### The 5 Cities Study UIC ENGINEERING

THE UNIVERSITY OF ILLINOIS AT CHICAGO

**UIC** 

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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 <u>large amount of aromatic hydrocarbons</u> 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 **<u>substitutes</u>** and **<u>dilutes</u>** aromatics in gasoline.
  - Moreover, ethanol also <u>alters the distillation curve</u> 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 <u>ethanol blended into gasoline</u> the reforming unit severity is adjusted to lower RON numbers, which generally results in <u>lower benzene and aromatics content</u>





#### U.S. Domestic Blending Behavior

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

PA United St Environm Agency	tates nental Prote	ction Co	CG= onventior Gasoline	nal				
	1990	2000		2016 RFG	r	2016 CG	r	
Property	Baseline	RFG Average	CG Average	Average	95%	Average	<b>95</b> %	
Sulfur (ppm)	339	126	324	23.1	48.2	22.5	51.0	1
Benzene (vol%)	1.53	0.59	1.15	0.51	0.86	0.63	1.27	1
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.Z	47.9	54.8	53.0	61.4	w
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	gq
Ethanol (vol%)	0.6	1.14	0.84	9.61	9.97	9.28	9.8	
		+			-		4	4

CG= Conventional Gasoline; RFG= Reformulated Gasoline

#### Groups and Derivatives of Hydrocarbons



# Primer

• Aldehyde:

an organic compound containing the group —CHO, <u>formed by the oxidation of alcohols</u>. Typical\_aldehydes include methanal (formaldehyde) and ethanal (acetaldehyde). Many aldehydes are either gases or volatile liquids.

• Aromatic Hydrocarbons:

Aromatic hydrocarbons are those which <u>contain one or more benzene rings</u>. 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 <u>multiple aromatic rings</u> (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 C4H6. At atmospheric conditions, 1,3-butadiene exists as a colorless gas.

#### <u>Vehicle Emissions</u> 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

d .	Pollutant		
	Benzene		
	Ethanol		
	1,3-Butadiene		
unds	Formaldehyde		
	Acetaldehyde		
	Acrolem		
	Methyl-Tertiary-Butyl Ether (MTBE)		
	2,2,4-Trimethylpentane		
	Ethyl Benzene		
	Hexane		
	Propionaldehyde		
	Styrene		
EPA-420-R-16-016	Toluene		
NUVEINDEI 2010	Xylene(s) <sup>1</sup>		

### Vehicle Emissions of Toxic Compounds

 Polycyclic Aromatic Hydrocarbons (PAHs)

		Pollutant				
IS		Acenaphthene				
		Acenaphthylene				
		Anthracene				
		Benz(a)anthracene				
		Benzo(a)pyrene				
		Denzo(0)Intorantinene				
		Benzo(g,h,i)perylene				
		Benzo(k)fluoranthene				
		Chrysene				
		Dibenzo(a,h)anthracene				
		Fluoranthene				
		Fluorene				
		Indeno(1,2,3,c,d)pyrene				
EDA 400 D 16 0	6	Naphthalene				
November 2016	10	Phenanthrene				
November 2016		Pyrene				

### 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).</li>

## 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



#### • 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 <u>acute myeloid leukemia</u> (acute non-lymphocytic leukemia), and there is limited evidence that benzene may also cause acute and chronic lymphocytic leukemia, <u>non-Hodgkin's lymphoma</u> 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 <u>leukemia</u>." 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 <u>nasal tumors in animals</u> 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): <u>Lung</u>, Gastrointestinal, Respiratory
  - Tumor type(s): <u>Squamous cell neoplasia in the larynx, pharynx, trachea, nasal cavity, esophagus, and forestomach</u>. (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 <sup>3</sup> )	Relative Potency	
Acetaldehyde	2.7 × 10 <sup>-6</sup>	0.002	
Benzene	2.9 × 10 <sup>-5</sup>	0.026	
Benzo[a]pyrene	1.1 × 10 <sup>-3</sup>	1.00	
1,3-Butadiene	1.7 × 10 <sup>-4</sup>	0.155	
Formaldehyde	$6.0  imes 10^{-6}$	0.005	



Source: California Environmental Protection Agency



- 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-Butadier		Formaldehyde			
E10 Fuel								
Beijing	5.2	-79.0	-30.6	-97.9	-3.3			
Delhi	3.9	-95.7	-59.8	-107.8	-2.2			
<b>Mexico</b> 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			
E20 Fuel								
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			



• 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.





- Ethanol fuel blends were estimated to yield a net reduction of approximately <u>200-300 cancers</u> 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 <u>1,3-butadiene to 1 ppm</u> was estimated by OSHA to avoid <u>59 cancers among approximately 9000 exposed</u> <u>workers over a working lifetime of 45 years, or 1.3 cancers per year</u>. 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 <u>reduction in the Permissible Exposure Limit for benzene from</u> <u>10 ppm to 1 ppm was estimated by OSHA to avoid 326 deaths from leukemia</u> <u>and other cancers over 45 years, or 7.2 cancers per year</u>; 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 CO<sub>2</sub> 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 <u>Environmental Protection Agency's Fuel Trend Report shows the link that ethanol</u> <u>reduces aromatics including benzene</u> in fuels which are carcinogenic.
  - Ethanol also reduces other carcinogenic subgroups of volatile organic compounds (butadiene).
  - <u>Ethanol also reduces a group of air toxics called PAHs</u> 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 <u>actual fuel samples</u> 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



### Contact

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