

PM and Benzene in Splash Blended Fuels with Ethanol

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Particulate Matter



Ethanol and Particulate Matter Emissions: Particulate Matter Index (PMI) Model

- The PMI-based predictive model for PM emissions from gasoline fuels was first proposed by Aikawa et al.
- It is based on the observed direct correlation between the weight fraction, vapor pressure, and Double Bond Equivalent (DBE) of gasoline fuel and the production of PM emissions.
- 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.**

Cook County Gasoline Sampling

- ERC sampled several Cook County retail stations (both regular & premium grade gasoline)
 - Splash blended E10 samples to E15, E20, E25, and E30 fractions
 - Analyzed samples for key fuel properties
- Intertek Labs Performed Detailed Hydrocarbon Analysis
- Calculated Particulate Matter Index (PMI)

Cook County Gasoline Sampling

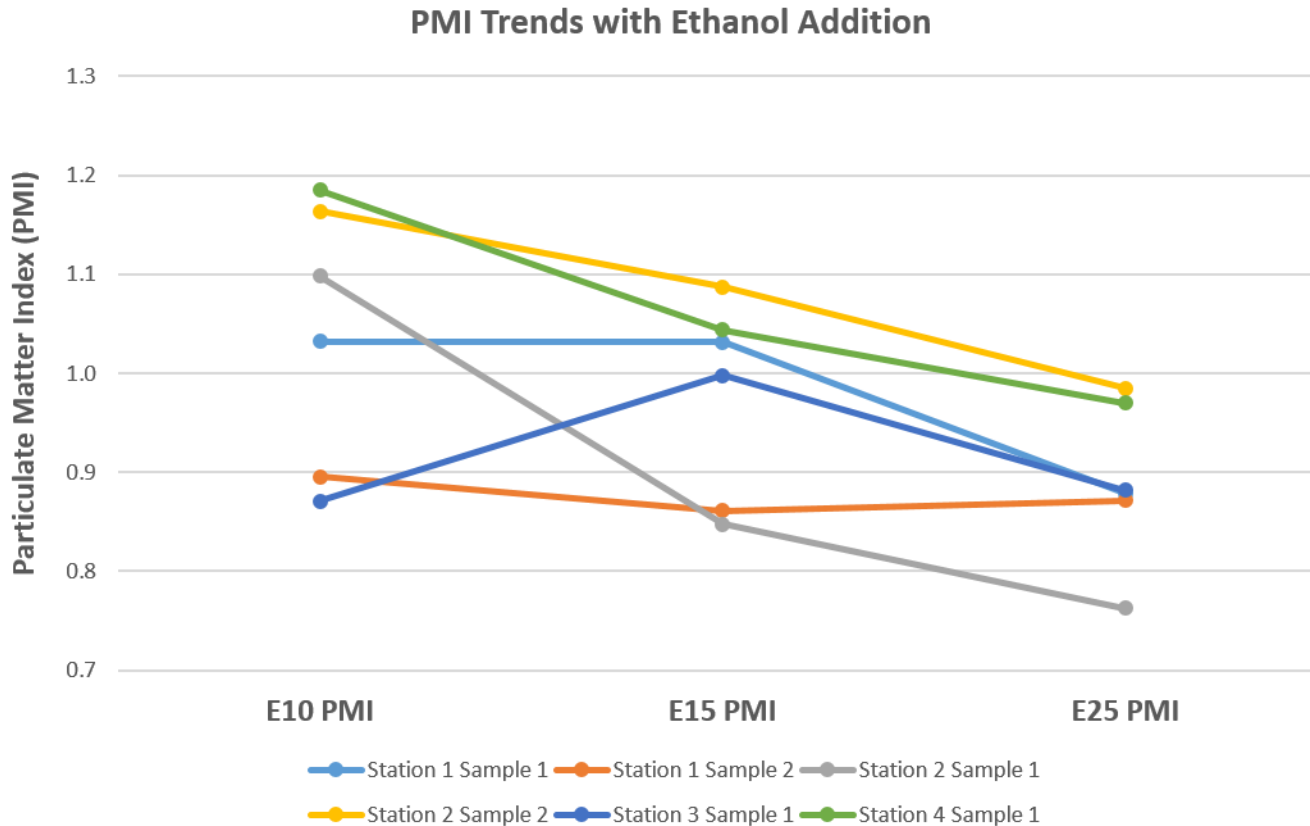
Sample Location	Fuel Grade	E10 (Original Sample)	E15	E20	E25	E30
Station 1 (2 samples)	Premium Gasoline	●	●	●	●	
Station 2 (2 samples)	Regular Gasoline	●	●		●	●
Station 3 (1 sample)	Regular Gasoline	●	●	●	●	●
Station 4 (1 sample)	Regular Gasoline	●	●	●	●	●

Sample Property	Test Method
Detailed Hydrocarbon Analysis, including total aromatic, olefin, and benzene content	ASTM D6730
Aromatics in Gasoline (GCMS)	ASTM D1319 correlated to ASTM D5769
Vapor Pressure (DVPE)	ASTM D5191
Ethanol Content	ASTM D4815
Distillation Curve (IBP, T10, T20, T30, T40, T50, T60, T70, T80, T90, T95, FBP, e200, e300)	ASTM D86
Heating Value (BTU)	ASTM D240
Octane	ASTM D2699 and ASTM D2700

* Detailed hydrocarbon analysis required for PMI calculations.



PMI Modeling Results



Finding:
PMI Model:
Samples behaved as expected - **Decreasing PMI value with the addition of ethanol.**

This is expected given ethanol's double-bond equivalent value of zero.

