per head (g CO ₂ e/head)	Total emissions (g CO ₂ e/MMBtu)	
Dairy	–20 ^a	3625	–351	2065	–200	–551
Beef	90	1850	807	143	62	869
Poultry	–12,564.6 ^b	–	NA	3.21	–195	–195
Swine	–220	37.5	–40	378	–403	–443
Total	NA	NA	416	NA	–736	–320

^aMature cows only.

^bPopulation changes the same as in [1] except for poultry, which has been reduced to reflect annual average population changes rather than changes in total head slaughtered.

g CO₂e/head = grams of carbon dioxide equivalent per head; g CO₂e/MMBtu = grams of carbon dioxide equivalent per million British thermal units.

native from managed grasslands. In CDL studies, the ‘grasslands’ category includes native grasslands, pasture, cropland pasture, grass-hay, and land in the USDA’s Conservation Reserve Program. Quantifying emissions adds another complexity because the emissions associated with any given pixel moving from grassland to cropland will depend on the prior grassland use and management practices. Satellite images do not show either. There is also the issue of allocating emissions among drivers. Farmers base land-use and production decisions on past and expected commodity prices. Since 2006, domestic and world corn and soybeans prices have been historically high. In addition to increased ethanol production, these high prices reflect global population growth, increases in global demands for livestock products, and a series of severe weather events that disrupted global and US commodity markets. Analyzing the high US corn prices between 2006 and 2009 relative to 2004, Babcock and Fabiosa [17] conclude that 32% of the higher annual prices were attributable to ethanol and 64% to other factors.

Finally, the CDL is one of several national-scale land-cover data products developed by US government agencies. Others include the Forest Service’s Forest Inventory Assessment, the USDA’s Natural Resources Inventory, and the US Geological Survey’s National Land Cover Database. Focusing on 20 counties in the Prairie Pothole Region between 2004 and 2014, Dunn et al. [18] show that estimates of conversions of grassland, forest, and wetlands to cropland vary significantly depending on the land cover product and analytical techniques used.

Domestic rice methane

US rice production is a source of CH₄ emissions due to organic material decomposing under anaerobic conditions

in flooded fields. In the RIA, a decrease in rice hectares accounts, in part, for the RFS2-driven increase in corn hectares. This results in a decrease in CH₄ emissions.

EPA used FASOM simulations for the control and corn only scenarios to project RFS2 corn ethanol mandate-driven changes in rice hectares in 2022 at –23,790. These hectares were allocated across domestic rice-producing regions and each region’s hectares were multiplied by a region-specific per-hectare emissions coefficient from EPA [19]. EPA estimated the RFS2-related change in CH₄ emissions from decreased rice production at –42,000 metric tons CO₂e, which converted to –209 g CO₂e/MMBtu [1].

Domestic rice is a small emissions category and little new information has emerged since 2010 indicating US rice area has responded to the RFS2 along a significantly different path than that projected in the RIA. Hence, we use the RIA change in total domestic rice hectares, but allocate them regionally based on their current distribution. As shown in Table 3, since 2010, EPA has increased the per-hectare CH₄ EFs for rice production and the IPCC has increased the GWP value for CH₄ from 21 to 25. We incorporate both adjustments in calculating changes in regional rice emissions. Summing emissions across regions and dividing by 9.84 billion liters yields a per-liter emissions value. Applying a heating value for ethanol of 20,166 Btu/L, our emissions value for Domestic rice methane is –1013 g CO₂e/MMBtu.

Domestic livestock

This category includes changes in CH₄ emissions from enteric fermentation and changes in CH₄ and N₂O emissions from manure management. These sources account for about 47% of GHG emissions from US agriculture [20]. Enteric fermentation from dairy cows and beef cattle and manure management on dairy, beef, and swine operations

Table 5. Reduced Methane Emissions from Distillers Grains as Animal Feed by Ethanol Plant Type.

Ethanol plant type	Ethanol market share (%)	Dried DGS yield (g/L)	Wet DGS yield (g/L)	Emissions reduced (g CO ₂ e/L)	Emissions reduced (g CO ₂ e/MMBtu)
Dry mill with out corn oil extraction	17.7	504.1	661.7	−50.46	−2506
Dry mill with corn oil extraction	70.9	482.2	632.9	−48.34	−2397
Wet mill	11.4	–	–	–	–
Per average liter	–	431.1	565.9	−43.21	−2143

g/L: grams per liter; g CO₂e/L: grams carbon dioxide equivalent per liter; g CO₂e/MMBtu: grams carbon dioxide equivalent per million British thermal units.

account for about 95% of US livestock emissions. Increases in US corn ethanol production affect changes in livestock emissions through changes in animal populations, feed prices, and feed mixes. Corn is the most important feed input used in confined dairy, beef, swine, and poultry operations. While increases in corn ethanol production have helped drive historically high corn and feed prices since 2005, feed price impacts have been moderated by increased production of feed co-products, mainly DGS. When substituted for corn in cattle feed, DGS (dried or wet) reduces CH₄ emissions from enteric fermentation [1].

In the RIA, the RFS2-driven impacts of higher corn ethanol production on feed prices, livestock numbers, and livestock-related emissions are assessed using FASOM simulations for the ‘control case’ and the ‘corn only case’. FASOM projected the RFS2 would increase feed prices; reduce the populations of dairy cattle, swine, and poultry; increase the population of beef cattle; and reduce livestock-related emissions of CH₄ and N₂O. FASOM assesses livestock-related emissions on a per-head basis. Hence, a change in animal numbers results in a change in emissions in the same direction. An adjustment is made to capture the lower per-head enteric fermentation emissions for cattle fed DGS in place of corn. For this source category, the RIA projected emissions in 2022 at −3746 g CO₂e/MMBtu.

Since 2010, little new information has appeared to indicate that the relationship between feed prices and domestic livestock populations has changed significantly from those in the RIA’s FASOM simulations. Given this, the relatively small magnitude of the emissions category, and annual corn ethanol production in the RIA being 56.78 billion liters from 2015 through 2022, we use the RIA’s 2022 projections for changes in dairy cow, beef cattle, and swine populations in our analysis. For poultry, we reduced the RIA population change by 75%, because the RIA appears to include changes in poultry slaughtered instead of the annual average poultry population. The time from hatch to slaughter for poultry species is generally 3 to 4 months. Hence, it takes 3–4 slaughtered birds to apply a per-head annual emissions factor. We combined the changes in animal populations with annual EFs from the official 2016 US greenhouse gas inventory [21]. These EFs incorporate changes EPA has made in methodologies for computing emissions for different types of livestock and the AR4 GWPs for CH₄ and N₂O. Table 4 shows changes in populations, per-head annual EFs, and total emissions by livestock type.

To capture CH₄ emission reductions associated with feeding cattle DGS in place of corn, we use emissions reduction factors from the GREET 2015 (i.e. 0.183 kg CO₂e/dry kg of dried DGS (DDGS) and 0.130 kg CO₂e/dry kg of wet DGS (WDGS) for every dry kilogram of DGS consumed by beef cattle). Based on Renewable Fuels Association data [22], beef cattle consume 45% of DGS. Table 5 shows, by plant type, wet and dry DGS yields per liter of ethanol and emission reductions per liter and

in g CO₂e/MMBtu). Table 5 also shows the ethanol market shares by type of plant, which we use to calculate the emissions reduction for an ‘average’ liter of ethanol.

Combining the reduced emissions from changes in animal populations (−320 g CO₂e/MMBtu) with the reduced emissions from using more DGS in livestock diets (−2143 g CO₂e/MMBtu) we assess domestic livestock emissions at −2463 g CO₂e/MMBtu. This is about two thirds the RIA value, and it reflects differences in the CH₄ emissions reduction factors associated with feeding beef cattle DGS in place of corn in the GREET 2009 and 2015 models.

International livestock

As in domestic feed markets, large increases in the US ethanol industry’s demand for corn have helped drive higher prices in international feed markets. This has affected changes in global livestock populations, which in turn has affected changes in CH₄ emissions from enteric fermentation and CH₄ and N₂O emissions from manure management.

The RIA grouped international livestock into seven regions (Canada, Western Europe, Eastern Europe, Oceania, Latin America, Africa, the Middle East, and India). Simulations of the Food and Agriculture Policy and Research (FAPRI) - Center for Agricultural and Rural Development (CARD) model for the ‘control case’ and the ‘corn only case’ were used to evaluate changes in regional populations of dairy and beef cattle, swine, sheep, and poultry in response to RFS2-driven changes in international feed prices. The changes in regional livestock populations were multiplied by region- and livestock-specific, per-head GHG EFs. The EFs for both the enteric fermentation and the manure management emissions reflected the default IPCC EFs, which account for differences in regional livestock systems [10]. EPA projected emissions for this category in 2022 at 3458 g CO₂e/MMBtu.

Since 2010, little new information has appeared to indicate that the FAPRI-CARD relationships between feed prices and international livestock production have changed significantly. Given this, the relatively small magnitude of the emissions category, and annual corn ethanol production in the RIA being 56.78 billion liters from 2015 through 2022, we use the RIA’s 2022 projections for changes in regional dairy cattle, beef cattle, swine, sheep, and poultry populations for our analysis. Population changes by region and livestock group are available in Rosenfeld et al. [5].

With one exception, we use the RIA’s region- and livestock-specific EFs for enteric fermentation and manure management; however, we adjust these factors to reflect the AR4 GWPs for CH₄ and N₂O. While updated activity EFs are available for a number of countries, it is difficult to justify applying these factors to changes in livestock populations in regions that are multi-county aggregates. The

Table 6. iLUC emissions by scenario, emissions factor set, and annualized emissions value.^a

Scenario	Emission factor (EF) data set	Emissions (g CO ₂ e/MMBtu) ^c
FAPRI-CARD	RIA [1] analysis Winrock	31,790
Scenarios making up composite iLUC emissions value used in this analysis		
GTAP 2013	CARB AEZ Model	17,802
GTAP 2013 ^b	Winrock	5913
GTAP 2013 adjusted with data in [26]	CARB AEZ Model	8464
GTAP 2013 adjusted with data in [26]	Winrock	1326
CARB 2015 [27]	CARB AEZ Model	20,890
Dunn et al. 2015 [11]	Winrock	5286
[11]	Woods Hole	3893

^aScenarios in [11] and the four scenarios we construct use land conversion results published by [26]. [27] modified some important factors and values within the GTAP-Bio model to produce their own unique land conversion results.

^bEmissions vary in these studies because within each region, [11] used an average of the individual country EFs, while we weight countries' EFs by their share of regional arable land.

^cAll studies assume emissions from land conversions occur over 30 years. This column shows annualized values. The RIA and GTAP-Bio 2013 consider different volume increases in corn ethanol production. Describing emissions in g CO₂e/MMBtu puts all emissions in a comparable metric.

Abbreviations: iLUC = international Land Use Change; g CO₂e/MMBtu = grams carbon dioxide equivalent per million British thermal units; RIA = Regulatory Impact Analysis; FAPRI-CARD = Food and Agriculture Policy Research Institute-Center for Agricultural and Rural Research model; GTAP = Global Trade Analysis model; CARB = California Air Resources Board; AEZ = Agricultural-Ecological Zone.

Table 7. Mode and distance assumptions.

Mode	Farm to stacks		Stacks to plant		Plant to blending terminal		Terminal to retail station		DGS ^a		Corn oil	
	% of total shipped	Distance (km)	% of total shipped	Distance (km)	% of total shipped	Distance (km)	% of total shipped	Distance (km)	% of total shipped	Distance (km)	% of total shipped	Distance (km)
Barge	0	0.0	0	0.0	13	837	0	0.0	2	837	0	0
Rail	0	0.0	0	0.0	79	1287	0	0.0	12	1287	20	644
Truck	100	16.1	100	64.4	8	129	100	48.3	86	80	80	161

^aThe values shown in these columns reflect a weighted average dry and wet distiller grains and solubles (DGS) co-product.

exception was Canadian cattle, where updated factors were available and the region consisted of only Canada.

Given these adjusted EFs, our emissions value for the international livestock source category is 3894 g CO₂e/MMBtu. This value is somewhat higher than the RIA value and reflects the updated EFs for Canadian cattle and the higher GWP for CH₄.

International land-use change

iLUC is the largest emissions category in the RIA LCA. It encompasses indirect emissions associated with farmers outside the United States shifting new land into commodity production in response to increases in global commodity prices driven by the RFS2 corn ethanol mandate. For the RIA, EPA used simulations of the FAPRI-CARD model to assess global agriculture's response to the RFS2. FAPRI-CARD can assess changes in area and production across 20 crops and 54 regions in response to changes in international and domestic commodity prices. For 2022, FAPRI projected the RFS2 corn ethanol mandate would increase cropland outside the United States by 789,000 hectares and decrease pasture by 446,000 hectares. Among regions, Brazil accounted for the largest share of new cropland (approximately 316,000 hectares) [1, see fig. 2.4-47].

While FAPRI can assess how much new land will shift into commodity production in response to a global commodity market shock, it cannot distinguish the types of land that shift. The FAPRI-CARD projected changes in regional land areas used for commodity production (crops and livestock) were analyzed by WI to determine the types of land, and the quantities of each land type, that would be affected. WI's methodology drew on MODIS (Moderate Resolution Imaging Spectroradiometer) satellite data covering the period 2001

to 2007 [23,24] and expert opinion to quantify, by region, conversions and reversions of land to commodity production from forest land, from grassland, and from cropland-pasture. Summed across regions, the RIA projected emissions in 2022 for the iLUC source category at 31,790 g CO₂e/MMBtu.

