

Health Impact of Corn Ethanol Blends



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Primer: Vehicle Emissions of Toxic Compounds

EPA-420-R-16-016
November 2016

Groups and Derivatives of Hydrocarbons

Formaldehyde;
Acetaldehyde

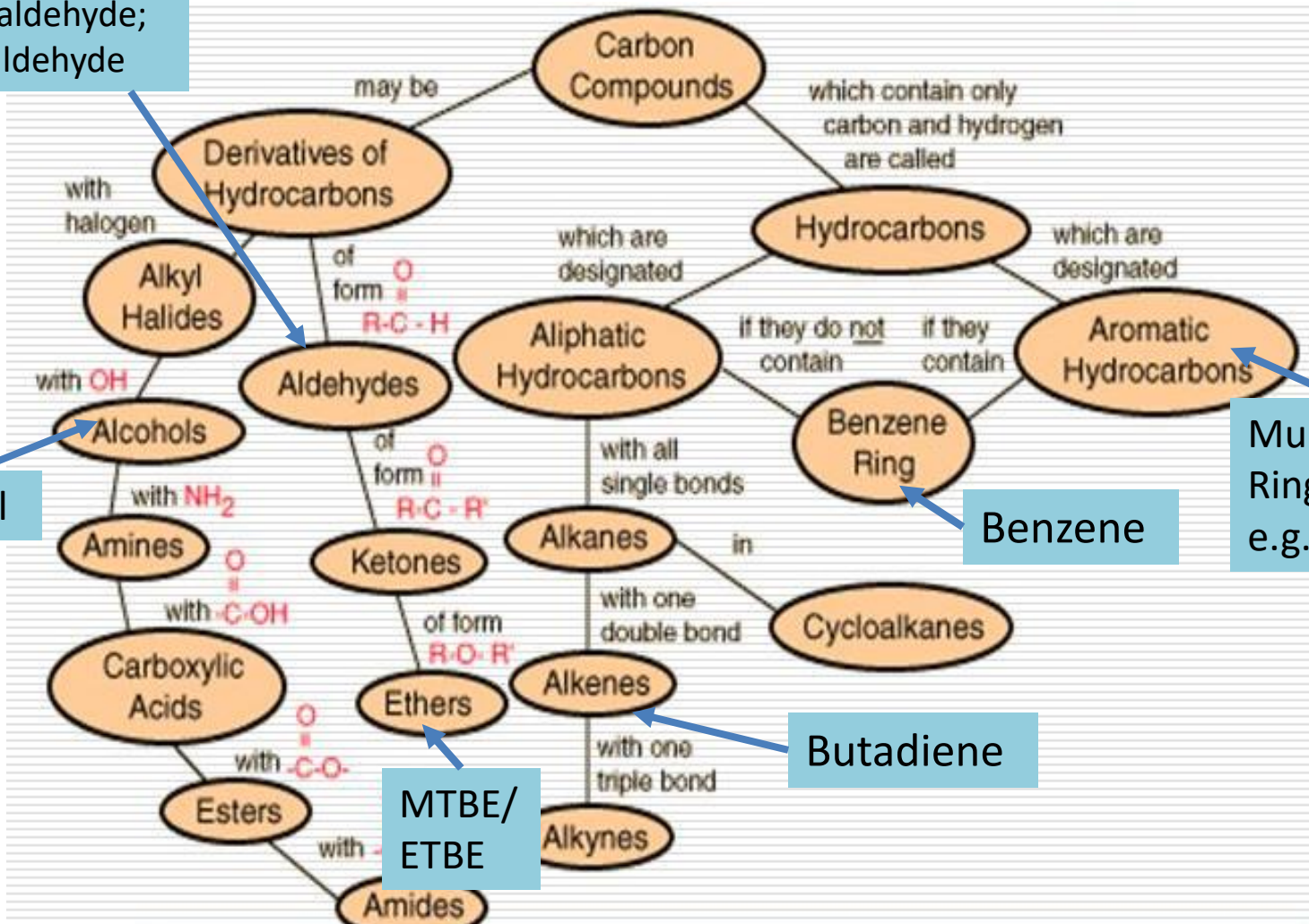
Ethanol

Benzene

Multiple Benzene
Rings = PAHs
e.g. Benzopyrene

MTBE/
ETBE

Butadiene



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

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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

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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).

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 the formation of toxic emissions in a vehicle.