Benzene



Benzene and Cancer Risk

- Unit risk factors represent long term cancer risk for exposure to compounds
- Only 4 organic compounds are “listed” carcinogens (high burden of proof)
- Normalize risk factor
 $CRF \times \text{tons/year}$ to show cancer potential
- Ethanol generally decreases 1,3 Butadiene and Benzene, increases aldehydes but the weighted sum results in reduced cancer risk

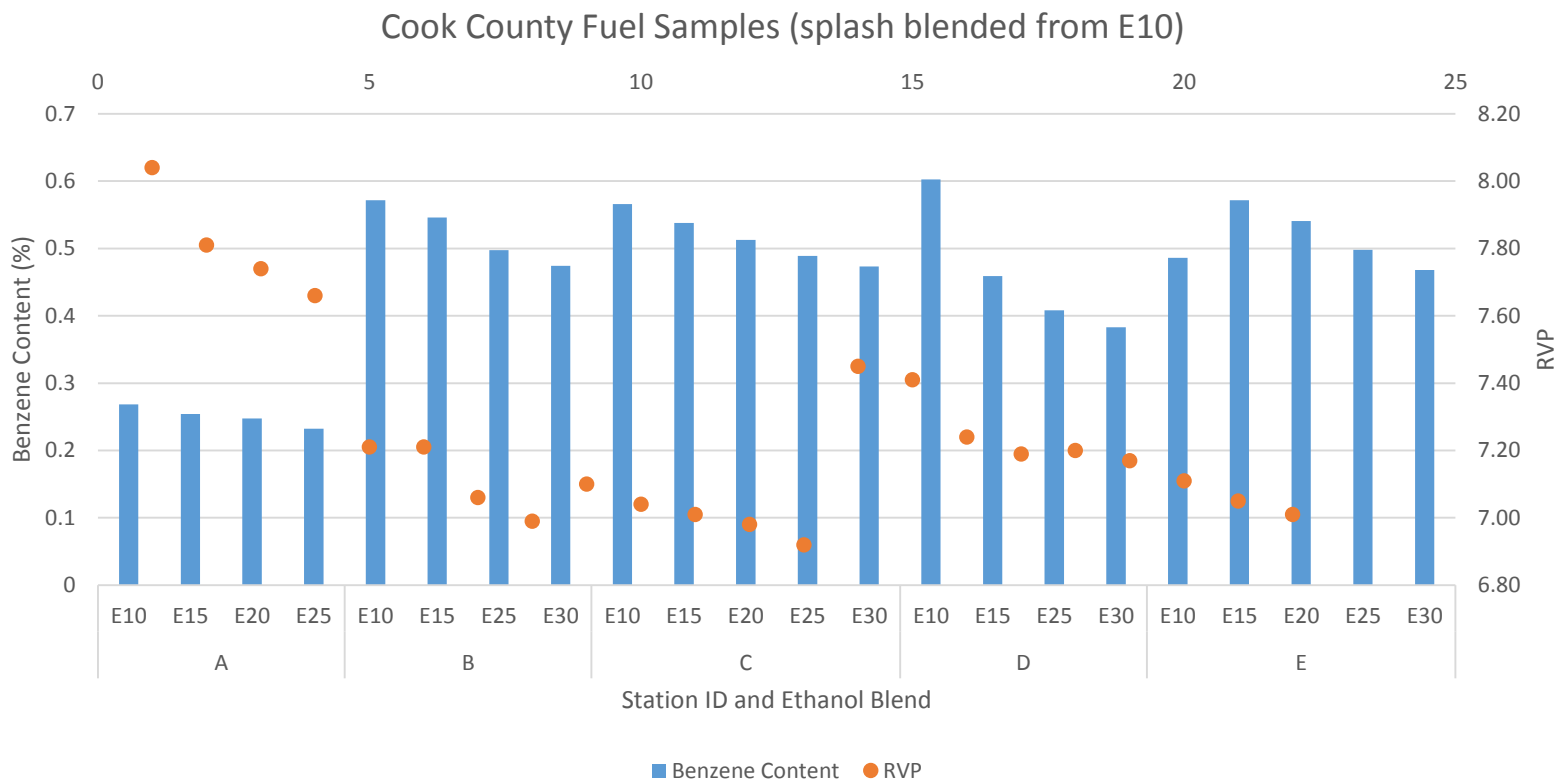
Species	Cancer Risk
Acetaldehyde	1
Formaldehyde	2.22
Benzene	10.74
1,3-Butadiene	62.96

Source: Budroe, J., Brown, J., Collins, J., & et al. (2009). Technical Support Document for Cancer Potency Factors.

Cancer Risk

- Stein et al./SAE In. J. Engines / Volume 6, Issue 1 (May 2013):
 - “Increased ethanol in gasoline should decrease emission of 1,3 butadiene and benzene and increase emissions of acetaldehyde and formaldehyde (later two due to incomplete combustion of ethanol). Due to much higher toxicity weighting factors, 1,3-butadiene and benzene dominate the weighted sum of these four toxics even in high ethanol content”
- “Unnasch and Henderson (2014) “Change in Air Quality Impacts Associated with the Use of E15 Blends Instead of E10”.
 - Analysis of CRC Study E80 showed that “a change from E10 to E15 results in a 6.6% reduction in toxic risk. Furthermore, a “reduction in 1,3 butadiene and benzene produces a decrease in impacts that is greater than their relative decrease in mass emissions””

Intertek Laboratories: Cook County Station Samples



Benzene Content Decreases with Increased Ethanol Blend