Since 2010, several new studies have assessed the iLUC impacts associated with the corn ethanol mandates in the RFS and RFS2 [11,12,25–28]. These studies employ data, modeling capabilities, and other information that were not available for the RIA. Viewed collectively, three results stand out. First, the studies all find significantly lower iLUC emissions than were projected in the RIA. Second, across studies, estimates of corn ethanol-driven iLUC emissions trend down over time. Finally, two research groups, the California Air Resources Board (CARB) [27, 29] and Dunn et al. [11, 25], look at the issue twice. Each finds iLUC-related emissions to be significantly lower (by 33–60%) in their second analysis. Given that the RIA projected emissions path for iLUC is flat from 2015 onward, the new research strongly indicates that actual iLUC emissions related to corn ethanol are much lower than was projected in the RIA.

Except for Babcock and Iqbal [26], the studies cited above employ some version of the Global Trade Analysis Project (GTAP) model. Most use the 2013 GTAP-Bio (for biofuels) model described in Tahierpour and Tyner [12]. Relative to the FAPRI-CARD model used in the RIA and the GTAP model used in CARB [29], the 2013 GTAP-Bio model has several upgrades that make it better suited to analyzing the iLUC impacts related to increases in US corn ethanol production. First, its base period is 2004. Hence, all simulations are relative to the year before implementation of the RFS. Second, the model includes region-specific land transformation elasticities developed from two United Nations Food and Agriculture Organization (FAO) land-

Table 8. Assumptions and inputs for fuel production modeling in GREET 2015.

Input category	Dry milling plant without corn oil extraction ^a	Dry milling plant with corn oil extraction ^a	Wet milling plant ^b
Total energy use for ethanol production (MJ/L)	28.33	27.88	50.02
Process fuel energy – natural gas, coal, and biomass (MJ/L)	25.66	25.18	50.02
Electricity use (kWh/L)	0.195	0.198	0.00
Co-product yield – dry DGS to animal feed (g/L ethanol)	504	482	0.00
Co-product yield – wet DGS to animal feed (g/L ethanol)	661	633	0.00
Co-product yield – CGM to animal feed (g/L ethanol)	0.00	0.00	162
Co-product yield – CGF to animal feed (g/L ethanol)	0.00	0.00	702
Co-product yield: Corn oil (actual g/L ethanol)	0.00	22.77	117
Ethanol yield (L/bushel)	10.6	10.7	9.88
GHG emissions (g CO _{2e} /MMBtu)	32,114	31,590	53,055

^aThese are composite refineries reflecting the 2014 mix of natural gas, coal, and biomass as a process fuel at the respective dry mill refineries.

^bElectricity consumption is included with process fuel energy.

Abbreviations: GREET = The Greenhouse Gas, Regulated Emissions, and Energy Use in Transportation Model; MJ/L = Mega Joules per liter; kWh/L = kilowatt hours per liter; g/L = grams per liter; L/bushel = liters per bushel; g CO_{2e}/MMBtu = grams CO₂ equivalent per million British thermal unit; RIA = Regulatory Impact Analysis; BAU = Business as Usual Scenario; HEHC = High Efficiency - High Conservation Scenario

cover datasets. Finally, the model explicitly accounts for the higher cost of converting forest to cropland relative to the cost of converting grassland. The complete set of global land-use changes generated by Taheripour and Tyner [12] is available in ANLs CCLUB model.

While commodity production data show that farmers in the US and in other regions did increase commodity production in response to historically high commodity prices over the period 2004–2012, Babcock and Iqbal [26] show most of these increases were achieved by farmers using existing cropland more intensely rather than by bringing new land into production. For example, comparing Brazilian data for 2004–2012 on planted, harvested, and double-cropped hectares, they found increased use of double cropping accounted for 76% of the increase in harvested area. For China and India over the same period, they found virtually all of the increases in harvested area were due to intensification. In China, the driver was increased use of double cropping, while in India the drivers were increased use of double cropping (33%) and decreases in idle cropland (67%). This is important from an LCA perspective because bringing new land into production generally entails much higher GHG emissions than does using existing cropland more intensely.

To see how increased intensification might affect the iLUC impacts in the GTAP 2013 land-use change results, we apply the Babcock and Iqbal [26] intensification measures for five regions (i.e. Brazil, China, India, Indonesia, and sub-Saharan Africa) to their cropland increases in the 2013 GTAP results. Regional conversions to cropland from forest, grassland, and cropland pasture in the 2013 GTAP-Bio simulation are shown in Rosenfeld et al. [5, table 2-37] both with and without the regional intensification adjustments. Aggregated across regions, intensification reduces hectares converted by 775,000, which is almost 60% of total hectares converted in the 2013 GTAP results.

To assess iLUC emissions associated with increases in US corn ethanol production requires linking regional shifts of land into commodity production with a set of associated EFs. The RIA employs a set of iLUC EFs developed by WI. The WI EFs reflect historical land-use trends identified using MODIS satellite imagery from 2001 and 2007, and include region-specific factors by type of land converted. A second set of EFs are those developed by WH. The WH EFs incorporate region- and biome-specific values for belowground carbon, biomass carbon, and carbon growth factors. The WI and WH EF sets are options in the ANL CCLUB model, but neither aligns exactly with the GTAP 2013 AEZ structure.

Hence, using GTAP 2013 iLUC results with either the WI or WH EF set requires some aggregation of land conversions across land types and AEZs within each region.

A third set of iLUC EFs is available from the Low Carbon Fuel Standard Agro-ecological zones (AEZ) model (a GTAP model tailored to California) used by CARB [27]. The CARB AEZ EFs are not included in the ANL CCLUB model but are completely consistent with the 2013 GTAP region-AEZs structure. This makes computing iLUC-related emissions for GTAP 2013 simulation results relatively straightforward.

To assess the contribution of iLUC emissions to corn ethanol's GHG profile, we compute the average iLUC emissions for seven scenarios. Three scenarios are directly from CARB [27] and Dunn et al. [11]. Four scenarios we construct using the regional iLUC impacts from Tahierpour and Tyner [12], the CARB and WI EFs, and the regional data on intensification in Babcock and Iqbal [26]. Table 6 details the seven scenarios, their EF sets, and their iLUC emissions values. The average annual iLUC emissions of these seven scenarios is 9082 g CO_{2e}/MMBtu. This is our emissions value for the iLUC category.

International farm inputs and fertilizer N₂O

This category includes emissions related to changes in the use of chemical and energy inputs by farmers outside of the United States responding to changes in global commodity markets driven by increases in US corn ethanol production. EPA utilized FAPRI-CARD simulations to assess changes in harvested area and production by crop and country. Fertilizer application rates per hectare came from the International Fertilizer Industry Association (IFA) [30] and FAO [31]. Herbicide and pesticide activity data came from FAO [31] and, for China, USDA's Economic Research Service (ERS) [32]. EFs for fertilizers, herbicides and pesticides came from GREET 2009 [33]. Direct and indirect N₂O emissions from synthetic fertilizer were estimated using an approach analogous to that used for domestic direct and indirect N₂O emissions.

For energy inputs, EPA used International Energy Agency (IEA) data on farm-sector use of diesel, gasoline, and electricity by country [34]. Emissions associated with use of these inputs were calculated using IEA country-level GHG EFs. Farm-sector emissions were scaled up to life-cycle emissions based on the ratio of combustion to life-cycle GHG emissions from US electricity and fuel use [34]. For each country, dividing the total life-cycle emissions by the area of arable land in the FAOstat land area database [31] yielded per-hectare LCA emissions.

Multiplying the per hectare emissions by the FAPRI-CARD country-level changes in harvested hectares yielded total fuel-related emissions related to the RFS2 corn ethanol mandate. Summed across countries and inputs, the RIA projected emissions in 2022 for this category at 6601 g CO₂e/MMBtu. This projection, however, reflects the FAPRI-CARD extensive margin response of international agriculture to the RFS2-driven increase in US corn ethanol production. As discussed, information not available in 2010 indicates international agriculture's primary response to increases in US corn ethanol production has been to use existing cropland more intensely. Since the RIA overestimates the amount of new land shifted into commodity production, it overestimates the emissions associated with the use of chemical and energy inputs.

We assess emissions for the international farm inputs and fertilizer N₂O category based on the international acreage responses to increased US corn ethanol production in the GTAP 2013 results available in ANL's CCLUB model [11]. Since the base year for the GTAP 2013 model is 2004, its iLUC results reflect the new land brought into commodity production outside the United States in response to the ethanol mandates in the original RFS and the RFS2. That is, the GTAP 2013 iLUC results reflect an increase of 43.87 billion liters of US corn ethanol. To make the 2013 GTAP iLUC numbers more directly comparable to the FAPRI-CARD values in the RIA, we convert both to new hectares brought into commodity production per million liters increase in US corn ethanol. The GTAP 2013 and FAPRI-CARD values are 29.59 and 80.05 ha/million liters, respectively.

We follow the general RIA approach to estimate average per-hectare emissions associated with international agriculture's use of chemical and energy inputs. Country-level per-hectare application rates are from FAO and IEA data compiled in FAOStat [31]. We update the herbicide and pesticide use data to reflect the most current data available from FAO's FAOStat dataset for pesticide consumption [31]. For multi-country GTAP regions, we compute weighted average application rates with the weights being each country's share of its region's stock of arable land. Arable land area came from FAO [31]. Life-cycle EFs for nitrogen, phosphate, potassium, calcium carbonate, and insecticide are from GREET 2015. Life-cycle EFs for herbicides and insecticides are from ecoinvent v2 found in SimaPro [9].

We calculate direct and indirect N₂O emissions based on IPCC guidance [10]. The guidance uses applied nitrogen fertilizer rates to assess the direct impacts including the N additions from fertilizer, and the N mineralized from soil due to the loss of soil carbon. The N fertilizer application rate is also used to calculate the indirect emissions from volatilization and leaching [10].

Emissions associated with the use of energy inputs are calculated using IEA data on total CO₂ emissions from agricultural fuel combustion by country. These emissions are combined with country-level emissions related to agriculture's use of electricity. The total emissions are then scaled to represent the full life-cycle GHG emissions for each country. We did not update the RIA EFs for energy inputs because IEA no longer releases country-specific EFs.

The per-hectare emission rates developed for chemical and energy inputs are multiplied by the amount of new land in each GTAP region shifting into commodity production in response to increased US corn ethanol production. Converted

to the common energy metric, we assess emissions for this category at 2217 g CO₂e/MMBtu. This value is about a third of the RIA value and reflects the much lower LUC response per million liter increase in US corn ethanol production in GTAP 2013 relative to the 2010 FAPRI-CARD model.

International rice methane

This category captures CH₄ emissions related to RFS2-driven changes in rice area outside of the United States. EPA projected these emissions based on IPCC guidance [10], country-level data on rice area harvested and length of growing season, and default IPCC EFs for irrigated, rainfed lowland, upland, and deepwater rice production systems [10]. Country values for the rice-growing season came from the International Rice Research Institute (IRRI) [35]. FAPRI-CARD simulations projected annual country-level values for rice production and harvested acres under the 'control case' and the 'corn only case' scenarios. Comparing these simulations, the RIA projected international rice area in 2022 would increase by 58,344 hectares in response to the RFS2 corn ethanol mandate.

Multiplying the country-specific changes in rice acres by the appropriate production system EF(s) and summing across countries, the total projected change in CH₄ emissions in 2022 was 19,918 Mg CH₄. This converted to 2089 g CO₂e/MMBtu [1]. Country values for changes in rice area and emissions are in Rosenfeld et al. [5, table 2-48].

International rice methane is a relatively small emissions category in the RIA and very little new information indicates a need to change the RIA methodology or emissions estimate. Hence, we use the RIA's country-specific changes in rice acres and CH₄ emissions (i.e. 19,918 Mg CH₄). We multiply these emissions by the AR4 CH₄ GWP to get the CO₂ equivalent. We then divide the CO₂ equivalent by 9.84 billion (i.e. the RFS2-related increase in US corn ethanol production in 2022) to get an equivalent emissions per liter. We convert this to g CO₂e/MMBtu using the heating value 20,166 (Btu/L). Our value for the international rice methane emissions is 2483 g CO₂e/MMBtu.

Fuel and feedstock transport

CO₂ emissions from combusting gasoline and diesel fuels occur in transporting corn from farm to refinery, ethanol from refinery to retail station, and co-products from refinery to end users. While this category accounts for 5–6% of ethanol's GHG profile, transportation vehicles and systems have become more fuel and GHG efficient since 2010 [36].

The RIA drew on a combination of sources to determine fuel and feedstock transportation emissions. From GREET 2009, corn was assumed to move 10 miles by truck from the farm to a central collection point (i.e. the stack) and 40 miles by truck to the refinery. An Oak Ridge National Laboratory (ORNL) study provided projected 2022 fuel transportation modes and distances for ethanol from refinery to the blending terminal [37]. For co-products, the EPA obtained data from the USDA on modes and distances for transporting DGS from refineries to final users [1]. For each mode of transportation and associated distance traveled, GREET default assumptions and EFs were used. The

RIA projected 2022 emissions for the fuel and feedstock transport category at 4265 g CO₂e/MMBtu. The RIA did not consider transportation requirements for corn oil.