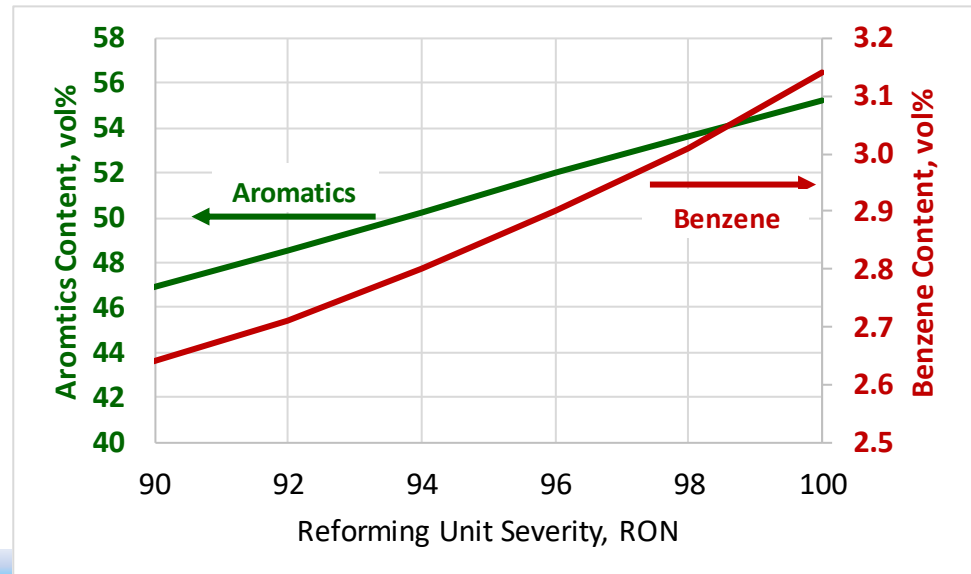


Tailpipe Emissions Reductions from Corn Ethanol

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?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



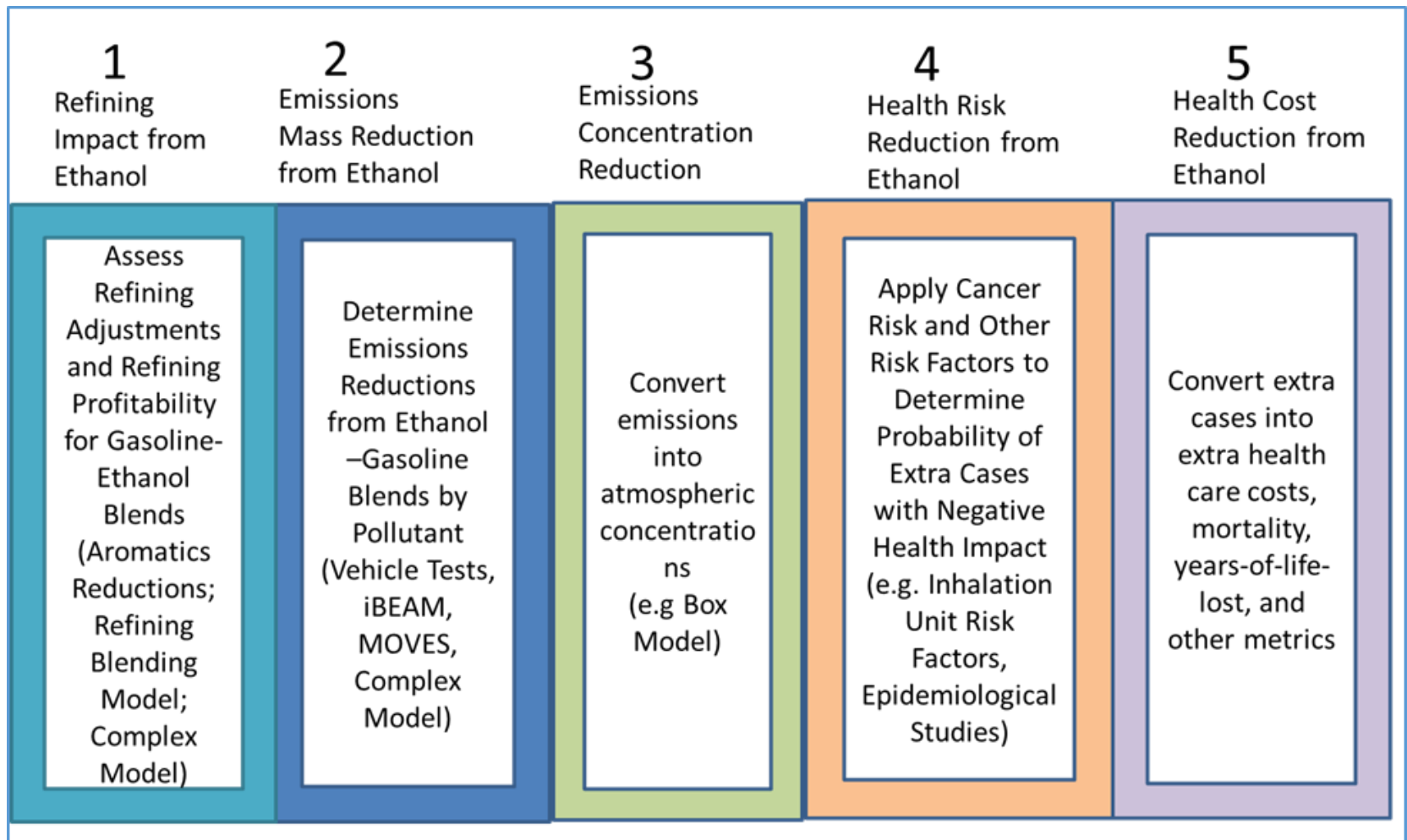
CG= Conventional Gasoline; RFG= Reformulated Gasoline