Our method is similar to that of the RIA but incorporates updated assumptions, transportation mode and distance traveled data, and EFs from GREET 2015. Relative to GREET 2009, GREET 2015 includes: (1) new LCA EFs for five types of diesel and gasoline freight vehicles; (2) new transportation mode and distance traveled data for ethanol moving from refinery to blending terminal and from blending terminal to retail station; and (3) new life-cycle freight EFs for rail, barge, and truck [36]. For corn oil, transportation emissions reflect the same emissions per ton-mile as for DGS. Table 7 shows the modes and distances for transporting corn, ethanol, DGSs, and corn oil used in our analysis. For the columns labeled Farm to stacks, Stacks to plant, and DGS, the values are the same as in the RIA. We assess emissions for this category at 3,432 g CO₂e/MMBtu. Of this, 57.3%, 33.8%, 8.3% are for the transportation of, respectively, corn, ethanol, and DGS.

Fuel production

This category includes emissions related to energy use at refineries. Across refineries, energy use per unit of ethanol varies significantly. Major determinants are the type of refining process (i.e. wet or dry milling), the process fuel used (i.e. natural gas, coal, or biomass), the set of co-products produced (wet DGS, and dry DGS), and the quantity of electricity purchased from the grid. For the RIA, EPA developed a table from various sources detailing projected 2022 energy use by refineries across these factors [1, table 2.4-55].⁸ Based on these energy use values, various EFs from the GREET 2009 model, and assumed yields of ethanol per kilogram of corn (0.40 L for dry mill plants and 0.37 L for wet mill plants), EPA projected 2022 emissions profiles for a variety of refinery configurations [1, fig. 2.6-3]. The GREET model coefficients included: (1) emissions from combustion of natural gas and coal; (2) upstream emissions for natural gas, coal, and biomass; and (3) emissions associated with the production and use of purchased electricity [1, 33].

For the RIA LCA, EPA constructed a 'representative' new dry mill refinery in 2022 that uses natural gas for a process fuel, produces a DGS mix that is 63% dry and 37% wet, and has a fractionation technology in place for extracting corn oil from the DGS. EPA projected emissions for the fuel production category at 28,000 g CO₂e/MMBtu in 2022.

Since 2010, production efficiencies have improved and GHG intensities have fallen in the US corn ethanol industry. There has been an ongoing shift from coal to natural gas as a process fuel. The use of new enzymes and yeast strains has increased efficiencies in starch conversion and fermentation so refineries are getting more ethanol per bushel of corn [38]. Finally, many refineries now recover corn oil as a co-product. We draw on the set of corn ethanol production pathways and their associated EFs available in GREET 2015. Many of these pathways are new or updated relative to GREET 2009 and better reflect the production technologies and energy use at refineries today. The updated pathways include: (1) an ethanol industry average – 92% natural gas, 8% coal; (2) dry mill – 100% natural gas; (3) dry mill – 100% coal; (4) dry mill – 100%

biomass (forest residue); and (5) wet mill – 72.5% natural gas, 27.5% coal. Table 8 shows the assumptions on energy use, co-product yields, ethanol yields, and GHG emissions for these pathways.

For co-products, drying DGS and extracting corn oil requires energy. When accounting for DGS as a co-product, we used the displacement method (described previously). The energy and emissions related to DGS drying are allocated to the fuel production category and a credit is given for DGS displacing corn grown for animal feed. As noted, we allocate the entire co-product credit to the *domestic farm inputs and fertilizer N₂O* category. For corn oil, we used the marginal method, which does not allocate the energy or the emissions related to corn oil extraction to the ethanol production process and does not award the process a credit based on reducing the GHG intensity of downstream products or replacing other feedstocks.

To assess fuel production emissions, we construct a composite refinery reflecting a weighted average of current dry and wet milling production processes (18% dry milling without corn oil extraction, 71% dry milling with corn oil extraction, and 11% wet milling). Our weighted industry average emissions level is 34,518 g CO₂e/MMBtu. This value is higher than in the RIA and reflects some refineries still using coal as a process fuel.

Tailpipe

Combusting ethanol in motor vehicles emits CO₂ from the tailpipe. These emissions are biogenic and are assumed to be offset by the removal of CO₂ from the atmosphere during new biomass growth. Ethanol combustion also emits CH₄ and N₂O, which remains in the atmosphere. Using the 2009 Motor Vehicle Emission Simulator (MOVES), EPA projected these emissions at 269 g CO₂e/MMBtu for CH₄ and 611 g CO₂e/MMBtu for N₂O [1, 39].⁹ Summing these values, the RIA projected tailpipe emissions in 2022 at 880 g CO₂e/MMBtu.

Since 2010, new estimates of the CH₄ and N₂O emissions associated with combusting ethanol have been published by the Washington Department of Ecology [40] (187 g CO₂e/MMBtu), the State of California GREET model [41] (613 g CO₂e/MMBtu) and GREET 2015 (578 g CO₂e/MMBtu). All three values are less than the value in the RIA. The GREET-affiliated estimates have a small downward bias because they reflect E85, not pure ethanol as in the RIA. The Washington Department of Ecology emissions estimate reflects pure ethanol but it has the largest difference from the RIA value. Given that this is the smallest emissions category and given our overall reliance on GREET 2015 EFs, we select 578 g CO₂e/MMBtu as the emissions value for this category.

Projected GHG LCA emissions in 2022 for BAU and HEHC scenarios

Starting with our current emissions profile of corn ethanol, we develop two projected emissions profiles for 2022. The first projection, labeled the BAU scenario, continues through 2022 current trends in: (1) per-hectare corn yields (increasing by 125.7 kg/ha/year [42]); (2) refineries switching from coal to natural gas as a process fuel; and (3) increasing fuel efficiency in heavy-duty diesel trucks. The BAU scenario reflects

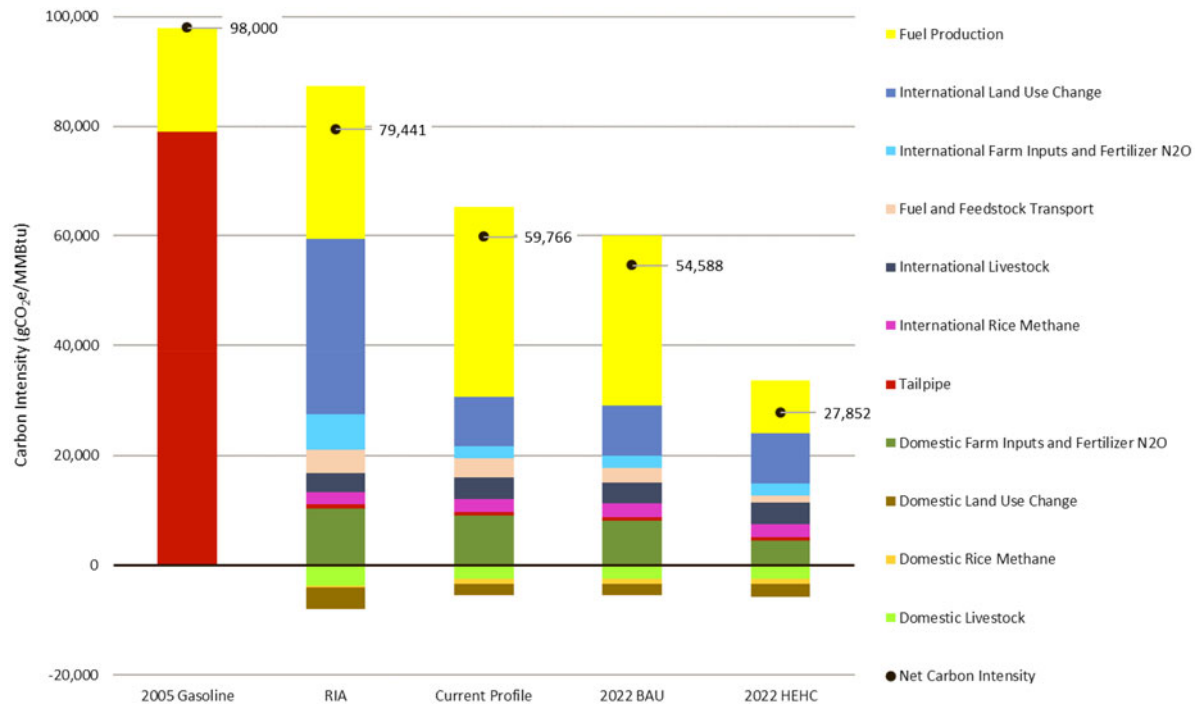


Figure 1. Life-cycle GHG emissions for gasoline and corn ethanol by scenario and source category. RIA: Regulatory Impact Analysis; BAU: Business as Usual Scenario; HEHC: High Efficiency - High Conservation Scenario; N₂O: Nitrous Oxide.

expected improvements in corn ethanol's GHG profile in 2022 without refineries acting to reduce emissions. The second projection, the HEHC scenario, adds to the BAU scenario several actions refineries could take to reduce the GHG intensity of corn ethanol. These include contracting with farms to grow corn using low-emissions practices (reduced tillage, cover crops, and nutrient management), switching to sustainably produced biomass as a process fuel, and locating confined livestock operations close to refineries.¹⁰

Contracting with farmers (reduced tillage, nitrogen management, and cover crops)

The current and BAU GHG scenarios assume farmers grow corn for ethanol using conventional tillage. Relative to conventional tillage, reduced tillage systems increase soil carbon levels, decrease CO₂ emissions from fuel combustion in field operations, and decrease N₂O emissions from volatilization. For the HEHC scenario, we estimate increased soil carbon impact of farmers adopting reduced tillage by matching US corn hectares by AEZ from the GTAP 2013 simulation with the corresponding AEZ soil carbon emissions coefficients using both conventional and reduced tillage. Summed across AEZs, the emissions impact is -321 g CO₂e/MMBtu (in Table A2, compare the domestic LUC values for the 'current conditions' and the '2022 HEHC' scenarios). To account for the emissions impact of lower diesel fuel consumption, we decrease the use of diesel in farm operations from 76.36 L/ha under conventional tillage to 64.98 L/ha for reduced tillage [7]. Finally, the shift from conventional to reduced tillage reduces the volatilization rate of applied nitrogen. The COMET-Planner report attributes a 0.173 Mg CO₂e/ha/year reduction in emissions to reduced tillage relative to conventional tillage. This represents a 74.4% reduction in N₂O emissions from volatilization, which we incorporate into the HEHC scenario.

If they are not doing so already, farmers can reduce applied N and the associated N₂O emissions by targeting N applications and using N inhibitors [5]. The COMET-Planner report estimates

these practices can reduce N application rates by 15%. We make this adjustment to the application rates in the HEHC scenario. There is little publicly available data with which to quantify the upstream emissions associated with N inhibitors. As a proxy, we use an application rate of 5.53 kg/ha [43, 44] and manufacturing process emissions for the 'organophosphorus-compound' from the ecoinvent database [9].

Cover crops protect soils between harvest and planting. Using cover crops can reduce indirect N₂O emissions related to leaching of N fertilizer. The COMET-Planner attributes a 1.24 Mg CO₂e/ha/year reduction in emissions to cover crops. This is a 76.8% reduction in N₂O emissions from leaching, which we incorporate in the HEHC scenario.

Comparing the BAU and HEHC scenarios indicates that in 2022, refineries can reduce emissions by 4021 g CO₂e/MMBtu by contracting with farmers to grow corn using reduced tillage, nitrogen management, and cover crops (sum the differences in emissions for 'domestic farm inputs' and 'domestic LUC' between BAU and HEHC scenarios in Table A2).

Fuel production

For the current GHG profile of corn ethanol, we assess emissions for the fuel production category by constructing a composite process fuel reflecting a weighted average of fuels currently used by refineries. For the 2022 projections, we focus on refineries that use dry milling technologies. The ethanol industry has been shifting to dry milling due largely to the high capital costs of wet mill refineries [45]. In 2013, 83% of US corn ethanol refineries used dry mill technologies. Rosenfeld et al. [5] describe fuel production emissions for dry mill refineries, with and without corn oil extraction, and using different process fuels. Our BAU scenario assumes a dry mill refinery with corn oil extraction using natural gas as its process fuel. Fuel production emissions for this refinery are 31,006 g CO₂e/MMBtu. Our HEHC scenario assumes the same refinery using biomass as its process fuel. The HEHC scenario also incorporates a higher

ethanol yield per bushel of corn than in the BAU scenario, 0.44 versus 0.42 L/kg of corn. Fuel production emissions for the HEHC refinery are 9695 g CO₂e/MMBtu.

Fuel and feedstock transportation

For the current GHG profile of corn ethanol, we use default GREET 2015 transportation and distribution EFs, mode allocations (i.e. barge, truck, or rail), and distance assumptions to generate transportation-related emissions (see Table 7). For the 2022 BAU and HEHC projections, we adjust the default GREET 2015 emissions to reflect a 50% increase in fuel efficiency for heavy-duty diesel trucks and an increase in the use of liquefied natural gas (LNG)- and renewable LNG-powered heavy-duty trucks. The BAU includes a transition of feedstock, fuel, and corn oil transport to LNG and DDGS transported by diesel. The HEHC included a full transition to renewable LNG, increased in part due to renewable natural gas from landfills qualifying as an advanced biofuel. Additionally, the HEHC scenario assumes the location of confined animal feeding operations (CAFOs) near ethanol plants and we eliminate emissions related to transporting DDGS. For the BAU and HEHC scenarios, emissions related to transporting of fuel and feedstock are projected at 2641 and 1237 g CO₂e/MMBtu, respectively.

Discussion

Figure 1 shows the RIA GHG profile for gasoline, the RIA projected GHG profile for corn ethanol in 2022, our current GHG profile for corn ethanol, and our two projected GHG profiles for corn ethanol in 2022. Appendix Table A2 provides the emissions values by source category for each ethanol scenario.

In the RIA, EPA quantified the LCA emissions associated with its 'average' 2005 gasoline (see note 1) at 98,000 g CO₂e/MMBtu. For corn ethanol, the RIA projected emissions in 2022 at 79,441 g CO₂e/MMBtu. The ethanol is produced at a new natural gas-powered dry mill refinery, with a fractionation process in place for extracting corn oil, and producing a DGS mix that is 63% dry and 37% wet. Interestingly, the projected emissions for corn ethanol fall just short of the 20% reduction required in the RFS2 to qualify as a renewable fuel. EPA assumed there would be additional emissions reductions by 2022 related to increased efficiencies (e.g. in drying DGS). With these efficiency gains, EPA projected the life-cycle GHG emissions of corn ethanol in 2022 at 21% lower than gasoline.

Our current conditions scenario assesses the life-cycle emissions of corn ethanol at 59,766 g CO₂e/MMBtu. This is a 39% reduction in GHG emissions relative to gasoline; almost twice the reduction developed in the RIA. This scenario assumes ethanol plants use a composite process fuel that reflects today's mix of natural gas, coal, and other fuels used by refineries. The 39% reduction is the industry-wide average GHG reduction for corn ethanol relative to gasoline. However, most refineries today use natural gas as a process fuel. In Table A2, replacing the fuel production emissions in the current conditions scenario with the fuel production emissions in the BAU scenario indicates that the GHG profile of corn ethanol produced in these refineries is 42.6% lower than that of gasoline.

Our BAU scenario assumes a continuation through 2022 of current trends in average corn yields per hectare, process fuel switching from coal to natural gas, and increasing fuel efficiency in heavy-duty trucks. Based on these trends, we project life-cycle GHG emissions for corn ethanol in 2022 at 54,588 g CO₂e/MMBtu. This scenario indicates that even if the ethanol industry does not act to reduce emissions, the GHG profile of corn ethanol will continue to improve. By 2022, the emissions associated with producing and combusting corn ethanol will be, on average, 44.3% lower than the emissions associated with producing and combusting gasoline.

Our HEHC scenario assumes refineries actively reduce their GHG profile. Refineries use sustainably produced biomass as the process fuel, contract with farmers to grow corn using low-emissions practices, and locate CAFOs near refineries. Projected emissions for corn ethanol in 2022 are 27,852 g CO₂e/MMBtu, which is a 71.6% reduction in GHG emissions relative to gasoline. The main source of emissions reductions is the shift to sustainable biomass as the process fuel. While it is not likely the ethanol industry as a whole will undertake these changes, it does highlight the emissions reductions that are technically possible with currently available technologies. Given an appropriate incentive, some refineries will likely undertake these changes. The most likely source of such an incentive are opportunities to participate in new or expanding markets for low-carbon transportation fuels. As noted at the beginning of this paper, a number of these markets are now taking shape outside of the United States.

Finally, in the HEHC scenario refineries achieve an emissions reduction of 4021 g CO₂e/MMBtu by contracting with farmers to grow corn using low-emissions technologies and practices. The practices considered in this scenario are currently available and in use to some degree. Again, given an appropriate incentive, refineries could use such contracts to reduce ethanol's current GHG profile. Subtracting 4021 g CO₂e/MMBtu from the current emissions levels of a 'representative' refinery results in an emissions profile 43.1% lower than that of gasoline. For natural gas-powered refineries, the emissions reduction would be 46.7%.

Conclusions

This paper assesses the current greenhouse gas profile of US corn ethanol and two projected emissions profiles for 2022. The starting point is the GHG life-cycle analysis done by the US Environmental Protection Agency in 2010 for US corn ethanol as part of its Regulatory Impact Analysis (RIA) for the Revised Renewable Fuel Standard (RFS2). In the RIA, EPA projected that in 2022, the life-cycle emissions associated with ethanol would be 21% lower than those of an energy-equivalent quantity of gasoline.

We assess each of the 11 emissions categories in the 2010 EPA LCA in light of new data, technical papers, research studies and other information that have become available since 2010. Aggregated across the 11 categories, we find US corn ethanol is developing along an emissions pathway significantly lower than what EPA projected in 2010. Our analysis indicates the current GHG profile of US corn ethanol is, on average, 39% lower than that of gasoline. For natural gas-powered refineries, this value is

almost 43% lower. Finally, current trends in the ethanol industry and actions refineries could take to reduce emissions offer opportunities to lower the GHG profile of corn ethanol to between 47.0 and 70.0% relative to gasoline.

Our analysis is timely because many countries (e.g. Colombia, Japan, Brazil, Canada and the European Union) are now developing or revising their renewable energy policies. These policies typically require biofuel substitutes for gasoline to reduce GHG emissions by more than 21%. Our results could help position US corn ethanol to compete in these new and growing markets.

Notes

1. The US gasoline supply consists of gasolines imported from many foreign regions and gasolines refined domestically from petroleum extracted from numerous domestic and foreign regions. The gasoline assessed in the RIA is a composite product constructed to represent the 'average' gasoline consumed in the United States in 2005 [1, section 2.5].
2. To help readers quickly compare the methods of the RIA and our study, Appendix Table A1 identifies key differences in data, models, emission factors and other information used in the two studies by emissions source category.
3. To make our results familiar to a wider set of people in other disciplines, Appendix Table A2 presents emissions by source category for the RIA and our three scenarios in both g CO₂e/MMBtu and g CO₂e/MJ.
4. The regional breakdown, in acres, is in Rosenfeld et al. [5; table 2-6, p. 18].
5. ARMS is an annual survey that collects data on the financial condition, production practices, and resource use for US farms. Each ARMS samples about 5000 fields and 30,000 farms that are representative of that year's surveyed commodities.
6. For example, in Appalachia, 95.2% of acres apply nitrogen (N) and the average application rate is 173.01 kg/ha. Multiplying the adoption rate by the application rate gives an effective N application rate across the region of 164.70 kg/ha.
7. Our approach allows us to clearly distinguish between new acres brought into corn production due to increases in ethanol production, acres leaving corn production due to increases in supply of distiller grains and solubles, and the GHG impacts related to each set of acres (i.e. changes in emissions related to changes in farm input use and changes in soil carbon). Additionally, our approach allows us to account for the increase in average corn yields per hectare since 2010.
8. This table is reproduced in Rosenfeld et al. [5, p. 82].
9. MOVES estimates emissions for mobile sources covering a broad range of pollutants, and allows multiple-scale analysis.
10. The term 'sustainably produced biomass' abstracts from several emissions-related issues that could accompany a large-scale increase in the use of biomass as a process fuel by ethanol refineries. For example, LUC and farm input emissions could change if large areas of land are shifted into energy crop production. The nature and GHG intensity of feedstock production geared to supply large quantities of biomass to the ethanol industry would likely vary by region, and even by refinery location. While an analysis is beyond the scope of this paper, we acknowledge that our HEHC scenario is likely a relatively low-emissions case.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Appendix Table A1. Summary of Key Data Sources and Models Used in the Regulatory Impact Analysis (RIA) Life Cycle Analysis and the Current Greenhouse Gas (GHG) Profile.

Source category	RIA [1]	Current GHG profile
General – Global warming potentials (GWPs)	Second Assessment Report (1996) <ul style="list-style-type: none"> • Methane: 21 • Nitrous oxide: 310 	Fourth Assessment Report (2007) <ul style="list-style-type: none"> • Methane: 25 • Nitrous oxide: 298
Domestic farm inputs and fertilizer Nitrous Oxide (N ₂ O)	<ul style="list-style-type: none"> • Fertilizer application rates and fuel Consumption: Forestry and Agricultural Sectoral Optimization Model (FASOM version 2010) • Fertilizer and fuel production Emission factors: The Greenhouse Gas, Regulated Emissions, and Energy Use in Transportation Model (GREET) version 2009 • Fertilizer use emission factors: Daily Century (DAYCENT) Model (version 2010) 	<ul style="list-style-type: none"> • Fertilizer application rates: [6] • Fuel consumption: [7] • Fertilizer and fuel production emission factors: GREET (version) 2015 • Fertilizer use emission factors:[10] • Animal feed co-product credit: GREET (version 2015)
Domestic land use	<ul style="list-style-type: none"> • Acres: FASOM (version 2010) • Emission factors: DAYCENT Model (version 2010) 	<ul style="list-style-type: none"> • Acres: [12] • Emission rates: Century and Cole Models (version 2015)
Domestic rice methane	<ul style="list-style-type: none"> • Acres: FASOM (version 2010) • Emission factors: [19] 	<ul style="list-style-type: none"> • Acres: same as [1] • Emission factors: [21]
Domestic livestock	<ul style="list-style-type: none"> • Change in livestock populations: FASOM (version 2010) • Emission factors: [19] 	<ul style="list-style-type: none"> • Change in livestock populations: same as [1] except poultry • Livestock conventional feed emission Factors: [21] • Emission reductions from Distillers Grains with Solubles as feed: GREET (version 2015)
International livestock	<ul style="list-style-type: none"> • Populations: Food and Agriculture Policy Research Institute-Center for Agricultural and Rural Development (FAPRI-CARD) (version 2010) • Emission Factors: [10] 	<ul style="list-style-type: none"> • Populations: same as [1] • Emission factors: [10] except for Canada (2016) with a country-specific update
International land-use change	<ul style="list-style-type: none"> • Acres: FAPRI-CARD (version 2010) • Emission factors: Winrock International (2009) 	<ul style="list-style-type: none"> • Acres: [12]; in two scenarios, acres adjusted with data in [17] • Emission factors: Winrock International (2009), Woods Hole (2010) and California Air Resources Board (CARB) Agricultural - Ecological Zones (AEZ) (2015)

(continued)

Appendix Table A1. Continued.

Source category	RIA [1]	Current GHG profile
International farm inputs and fertilizer N ₂ O	<ul style="list-style-type: none"> • Acres and production: FAPRI-CARD (version 2010) • Fertilizer application rates: [30] and [31, version 2009] • Fuel use: [34] • Fertilizer and fuel production emission factors: GREET (version 2009) • Fertilizer use emission factors: Methodology similar to domestic 	<ul style="list-style-type: none"> • Acres and production: [12] • Fertilizer application rates: [31, version 2015] • Fuel use: same as [1] • Fertilizer and fuel production emission Factors: GREET (version 2015) • Fertilizer use emission factors: [10]
International rice methane	<ul style="list-style-type: none"> • Acres: FAPRI-CARD (2010) • Emission factors: [10] 	<ul style="list-style-type: none"> • Acres: same as [1] • Emission factors: same as [1]
Fuel and feedstock transport	<ul style="list-style-type: none"> • Transport distances: GREET (version 2009) • Emission factors: GREET (version 2009) 	<ul style="list-style-type: none"> • Transport distances: GREET (version 2015) • Emission factors: GREET (version 2015)
Fuel production	<ul style="list-style-type: none"> • Process energy: GREET (version 2009) • Emission factors: GREET (version 2009) 	<ul style="list-style-type: none"> • Process energy: GREET (version 2015) • Emission factors: GREET (version 2015)
Tailpipe	<ul style="list-style-type: none"> • Emissions: [39] 	<ul style="list-style-type: none"> • Emissions: GREET (version 2015)

Appendix Table A2. Emissions by scenario and category.

Emissions category	Estimated Greenhouse Gas (GHG) emissions (in grams carbon dioxide equivalent per million British thermal units)			
	RIA (2010)	Current	2022 BAU	2022 HEHC
Domestic farm inputs	10,313	9065	8190	4490
Domestic Land Use Change	-4000	-2038	-2038	-2359
Domestic rice methane	-209	-1013	-1013	-1013
Domestic livestock	-3746	-2463	-2463	-2463
International Land Use Change	31,790	9094	9094	9094
International farm inputs	6601	2217	2217	2217
International rice methane	2089	2482	2482	2482
International livestock	3458	3894	3894	3894
Fuel and feedstock transport	4265	3432	2641	1237
Fuel production	28,000	34,518	31,006	9695
Tailpipe	880	578	578	578
Total	79,441	59,766	54,588	27,852
	Estimated GHG emissions (in grams carbon dioxide equivalent per Mega Joule)			
Domestic farm inputs	9.77	8.59	7.76	4.26
Domestic Land Use Change	-3.79	-1.93	-1.93	-2.24
Domestic rice methane	-0.20	-0.96	-0.96	-0.96
Domestic livestock	-3.55	-2.33	-2.33	-2.33
International Land Use Change	30.13	8.62	8.62	8.62
International farm inputs	6.26	2.10	2.10	2.10
International rice methane	1.98	2.35	2.35	2.35
International livestock	3.28	3.69	3.69	3.69
Fuel and feedstock transport	4.04	3.25	2.50	1.17
Fuel production	26.54	32.72	29.39	9.19
Tailpipe	0.83	0.55	0.55	0.55
Total	75.30	56.65	51.74	26.40

USDA Factsheet: Lifecycle Greenhouse Gas Emissions of Corn-Based Ethanol

Background

The 2018 USDA and ICF report, titled *“A Life-Cycle Analysis of the Greenhouse Gas Emissions from Corn-Based Ethanol,”* finds that GHG emissions associated with producing corn-based ethanol in the United States are, on average, **39 percent lower than gasoline** when measured on an energy equivalent basis. Unlike previous studies of GHG benefits, which relied on forecasts of future ethanol production systems and expected impacts on the farm sector, this study reviewed how the industry and farm sectors have performed over the past decade to assess the current GHG profile of corn-based ethanol.