UIC 5 Cities Study

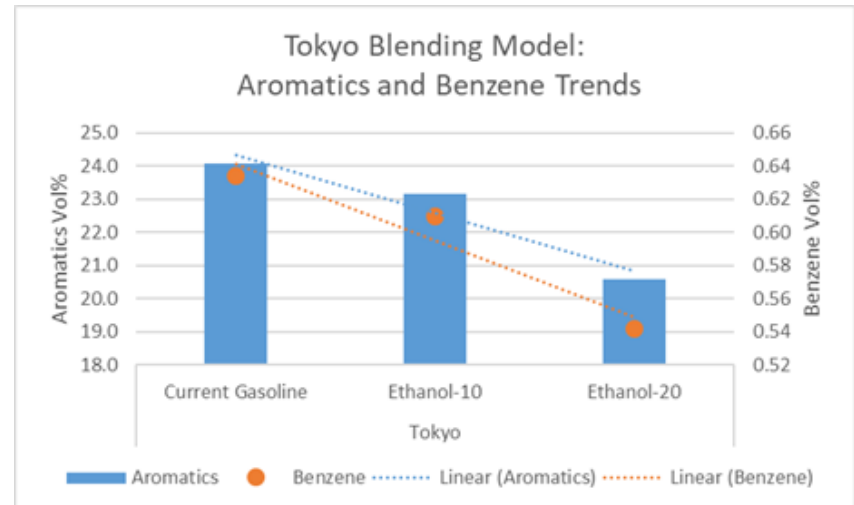
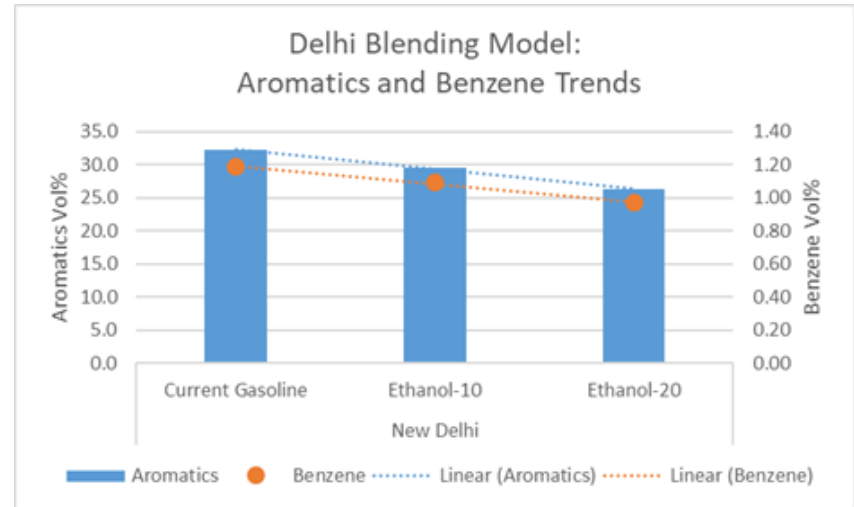
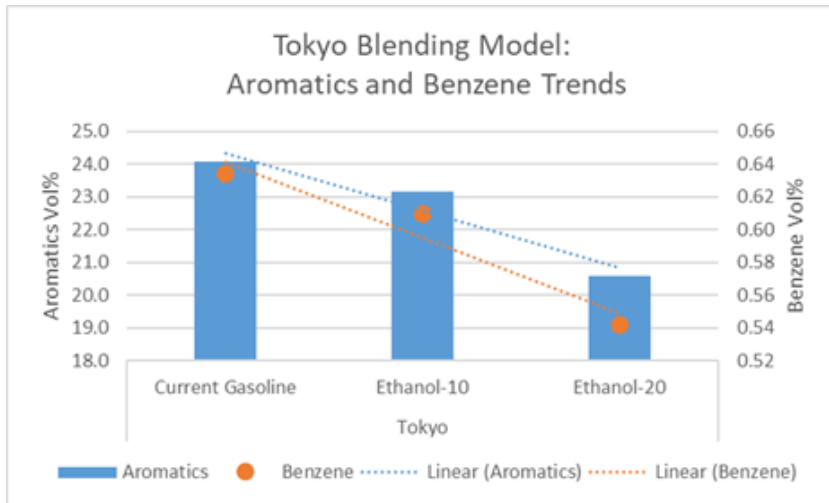
Biofuels Emissions Modeling Study for International Markets