The report shows that the reductions in GHG emissions resulted from a variety of improvements in the total ethanol supply chain. Farmers are producing corn more efficiently and using conservation practices that reduce GHG emissions, including reduced tillage, cover crops, and improved nitrogen management. Both corn yields and the efficiency of ethanol production technologies are also improving. Additionally, previous estimates of ethanol’s GHG balance report lower efficiencies, largely due to anticipated conversion of grasslands and forests to commodity production as a result of increased demand for corn used in ethanol production. However, recent studies of international agricultural land-use trends show that since 2004, the primary land-use change response of the world’s farmers to rising commodity prices has been to use available cropland more intensely rather than to bring new land into production.

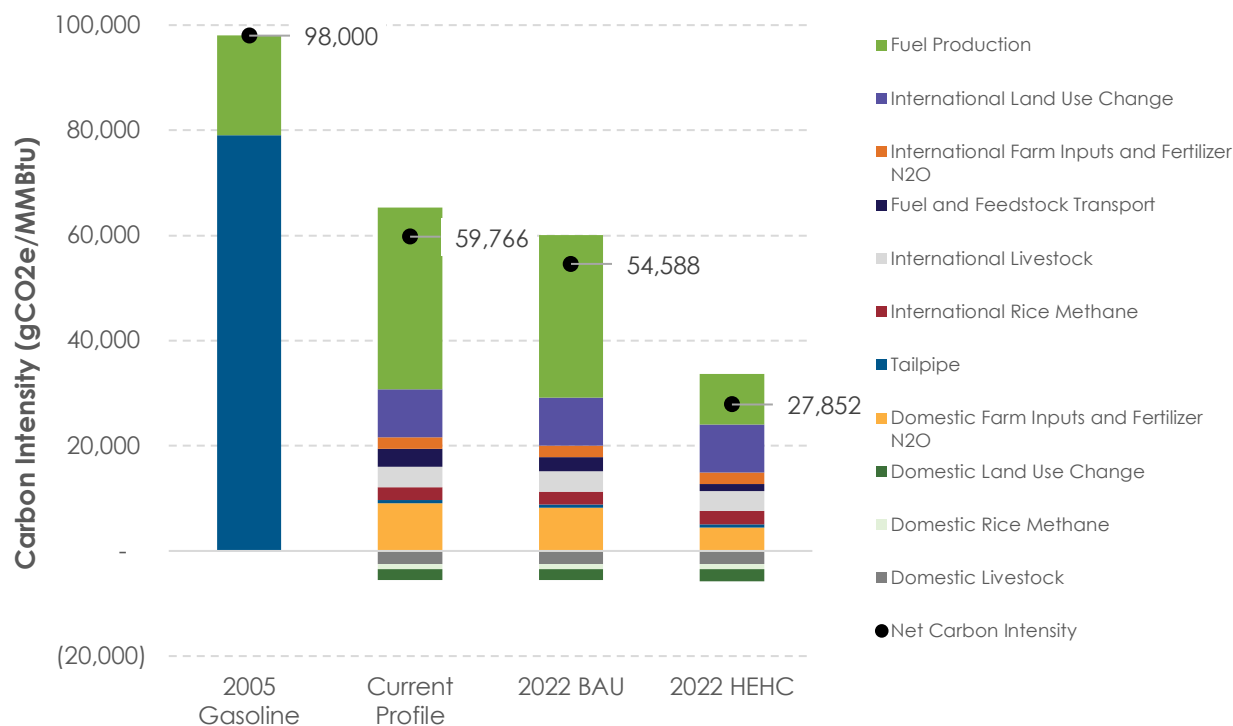
Ethanol GHG Balance Highlights

- Between 2005 and 2015, corn ethanol production in the United States increased from **3.9 to 14.8 billion gallons per year**.
- The current LCA value for corn ethanol produced in an “average” plant is 39 percent lower than gasoline. The value for ethanol refined at a **natural gas powered plant is 43 percent lower**.
- Given current trends, **by 2022 the LCA emissions for corn ethanol will be 44.3 lower** than gasoline.
- If refineries take steps to reduce emissions, by 2022 the LCA emissions for corn ethanol could be over **70 percent** lower than gasoline.
- Refineries can reduce LCA emissions **7 percent** by contracting with farmers to grow corn using low GHG-emitting practices (e.g., reduced tillage, cover crops, and nitrogen management).
- Ethanol produced in refineries powered by natural gas and that also contract with farmers to use low-emitting production practice has an LCA value **47 percent lower than gasoline**.

Carbon Intensity of Corn Ethanol under Different Scenarios

The chart below shows the GHG balance of gasoline (in 2005) compared to three emissions scenarios developed in the newly released ICF report. Specifically, the current lifecycle GHG balance of corn ethanol, the projected corn ethanol LCA GHG emissions in 2022 based on current trends (2022 BAU), and the projected corn ethanol LCA GHG emissions in 2022 assuming refineries adopt specific GHG-reducing technologies and practices (2022 HEHC).

Full Life-Cycle Emissions for Gasoline and ICF Corn Ethanol Scenario



Notes on Revisions to the January 2017 Report

The 2018 report updates a similarly titled ICF report that USDA released in January of 2017. The January 2017 report received considerable attention from entities in the ethanol industry, the larger renewable fuels sector, and among private sector and non-profit organizations with interests in ethanol and renewable fuels. A number of stakeholders commented on various aspects of the 2017 report. In reviewing the comments, USDA and ICF concluded there was a methodological error in the computation of GHG emissions associated with the domestic and international rice source categories. Domestic and international rice are relatively small emissions source categories in corn ethanol's GHG profile and correcting the methodological error did not significantly alter the results in the 2017 ICF report. However, in the interests of transparency and in conveying the most accurate information, USDA felt it important to provide the correct calculations. Additionally, the comments identified a number of errors in the report's text. The revised 2018 report both addresses these errors, and updates the rice source categories.

Air Pollution from Gasoline Powered Vehicles and the Potential Benefits of Ethanol Blending

A Review of Particulate, Nitrogen Oxide, and
Volatile Organic Compound Pollution

Sadaf Sobhani

Energy Future Coalition
United Nations Foundation


October 2016

Introduction

Each gallon of hydrocarbon-rich petroleum fuel that is used to power vehicles today produces nearly 20 pounds of carbon dioxide (CO₂), resulting in the annual emission of over 1.5 billion metric tons of CO₂, or roughly 1/3 of the total greenhouse gas emissions in the United States [1]. Efforts to curb climate change effects and reduce the greenhouse gas emissions from the transportation sector have resulted in stricter Corporate Average Fuel Economy Standards (CAFE) and policies such as the Renewable Fuel Standard (RFS) to develop alternative fuels. In addition to CO₂ emissions and its global warming effects, the concerns regarding vehicle emissions include toxic compounds such as carbon monoxide (CO) and nitrogen oxides (NO_x), which have significant epidemiological and environmental consequences. Control of hydrocarbons and CO first began in California in 1966, followed by standards set by the federal government in 1968. The 1970 amendment to the Clean Air Act (CAA) tightened the initial emissions standards and added NO_x as the third major pollutant emitted by vehicle engines [2]. Under the current CAA, the U.S. Environmental Protection Agency (EPA) is required to set standards for six principal air pollutants: ozone, particulate matter, lead, CO, nitrogen dioxide and sulfur dioxide. Airborne pollutants, including both primary tailpipe emissions (e.g. CO) as well as secondary chemical species formed via atmospheric reactions (e.g. ozone), can travel into the respiratory system and through the human body, causing potentially chronic health effects. Ambient and indoor air pollution result in over 5 million deaths a year, globally. In 2013, air pollution was the 4th highest ranking risk factor for death in the world [3]. Although exhaust emissions regulation in the last 50 years has resulted in significantly lower concentrations of toxic airborne pollutants in the United States, an estimated 9,320 deaths in 2013 were attributed to air pollution exceeding the American Thoracic Society (ATS) recommended standards [4]. This statistic is comparable to the 10,076 alcohol-related traffic deaths that occurred in that same year, illustrating that air pollution control remains as a highly relevant national public health concern that necessitates strong policies in parallel to those initiated to reduce CO₂ emissions. This report reviews the recent literature on particulate matter, NO_x, and volatile and semi-volatile organic compounds that result in ozone pollution. Emissions from automobiles are directly linked to fuel composition and engine technology, therefore this report also reviews the key concepts in engine performance (e.g. fuel octane rating, fuel injection technique, etc.). Results from numerous scientific studies are presented to show the current understanding of the sources and potential impacts of emissions from automobiles, focusing on the influences of specific gasoline components and ethanol-gasoline blending.

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1. Fundamentals of Fuel Octane Rating

Since the advent of modern automobiles, the spotlight has been mostly focused on one key feature of its operating fuel - the octane rating. This number quantifies a fuel's capacity to resist auto-ignition when compressed. Vehicles with spark-ignition (SI) internal combustion engines, which run on gasoline, comprise over 90% of the U.S. fleet. SI engines operate by first compressing the fuel-air mixture in the combustion chamber and then, at a carefully determined time, igniting that compressed mixture to transfer chemical energy to mechanical energy. If the fuel auto-ignites before the ignition is initiated by the spark plug, the engine experiences knocking, which can have negative performance effects or even damage the engine (Fig. 1.1). Proper functioning of an SI engine relies on high-octane gasoline fuels, since they have higher anti-knock properties. Automakers design the extent of piston compression of their engines to be compatible with current fuel octane standards. An engine's compression ratio (CR) is the proportion of the cylinder volume at the bottom of the piston stroke to the top of the stroke. CR directly correlates to engine efficiency therefore, extending octane ratings beyond the current minimums can enable automakers to produce engines with better performance and fuel economy.

1.1 History of Octane

Two pure compounds with opposite knocking behavior, n-heptane and isooctane (2,2,4-trimethylpentane), were used to establish the octane scale in 1927. As the name implies, isooctane has superior anti-knock properties and was assigned an octane rating of 100, while n-heptane was assigned a 0 rating. Gasoline and other fuel blends are tested for knock and compared to various mixtures of n-heptane and isooctane. A sample is assigned an octane rating corresponding to the ratio of n-heptane and isooctane required to match its knocking properties. The composition of the mixture that matches the observed knocking of the sample is assigned as the octane rating of that fuel [5]. The Research Octane Number (RON) tests the fuel performance under standard conditions, whereas the Motor Octane Number (MON) simulates more severe operation representative of conditions at high-load or speed. The average of a fuel's RON and MON is referred to as its Anti-Knock Index (AKI). Figure 1.2 shows the trend in fuel AKI, and illustrates the correlation between the rating and engine CR.

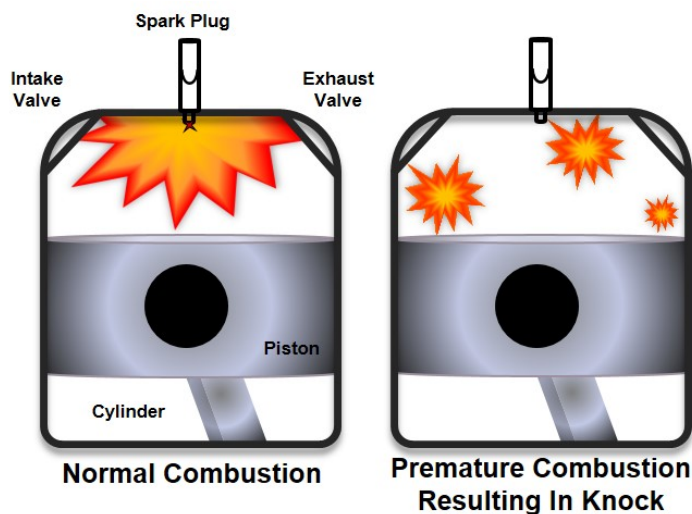


Figure 1.1: Cartoon of internal combustion engine. Under normal operation, the spark plug initiates the propagation of a premixed flame in the combustion chamber. Premature combustion caused by low-octane fuel results in uneven burning, which reduces the power output and can damage valves, pistons, and other engine components.

Today, the AKI federal standard for regular grade gasoline is 87.

Anti-knock agents, also called octane enhancers, are added to gasoline to help meet these federal standards. One of the most widely used octane enhancer for many years was tetra-ethyl-lead (TEL), which at approximately 3 $\frac{3}{4}$ gal gives a 10- to 15-point increase in AKI. As observed in Figure 1.2, lead compounds were phased out of gasoline beginning in 1975. Lead deposits damage the vehicle's catalytic converter, motivating the transition to unleaded gasoline, which increases engine life by as much as 150 % [6]. Lead is also highly toxic for humans; therefore, the transition was both economically and epidemiologically advantageous.

Octane enhancers, such as methyl t-butyl ether (MTBE), were first developed to replace lead. MTBE has both a high AKI rating and causes minimal corrosion to the engine and other parts. However, when gasoline containing MTBE leaks from underground storage tanks, it contaminates the groundwater, resulting in an unpleasant taste and odor in drinking water. This led to limitations on MTBE blending in gasoline, and in certain areas of the country, a total ban on its use. Today, refiners have focused their attention on petroleum refining and blending techniques to increase the concentrations of high-octane hydrocarbons in their gasoline.

1.2 Gasoline Composition

The crude oil that is pumped out of the ground is a complex mixture of several thousand organic compounds. These compounds include:

- straight-chain alkanes (paraffins),
- cycloalkanes (naphthenes),
- aromatic hydrocarbons (aromatics),
- alkenes (olefins).

These are natural constituents of crude oil, but can also be produced in various refining operations.

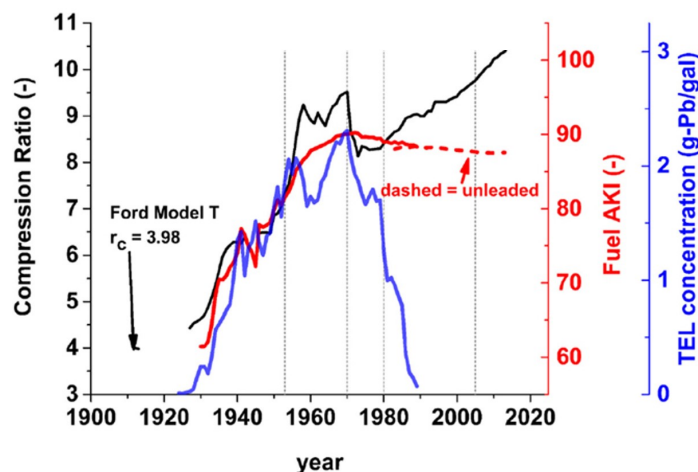


Figure 1.2: Averaged trends in compression ratio (black), fuel AKI (red), and fuel TEL concentration (blue) for the U.S. as a function of year. Plot adapted from Splitter et al. [7].

Techniques such as catalytic cracking and reforming are used to convert lower-demand components to high-demand products or to high-octane streams. By molecular rearrangement or dehydrogenation, catalytic reforming converts low-octane, heavy naphthas into aromatic hydrocarbons, which are added to gasoline components known as reformates. Alkylation and isomerization are also used to convert low-octane straight-chain paraffins to higher-octane branched paraffins, called alkylate, used in premium gasoline blending stocks for its exceptional anti-knock quality.

Some of these solutions have created public health problems of their own. For example, the increased use of benzene and other aromatics has led to concerns over human exposure to known carcinogens. Furthermore, aromatics are known to form polycyclic aromatic hydrocarbons (PAHs), which are precursors to soot and contribute to secondary organic aerosol (SOA) formation. Studies estimate that approximately 3,800 premature mortalities nationwide are due to the aromatics content of gasoline [8]. These health factors, along with an effort to lower the cost of refining, have increased interest in the use of alternative, low-cost, octane boosting oxygenates such as ethanol with RON = 109 [9].

1.3 Ethanol as an Octane Enhancer

Nearly all gasoline in the U.S. now contains 10% ethanol, by volume, sold as E10 [10]. The processes for producing E10 are similar to that of conventional gasoline, although the minimum AKI rating is no longer achieved with refining techniques alone. Refiners deliver a sub-octane fuel (AKI = 84) known as the Blendstock for Oxygenate Blending (BOB) to fuel terminals, where ethanol is blended into the fuel, raising the AKI rating by 2-3 points to meet the standard for regular grade gasoline. The advantageous properties of ethanol have sparked interest in raising the volume beyond 10% to achieve even higher octane rated fuels.

Scientists are actively researching the potential of biofuels in transportation, supporting governmental initiatives to reduce dependence on petroleum-based fuels and lower carbon emissions. Their studies give insights into the consequences of current and proposed ethanol blends not only on the octane rating, but also on emissions of greenhouse gases, particulates, and other toxic pollutants. Research shows that ethanol-gasoline blends have improved combustion processes due to

the oxygen content in ethanol. When compared to E0, ethanol-gasoline blends produce less exhaust emissions [11–17] along with PAH and soot emissions [18, 19]. Ethanol blends reduce combustion temperatures, which discourages nitric oxide production. Furthermore, these blends have faster flame speeds than pure gasoline, enabling complete combustion of the fuel. A review of the literature highlights a general reduction of engine out emissions and a positive effect of alcohol content on thermal efficiency.

Ethanol has been linked to higher evaporative emissions due to its volatility properties. Reid vapor pressure (RVP) and distillation profile of ethanol-gasoline blends are greatly affected by non-ideal mixture behavior. This behavior is a consequence of molecular interactions between the gasoline components and ethanol. Despite the fact that ethanol has a lower RVP than gasoline, blending 10% vol ethanol into gasoline increases the total RVP by about 6 kPa. In ethanol-gasoline blends, the nonpolar hydrocarbon molecules in gasoline interfere with the intermolecular hydrogen bonding between the polar ethanol molecules, and similarly do the ethanol molecules interfere with the hydrocarbons. These interferences with intermolecular bonding allow both types of molecules to more readily escape the liquid as vapor, which is manifested as increased vapor pressures and reduced distillation temperatures. The highest RVP of 68 kPa is observed when 10% vol ethanol is added to the gasoline, followed by a near plateau up to 20% vol. As ethanol content is increased above about 20% vol, RVP of the blend begins to decrease, and above 50% vol ethanol, the RVP becomes less than that of the gasoline [20]. Careful consideration of RVP is an important criteria for controlling evaporative emissions.

High-octane ethanol blends can also enable further engine downsizing and higher CR. Splitter and Szybist [21] demonstrated that E30 fuel improves anti-knock tendencies and high torque capability at stoichiometric conditions. Celik [12] showed that the power obtained from E50 fuel is 29% higher at CR of 10/1 compared to E0 at CR of 6/1. These studies and reviews of alcohol-gasoline blending [22–25] suggest that mid-level alcohol blends can increase vehicle efficiency, in addition to certain emissions advantages. High-octane fuels are essential to the proper functioning of current internal combustion engines and to the potential for future innovations in engine design. Many anti-knock agents that help boost the octane rating of gasoline have significant negative consequences on public health and the environment. Increasing the volume of ethanol blending in gasoline is one potential means to achieve higher octane fuels without the side effects of lead, MTBE, and aromatic hydrocarbons. Furthermore, ethanol blends have been shown to reduce emissions of other harmful pollutants, as discussed in the following chapters.



2. Particulate Pollution

Air pollution exists in both particle and gas phases. Unlike gases, which have defined chemical structures and specific physical properties, particulate matter (PM) come in all shapes and sizes (Fig. 2.1). PM, released from both anthropogenic and natural origins, also vary in their impact on public health and the environment. Once the liquid or solid particles become suspended in the atmosphere, often referred to as aerosols, they can travel into the respiratory system and blood stream, transporting toxic compounds and disrupting normal cell functions. From an environmental standpoint, they are able to scatter and absorb sunlight, which translates to a direct influence on the earth's temperature, climate, and air visibility. Control of PM emissions has developed as one of the main functions of air pollution control agencies. Unlike biogenic PM that can originate from mechanical processes such as sea spray or volcanic activity, anthropogenic PM mainly arises from gas-to-particle chemical conversion and condensation. Therefore, analysis of the composition, origins, and formation mechanisms of anthropogenic PM is a field of active research. Human-made aerosols, which are found in higher concentrations in urban areas, are mainly composed of a carbonaceous nucleus and substances absorbed on its surface, such as polycyclic aromatic hydrocarbons (PAHs), metals, sulfates, and nitrates. Exhaust from the tailpipe of motor vehicles contributes significantly to particulate pollution, since it contains a complex mixture of hundreds of chemicals in the form of precursor gases, as well as particulate carbon. A better understanding of the relationship between fuel composition and exhaust composition can help motivate both technological innovations and policies that enable cleaner energy sources for transportation, particularly relevant for renewable fuel initiatives.

2.1 Health Impact

The size distribution of aerosols is trimodal, including coarse, fine, and ultrafine particles. Coarse particles consist primarily of suspended dust, soil, volcano ash, sea salts, and pollen particles. Fine particles have smaller diameters, generally only a few microns (one-thirtieth the width of a human hair), and are mainly derived from direct emissions of gasoline and diesel engines, coal burning, and industrial processes involving combustion. Ultrafine particles have even smaller diameters, typically less than or equal to 100 nm, but can rapidly grow through coagulation and condensation

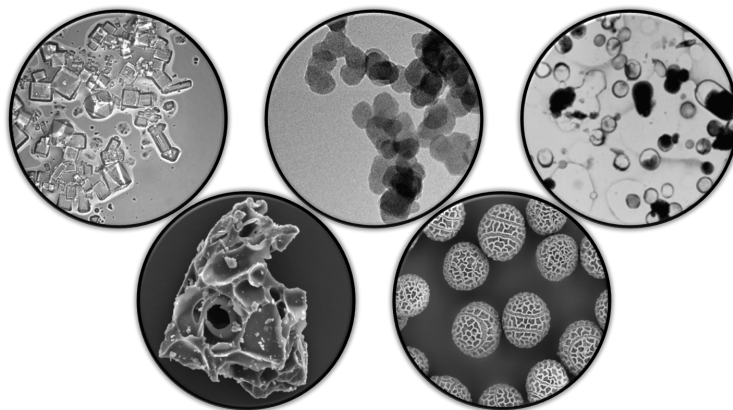


Figure 2.1: Electron microscope images of biogenic and anthropogenic PM, with the approximate dimension of each particle: sea salt (Chere Petty/Univ of Maryland, $\sim 15\mu\text{m}$), soot aggregates (Saffaripour et al. 2015, $\sim 0.5\mu\text{m}$), ammonium sulfate (Casuccio et al. 2002, $\sim 0.5\mu\text{m}$), volcanic ash (Tom Kircher/AVO/UAF-GI, $\sim 50\mu\text{m}$), pollen (Dartmouth E. M. Facility, $\sim 50\mu\text{m}$).

to form larger aggregates, therefore significantly contributing to fine particle exposure as well [26]. Similar to their larger counterparts, ultrafine particles are derived from combustion-related sources, and their emissions depend on specific fuel and engine properties. Once airborne, particles can enter human airways, attach onto surfaces in the respiratory tract and dissolve in body fluids, passing their chemical molecules into the bloodstream and circulating throughout the body. With their small size, fine and ultrafine particles can be breathed more deeply into the lungs and remain suspended for longer periods of time [26]. Public health policy is primarily concerned with the regulation of fine PM, comprised of sulfates, nitrates, ammonium, organic aerosols, and elemental carbon. The main effects associated with exposure to fine PM (referred to as $\text{PM}_{2.5}$) are premature mortality, aggravation of cardiovascular disease, aggravated asthma, acute respiratory symptoms and chronic bronchitis [27]. Nearly 200,000 premature deaths per year in the U.S. are attributed to $\text{PM}_{2.5}$ emissions [28], and the World Health Organization (WHO) estimates 3 million worldwide annual deaths caused by particulate pollution [29]. In 2012, the EPA lowered the primary annual fine particulate standard from $15\mu\text{g}/\text{m}^3$ to $12\mu\text{g}/\text{m}^3$ in an effort to combat these health effects.

2.2 Primary and Secondary Particulate Pollution

PM emissions from automobiles are directly linked to fuel composition and engine technology and are categorized as primary and secondary forms. The emissions that are already particulates at the tailpipe are referred to as primary PM, and those that form from the oxidation of gaseous precursors are secondary PM. The primary form of PM from automobiles, commonly referred to as soot, is composed of both elemental carbon (EC) and organic carbon (OC). EC has a chemical structure similar to graphite and is often interchanged with the term black carbon (BC). The strongest light-absorbing component of soot is BC, which can change the reflectivity of the Earth's surface when it lands on snow. For instance, the accumulation of black carbon aerosols in the Arctic and Himalaya is leading to increased melting of snow and consequent climate change effects [30]. As one of the most prevalent anthropogenic aerosols, soot not only affects global climate but also atmospheric visibility and human health.

In addition to the primary mode, OC can also be emitted as a result of condensation of low vapor

pressure gases onto existing aerosols. Secondary organic aerosols (SOAs) are formed as species such as hydroxyl radicals (OH) oxidize hydrocarbon molecules emitted from combustion. Vehicles typically emit a mixture of hundreds of gases, some of which are SOA precursors, such as single-ring monocyclic aromatics like toluene and xylene [31]. Furthermore, they can emit heavy PAHs, which can rapidly condense onto particles once emitted into the atmosphere, resulting in a higher proportion of these PAHs in smaller, respirable size particles [32]. Research has shown that the SOA fraction of fine organic PM can dominate over the primary organic aerosol fraction in certain areas [31].

Vehicle technology can also impact PM emissions. For instance, new technologies such as the gasoline direct injection (GDI) engines are shown to produce higher particulate emissions than conventional port fuel injection (PFI) engines. GDI engines improve the fuel efficiency of PFI engines by eliminating the throttle that controls the intake air flow into the engine, instead directly injecting the fuel into the cylinder per cycle. GDI-equipped vehicles are being rapidly integrated into the vehicle fleet, from less than 5% in MY2009 to 46% in MY2015 [33]. Although this technique increases efficiency, combustion of locally fuel-rich (Section 3.2) regions in the cylinder results in higher PM emissions [34]. Traditionally, PM emissions have been a concern for diesel engines, but new technologies in gasoline vehicles, along with better understanding of SOA production from gaseous precursors, are widening the focus of this field to both diesel- and gasoline-powered cars.

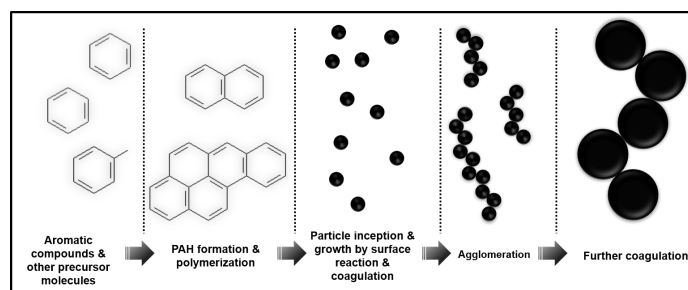


Figure 2.2: A growth mechanism for the formation of particulate carbon, or soot, from coalescence of PAHs.