- University of Illinois at Chicago with collaborators developed a spreadsheet based model called International Biofuels Emissions Analysis Model (iBEAM)
- The unique feature of the model/study is that it explores the comprehensive environmental linkages from fuel formulation at the refinery 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.
- Study includes 5 international mega cities

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

International Blending Model

Run: Example New Delhi

- The blending behavior from refiners whereby aromatics are reduced in anticipation of the addition of ethanol was also documented in the present study.
- Table shows the results from a blending model that changes the gasoline recipe based on the addition of ethanol.
- As can be seen the aromatics and benzene content drops with the addition of ethanol and the volume distilled at E200 and E300 increases.



		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 Reductions Literature Summary

		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%	

Legend:

THC = Total Hydrocarbon Emissions

NMHC = Non Methane Hydrocarbons

CO = Carbon Monoxide

NOx = Nitrogen Oxides



5 Cities Study Model Modeled Emissions Reductions

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





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

- 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



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^a 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 (MK1) + oxidizing catalytic converter	Diesel (MK3) without catalytic converter	Diesel (MK1) without catalytic converter
		<i>% of total B[a]P equivalents</i>				
Anthracene	0.0005	0.2	0.4	0.1	0.3	0.1
Benz[<i>a</i>]anthracene	0.005	0.2	0.3	0.1	0.4	^{d,e}
B[<i>a</i>]P	1	77	43	5.3	4.2	7.1 ^d
Benzo[<i>b</i> and <i>k</i>]fluoranthene	0.075	4.4	11	1.6	0.8	0.5 ^d
Benzo[<i>ghi</i>]perylene	0.02	1.4	1.4	0.2	^{d,e}	0.1 ^d
Chrysene/triphenylene	0.03 ^f	1.4	4.3	1.6	0.6	0.4
Fluoranthene	0.05	12	36	88	86	85
Indeno[1,2,3- <i>cd</i>]pyrene	0.1	2.3	1.4	0.5	0.2 ^d	0.7 ^d
Phenanthrene	0.0005	0.5	2.0	1.0	2.8	1.4
Pyrene	0.001	0.3	0.4	1.3	4.4	4.9
Total (µg/km)		8.6	0.7	1.9	4.8	1.4

^aNote 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.