2.3 The Role of Aromatics

Gasoline is a mixture of several hundred compounds, with varying concentrations based on the sample, including paraffins, olefins, and aromatics. The exact composition of gasoline varies widely, depending on the base crude oil and the refinery processes available, along with product demand and specifications. Aromatic hydrocarbons exhibit high anti-knock properties and can be blended in large volumes to boost the octane value of gasoline. Since the phasing out of toxic octane enhancers such as lead, refiners have used increasing volumes of aromatics to meet anti-knock requirements. Aromatics can be monocyclic, such as benzene and toluene, or polycyclic, such as naphthalene. Exposure to monocyclic aromatics such as benzene is linked to development of leukemia and lymphoma [35]. Several PAHs, found in fuels or produced during combustion, are also toxic and carcinogenic. Although the metabolic activation of PAHs in the body can vary among compounds, they generally convert to oxides and diol epoxides, which are the principal toxic metabolites involved in DNA replication and repair [36].

In addition to their inherent toxicity, PAHs are thought to be the molecular precursors to soot. Although most of the emitted PAHs are formed in the combustion process, higher fuel aromatic content does increase PAH emissions [37]. As shown in Figure 2.2, single-ring aromatics such as benzene can form into PAHs, which then coalesce into nascent soot particles. The growth

process from small molecules such as benzene to larger PAHs involves interaction and recombination reactions among the compounds of the fuel [38]. Although the first aromatic ring may be produced from non-aromatic species [39], higher concentrations of single-ring aromatics in the fuel have been shown to result in higher soot emissions [8]. Additionally, increasing PM emissions are accompanied by increasing PAH emission, of both gaseous and particulate-bound forms [37]. Pandis et al. [40] predicted that approximately 65% of SOAs result from the oxidation of aromatics, 15% from alkanes and 4% from olefins. These predictions are in agreement with that of Grosjean and Seinfeld [41], who also estimated SOA production resulting mostly from aromatics oxidation (58% for aromatics, 21% for alkanes, and 11% for olefins).

Numerous studies have been done to relate aromatic concentration to pollutant formation. Karavalakis et al. [8] studied the effects of aromatics in gasoline on both gaseous and PM emissions in PFI and GDI engines. This study was done on a fleet of seven light-duty gasoline vehicles and three gasoline fuel blends with 15%, 25% and 35% aromatics content, by volume. Their results showed a significant increase in emissions of CO, PM mass and number, and BC with increasing aromatics content for all seven vehicles. This and several other studies [37, 42, 43] illustrate that PM emissions increase with higher aromatic content in gasoline; however, there is currently no effective federal limit on aromatics content in gasoline. California has set limits for reformulated gasoline phase 3 of 25% vol for aromatics. Both the EPA and the California Air Resources Board (CARB) have classified benzene as a human carcinogen, with the federal limit of the percentage of benzene allowed in gasoline set to an average of 0.62% vol.

2.4 Effect of Ethanol Blending

Ethanol has superior anti-knock properties to gasoline, and is currently blended with a sub-octane blendstock to increase the octane rating and produce E10 fuel. Over 90% of gasoline in the U.S. is now blended with ethanol, which has instigated a surge of research and investigation into the efficiency and emissions implications of ethanol-gasoline blending. Storey et al. [19] compared PM emissions of both lean and stoichiometric GDI engines operated with E0, E10, and E20. Between E0 and E10, a 29% reduction of PM mass emissions was shown in the stoichiometric engine and a 42% reduction in the lean operating vehicles, both under the Federal Test Procedure 75 (FTP). Costagliola et al. [44] showed a 30–95% reduction of the number of particulates emitted for ethanol blends ranging from E10–E85. This suggests that the inclusion of more ethanol in the gasoline supply has a potential mitigating effect on PM emissions [18]. In addition to reducing the particle mass and number concentration, ethanol content in the fuel changes the composition of emitted particles. Dutcher et al. [45] showed that BC and particle-bound PAH concentrations decreased with ethanol content, with the greatest drop resulting from the change from E0 to E20. Therefore, ethanol-fuel blending may result in fewer emitted carcinogenic and light-absorbing particles (Fig. 2.3).

The Department of Energy, in collaboration with the EPA, also conducted a study in 2009 to assess the effects of fuel property changes on vehicle emissions. 27 fuels were tested in a fleet of 15 high-sales cars and light trucks from the 2008 model year over the LA92 cycle at 75°F. Four Flexible Fuel Vehicles in the test fleet were also tested on E85 fuel. The data and analysis on emissions properties were published in 2015 [46, 47]. The conclusion with respect to automobile PM emissions was that the most important factor increasing PM emissions is aromatic content, followed by temperature at 90% vol distilled (T90). These findings are in line with previous studies and theoretical combustion science of emission production, since aromatics are known soot precursors. The study also found that ethanol negatively impacted PM, which is a highly controversial and debated result. They attributed this behavior to ethanol's high heat of vaporization, compared to

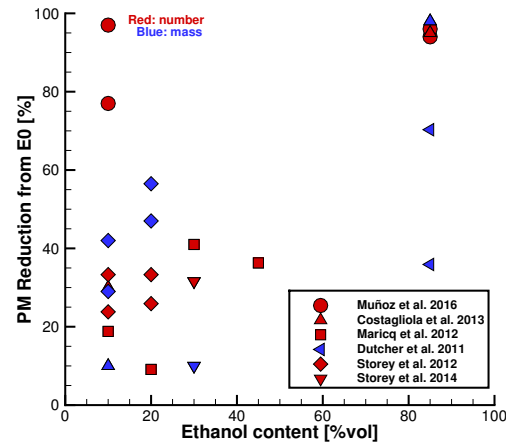


Figure 2.3: Studies showing emissions reductions of various ethanol blend concentrations compared to zero ethanol blends E0, based on total mass or number of particles.

the other hydrocarbons in the fuel. A high heat of vaporization results in lower temperatures after evaporation, making high boiling point aromatics even less likely to evaporate and mix with the air. This results in the production of more PM than would otherwise form without ethanol.

These studies shed light on the complexity of controlling fuel composition for emissions regulation. Clearly, the chemical properties of the base gasoline will affect the properties of the final fuel after blending with ethanol [48]. Although many studies have shown the beneficial effects of ethanol blending on fuel PM emissions, high levels of aromatics in the base mixture can cause conflicting results. A successful regulatory approach may be to control the total aromatic content in the base gasoline mixture, specifically limiting high-boiling point aromatics that contribute to soot formation. Ethanol can also be blended in higher volumes in gasoline to decrease gaseous and particulate emissions and further decrease the relative concentration of aromatics.

3. Nitrogen Oxide Pollution

Nitrogen oxide (NO_x) emissions consist of nitric oxides (NO) and nitrogen dioxides (NO_2). At high temperatures, characteristic of the combustion chamber of engines, nitrogen molecules in air react with oxygen to form NO gas. NO_2 is predominantly formed from the reaction of NO and peroxy radicals, but is rapidly converted back to NO at high-temperature environments containing an abundance of H and O radicals. Much of the NO gas emitted from the tailpipe is oxidized to NO_2 in the atmosphere, therefore exposure to NO_x is often represented by NO_2 concentrations.

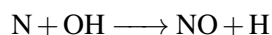
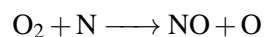
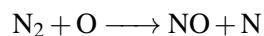
NO_2 is a highly toxic gas that can trigger cell damage and inflammatory processes in the respiratory system [49]. Secondly, ultraviolet radiation from the sun drives the chemical reactions between NO_x and other pollutants, producing ground-level ozone, or smog, which can also trigger serious respiratory problems. In the presence of sulfur dioxide, NO_x react to form acids that fall to the earth with rain, snow, or fog. Acidic droplets can damage forests and vegetation, and disturb the habitats of freshwater organisms. The federal annual mean standard for concentrations of NO_2 in the air, as set by the National Ambient Air Quality Standards (NAAQS), is 0.053 parts per million (ppm). The California standard is set to 0.030 ppm.

Due to the health and environmental consequences of NO_x pollution, regulation of these compounds remain as a major obligation of air quality agencies. In 2015, Volkswagen admitted that 11 million of its vehicles produced NO_x emissions nearly 40 times the permissible levels, resulting in one of the largest consumer class-action settlements in U.S. history. Although this case related to diesel cars, which produce higher amounts of NO_x than gasoline cars, it signifies the importance and relevance of continued NO_x regulation among the U.S. fleet and a continued effort to develop new technologies and fuel-blends which help curb emissions.

3.1 Formation Pathways

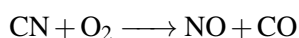
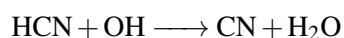
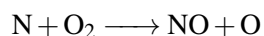
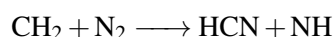
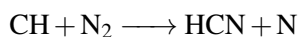
The nitrogen atoms in the formation of NO_x primarily come from the nitrogen in air, which is composed of 78% N_2 . The nitrogen atoms in some fuels (e.g. coal) can also contribute to NO_x emissions, but this is not relevant for most transportation fuels. NO can be formed via a number of reaction mechanisms, the two most significant being thermal and prompt NO formation:

- Thermal NO : This mechanism for NO formation is considered relevant at temperatures above 1,800K where the strong N_2 bond can be broken to initiate the following series of reactions:



This mechanism is the dominant source of NO in fuel-lean and stoichiometric conditions (Section 3.2) [50].

- Prompt NO : This mechanism is responsible for the formation of NO in the colder part of the flame and becomes significant under fuel-rich conditions, since it requires a high concentrations of the hydrocarbon radical species to initiate the sequence of reactions. These reactions first produce cyanonitrene (NCN) and hydrogen cyanide (HCN), which undergo further reactions to form NO [15]:



3.2 Ratio of Air to Fuel

An important operating condition of an engine is the air-fuel ratio, λ . For any combustion process, both fuel and oxidizer are required for a chemical reaction. If the exact right amount of air is supplied to burn off all of the fuel, this proportion of air to fuel is referred to as stoichiometric ($\lambda = 1$). If there is not enough air to burn all of the fuel, the mixture is called fuel-rich ($\lambda < 1$). Lastly, if there is excess air, the mixture is called fuel-lean ($\lambda > 1$). For gasoline, the stoichiometric air-fuel ratio is 14.7. Figure 3.1 shows the emissions associated with each combustion regime.

At higher loads, engines often operate at rich conditions for maximum power. The higher flame speed of ethanol helps in achieving complete combustion for rich mixtures. Most SI engines are designed to operate at stoichiometric or lean conditions and to minimize fuel enrichment, except during short periods of high-load (e.g. acceleration).

The various operating conditions of the engine have respective NO_x emissions. However, these values of NO_x are all well within the capacity of three-way catalytic converters, which convert NO to N_2 in order to meet regulatory standards. He et al. [13] report both engine-out and tailpipe emissions, and showed that catalytic conversion decreases NO_x emissions by up to a factor of 200 (Fig. 3.2b). With a properly functioning three-way catalytic converter, NO_x emissions are typically below 1ppm [51]. Techniques and fuel blends designed to lower engine-out NO_x can reduce the load on the catalytic converter and potentially enable lighter and less expensive catalysts.

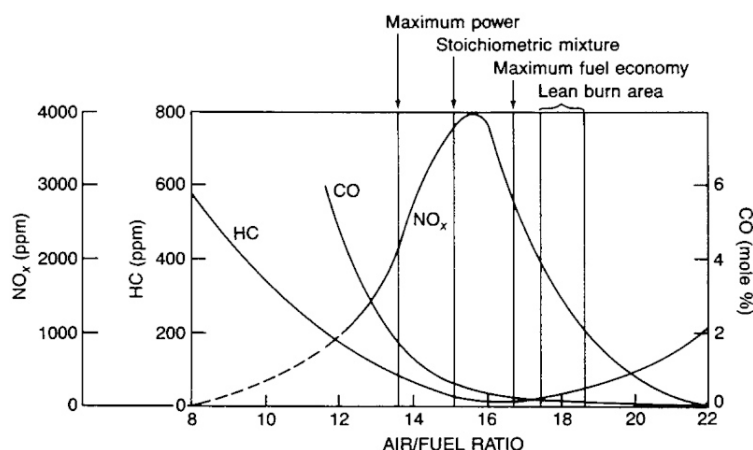


Figure 3.1: Concentrations of HC, CO, and NO_x emissions as a function of air-fuel ratio in a typical gasoline engine. Stoichiometric mixture ($\lambda = 1$) corresponds to an air/fuel ratio of 14.7 [9].

3.3 Effect of Ethanol Blending

Efforts to better characterize the chemical interactions between hydrocarbons, alcohols, and existing engine technologies have resulted in numerous scientific research publications on this subject. These researchers not only investigate the fundamental properties of ethanol-gasoline blends, but also study the effect of different blend concentrations on engine efficiency, greenhouse gas emissions, particulate pollution, and economic cost. There is a sensitivity of emissions testing to engine technology (i.e. direct injection vs. port-fuel injection), operating conditions (i.e. air-fuel ratio λ), mixing of fuel and oxidizer in the combustion chamber, and base-gasoline composition before it is blended with ethanol. Despite the complexity of this subject, key insights into the nature of ethanol-gasoline blends have been developed.

As outlined, the formation of NO is often dependent on high gas temperatures via the thermal NO mechanism. One strategy for reducing NO is to reduce the burned gas temperature. Ethanol blending is shown to be an effective way to reduce the burned gas temperature and consequently NO formation. This behavior is a direct consequence of two key properties of ethanol-gasoline blends. First, ethanol has a higher heat of vaporization than gasoline, which translates to lower compressed gas temperatures during the compression stroke (i.e. charge cooling). This difference in temperature is further increased in the expansion stroke post ignition, which leads to the second key property of ethanol combustion – lower adiabatic flame temperatures, or peak temperatures. Charge cooling and lower temperatures post combustion decrease NO production.

The blended fuel chemical structure also reduces prompt NO formation. This reaction mechanism depends on the presence of hydrocarbon radical species (HC). Alcohols, such as ethanol, are organic compounds in which the hydroxyl functional group (-OH) is bound to a carbon atom. In alcohol flames, the presences of the hydroxyl functional groups act to reduce the level of hydrocarbons produced in the flame, thereby lowering NO formation through the prompt route [22]. Furthermore, the higher flame speed of ethanol-gasoline blends compared to pure gasoline decreases the residence time of the mixture within the prompt-formation region of the flame. Therefore, ethanol blends fundamentally produce less NO_x at the same air-fuel ratio than pure gasoline. Some studies show conflicting results (i.e. increase of NO_x with ethanol blending) [52], illustrating the inherent complexity in these studies created by the wide flexibility in operating parameters and by engine-

specific complications. Furthermore, since ethanol is an oxygenated fuel, during high-load fuel-rich operation, it also effectively increases λ towards stoichiometric conditions where adiabatic flame temperatures are higher. Although this is advantageous for complete combustion of the fuel and enhances the efficiency of the engine, it may increase NO_x emissions compared to the fuel-rich conditions of pure gasoline [53] (Fig. 3.1).

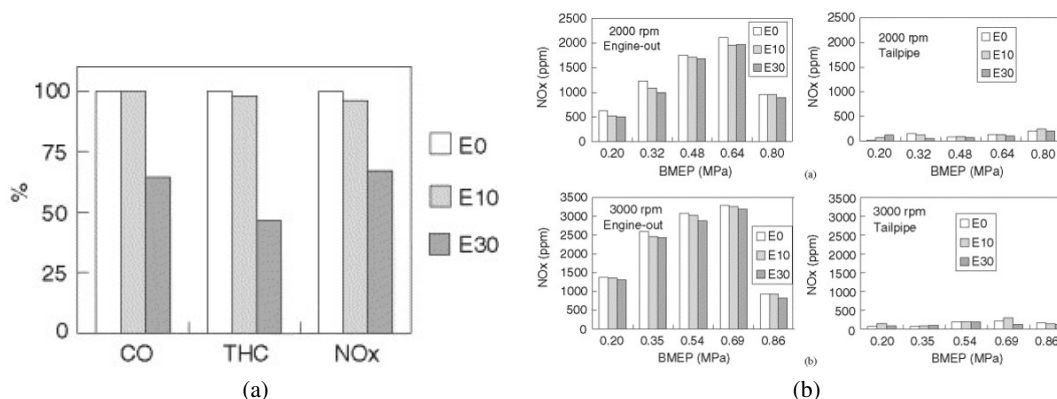


Figure 3.2: (a) Engine-out emissions at idle speed, relative to E0. Plot shows relative emissions versus brake mean effective pressure (BMEP). (b) Ethanol does decrease engine-out NO_x emissions, but tailpipe emissions are similar, due to the catalytic converter. Plot shows emission in parts per million (ppm) versus BMEP [13].

Numerous studies have experimentally investigated the effects of ethanol blending on emissions. Compared to E0, Jung et al. [14] reported a 25% - 45% decrease in NO_x for E85, Canakci et al. [11] reported an 11% decrease for E5 and 15.5% for E10, He et al. [13] reported up to 33% decrease for E30, Celik [12] reported a 33% decrease for E50, and Nakata et al. [16] reported a 25% decrease for E50 and 40% decrease for E100. These studies were performed on common engines such as those in the Toyota Corolla and Honda Civic, and reflect nearly constant load and speed conditions for stoichiometrically operated engines ($\lambda = 1$). Vertin et al. [17] studied the effects of ethanol blending on long-term emissions. For four of the six models tested, the vehicles aged on E0 fuel had higher exhaust emissions compared to vehicles aged on E15 or E20 fuel. The 2009 Honda Odyssey aged using E0 fuel had higher CO and NO_x emissions at 120,000 miles compared to the vehicles aged on E20 with 95% confidence. NO_x emissions from the 2009 Ford Focus aged using E0 fuel were higher than that those of E15 at 90,000 miles and E20 at 120,000 miles.

Overall, the effects of ethanol blending are advantageous both for short and long-term NO_x emissions. Catalytic converters today are designed to transform toxic engine-out NO_x emissions, along with other pollutants, to their non-toxic counterparts. Although alcohol-fuel blends inherently enhance the combustion process and reduce NO_x emissions by roughly 30% for mid-level blends, a properly functioning catalytic converter will absorb changes of this scale along with other fluctuations in transient engine operation.



4. Volatile Organic Compound Pollution

Air pollution results from the interaction between emissions and weather. To mitigate the public health consequences of pollution, air quality agencies work to set and enforce emission standards for the most toxic pollutants. It is also important to understand and acknowledge the complex chemistry and interdependence of these pollutants as they react in the atmosphere according to external conditions. For instance, in addition to their inherent toxicity, certain vehicle emissions can react with each other or with biogenic compounds to form secondary pollutants. Organic compounds in the atmosphere are partitioned between gases and aerosols, depending on their vapor pressures and chemical properties. Mostly, organic compounds that have low vapor pressures ($<10^{-11}$ atm) at ambient temperatures exist as aerosols and those with high vapor pressures ($>10^{-5}$ atm) exist in the gas-phase, often termed volatile organic compounds (VOCs) [54]. Essentially, VOCs refer to a large set of compounds that are able to evaporate easily. Aromatics constitute 20-30% of total VOCs in the urban atmosphere [55]. Compounds with intermediate vapor pressures are known as semi-volatile organic compounds (SVOCs). VOCs and SVOCs include pollutants of major concern to public health, such as benzene, toluene, ethylbenzene, xylene, and polycyclic aromatic hydrocarbons (PAHs). Furthermore, they contribute to the formation of ozone and secondary organic aerosols (SOAs).

Almost all of the weather on Earth occurs at the lowest layer of the atmosphere, known as the troposphere. Starting at Earth's surface and spanning up to 20 km above sea level, the troposphere holds nearly 80% of the mass of the atmosphere, comprised of air and water molecules. In this layer are also hundreds of thousands of organic compounds, originating from both biogenic and anthropogenic sources. The chemistry of the urban atmosphere differs from that of the natural troposphere due to the high concentrations of industrial and vehicle emissions such as nitrogen oxides and organic compounds. On a global scale, emissions of VOCs from vegetation are much greater than those from anthropogenic sources [54]. However, in urban areas, vehicular emissions contribute significantly to atmospheric VOC concentrations. Long-range transport strongly influences observed concentrations of ozone and ozone precursors. For example, studies at the west coast of

North America identified the influence of Asian emissions on ozone, hydrocarbons, nitrates, and sulfur concentrations [56].

4.1 Health Concerns and Regulation

Toxic and carcinogenic compounds such as PAHs are SVOCs emitted from vehicle engines and other combustion processes. The World Health Organization (WHO) has classified the PAH Benzo(a)pyrene as a human carcinogen, and numerous other PAHs as probable human carcinogens. PAHs can metabolize to form oxides and diol epoxides, the principal toxic metabolite involved in DNA replication and repair [36]. Exposure to VOCs such as benzene is linked to development of leukemia and lymphoma [35]. Surface ozone is produced by the reaction of VOCs and nitrogen oxides (NO_x) under the influence of sunlight [57, 58]. Ozone is the main component of smog, which can reduce lung function, aggravate asthma and emphysema, and lead to a wide range of respiratory symptoms [59].

Prior to 1966, vehicle manufacturers were not required to meet any exhaust emissions standards, both at the state and federal levels. As concern grew regarding the public health effects of direct and indirect pollution from automobiles, policies emerged to limit emission of the most toxic compounds. Today, the federal standards for Tier 3 vehicles are 4.2 g/mi CO and 0.05 g/mi total NO_x and non-methane hydrocarbon emissions [60]. Prior to emissions control in 1966, unregulated vehicles emitted about 10 g/mi hydrocarbons, 4 g/mi NO_x , and 80 g/mi CO [2]. In California, VOC emissions have decreased by nearly 50 times in the last 50 years (average of 7.5% a year) while fuel usage has tripled in that time [61]. Development of catalytic converters and air pumps that improve combustion efficiency have enabled these tremendous emission cuts. However, the significant health consequences of air pollution today motivate regulatory agencies and automakers to continue to seek innovative solutions to further decrease harmful emissions.

4.2 Ozone Formation

Ozone (O_3) is produced in the atmosphere from the chemical reaction between atomic and molecular oxygen, and any third body molecule (M) such as N_2 . In the troposphere, the oxygen atom required for this reaction is produced from the photo-dissociation of NO_2 to NO, which rapidly reacts with ozone to regenerate NO_2 :



In this reaction path, one ozone molecule is required to regenerate NO_2 , therefore there is a balance between produced and consumed ozone molecules. However, in the presence of hydrocarbons, NO_2 production can circumvent reaction 4.3, and result in the accumulation of ozone. Reaction between the hydroxyl radical (OH) and hydrocarbons generates peroxy radicals (RO_2 , where R is an alkyl group). RO_2 reacts with NO to form NO_2 , which is how the balance between produced and consumed ozone molecules is disrupted and begins to shift towards ozone accumulation.

Reducing anthropogenic VOC and NO_x emissions has been the main method of controlling ground-level ozone in the U.S. It is important to note that although ground-level ozone in the troposphere has harmful effects and requires control, ozone in the upper atmosphere (stratosphere) is beneficial in shielding the planet from excess ultraviolet light.

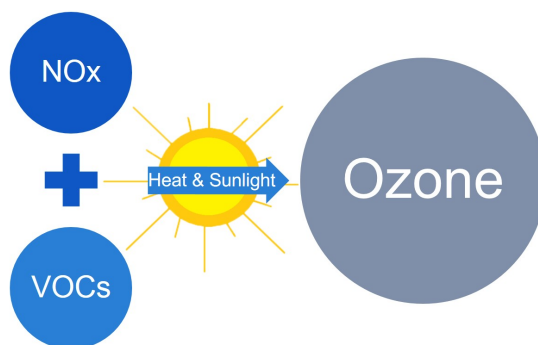


Figure 4.1: Ground-level ozone is not emitted directly into the air, but is formed by photochemical oxidation of NO_x and VOCs, which are emitted from industrial facilities and vehicle exhaust.

4.3 Effect of Ethanol Blending

Costagliola et al. [44] showed a 30–70% reduction in PAH emissions for ethanol blends, and a 50% reduction of benzene and 1,3-butadiene emissions with E85, compared to E0. Hsieh et al. [62] found a 20–80% reduction of hydrocarbon emissions with increasing ethanol content from 5% to 30% vol, compared to pure gasoline. Similarly, Koç et al. [23] found close to 20% and 30% hydrocarbon reductions with E50 and E85 blends. Muñoz et al. [51] concluded that blending of gasoline with ethanol substantially reduced PAH emissions in GDI vehicles. With E10, mean emissions of 2-, 3-, 4-, 5-, and 6-ring PAHs decreased by 67, 77, 74, 88, and 96%. Furthermore, with E85, mean emissions of these PAHs reduced by 85, 82, 91, and 97%. Their research is especially significant due to the recent rapid replacement of PFI vehicles with GDI, which produces more particulates and other harmful emissions. They conclude that pollution consequences from this transition can partly be compensated with ethanol blending, which suppresses particulate and PAH formation. As with particulates, the blending of ethanol in gasoline reduces harmful pollutants resulting from incomplete combustion and lowers the concentration of carcinogenic compounds both in the input fuel and output emissions.



5. Conclusion

Air pollution is a major public health concern, and policy measures are needed to help mitigate its impact from the transportation sector, specially in urban areas. Pollutants derived from vehicular exhaust are not only harmful at a local level, but become airborne and transport their toxic effects more broadly. Furthermore, interactions of PM, NO_x, and VOC emissions with atmospheric factors and other compounds in the air make emissions control a challenging research and regulatory problem.

Clear scientific evidence show that higher concentrations of aromatic hydrocarbons in gasoline result in increased gaseous and particulate pollution. Aromatics, often blended in high concentrations to boost the anti-knock property of the fuel, are found to be precursors of soot. Several monocyclic and polycyclic aromatic hydrocarbons are themselves known carcinogens. Ethanol can also be blended in higher volumes in fuel to decrease gaseous and particulate organic emissions, while also being advantageous both for short and long-term NO_x emissions. Alcohol fuel blends such as mid-level ethanol blends are shown to reduce NO_x production by roughly 30%. When blended into gasoline, ethanol increases the octane rating of the fuel enabling higher efficiency engines and is shown to decrease the emissions of several harmful pollutants.

Emissions from automobiles have a tremendous impact on public health and the environment. The wide scope of impact on both human health and the environment, along with the diverse origins and dispersion qualities of pollution, requires the expertise and collaboration of scientists, medical professionals, and policy makers in order to identify the appropriate mitigation plans. Furthermore, controlling human-made emissions from mobile sources involve automotive manufacturers, oil refiners, and regulatory environmental agencies, who all help to implement the scientific conclusions and policy decisions made to protect public health and the environment.



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