Study Results: Reduction in Cancer Cases with Ethanol Blends

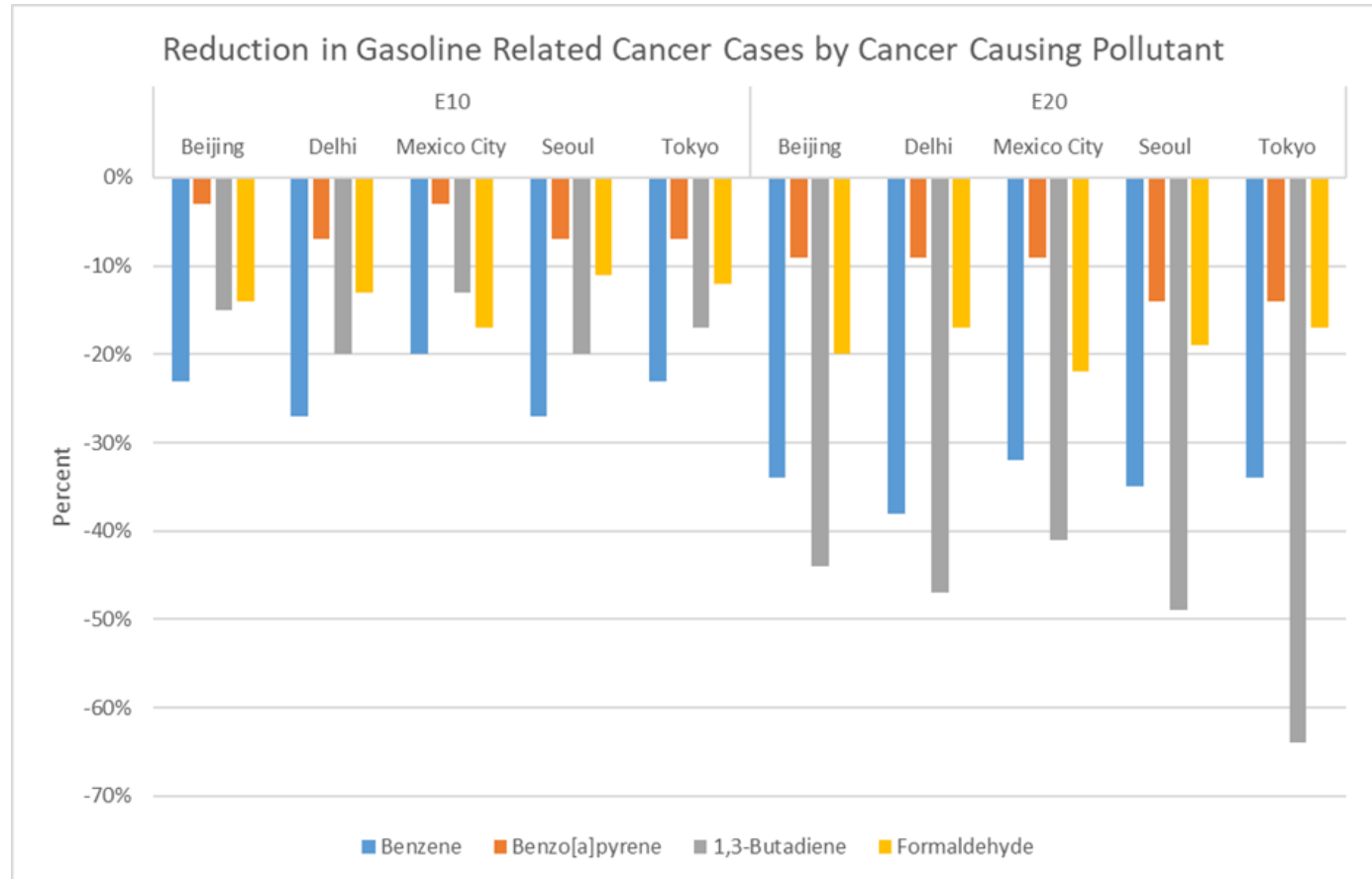
- Air Toxins Cause Increases Cancer Cases
- Ethanol Overall Reduces Cancer Cases from Selected Pollutants. Note slight increase in cancer cases from acetaldehyde is outweighed by significant decreases from other pollutants.

	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

- 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.



Years of Life Lost

- The carcinogenic pollutants considered in this study each cause a variety of cancers, each of which have different prognoses. The table below from cancer.gov citation summarizes the years of potential life lost per patient for the cancers relevant to the pollutants studied

	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





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
- Ethanol Overall Reduces Years of Life Lost and Reduces Economic Damage. Note slight increase in years of life lost from acetaldehyde is outweighed by significant decreases from other pollutants.

	Acetaldehyde	Benzene	Polycyclics/ Benzo[a]pyrene	Butadiene	Formaldehyde	Total	Years of Life Value Saved
E10 Fuel							
Beijing	76	-1,135	-487	-1,667	-48	-3,262	-\$489,246,26
Delhi	57	-1,375	-951	-1,835	-32	-4,136	-\$620,409,00
Mexico City	154	-1,770	-692	-2,431	-138	-4,877	-\$731,507,14
Seoul	43	-488	-641	-1,422	-20	-2,529	-\$379,311,49
Tokyo	40	-566	-676	-1,303	-21	-2,527	-\$379,052,10
E20							
Beijing	200	-1,671	-1,583	-4,894	-67	-8,015	-\$1,202,226,52
Delhi	156	-1,967	-1,357	-4,286	-40	-7,494	-\$1,124,045,01
Mexico City	401	-2,767	-1,521	-7,775	-182	-11,843	-\$1,776,517,78
Seoul	106	-638	-1,259	-3,537	-35	-5,363	-\$804,397,71
Tokyo	106	-828	-1,486	-4,918	-30	-7,155	-\$1,073,306,07



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.

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.

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