

HEAT OF VAPORIZATION AND SPECIES EVOLUTION DURING GASOLINE EVAPORATION MEASURED BY DSC/TGA/MS FOR BLENDS OF C1 TO C4 ALCOHOLS IN COMMERCIAL GASOLINE BLENDSTOCKS

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Background: Approaches to Increasing SI Engine Efficiency

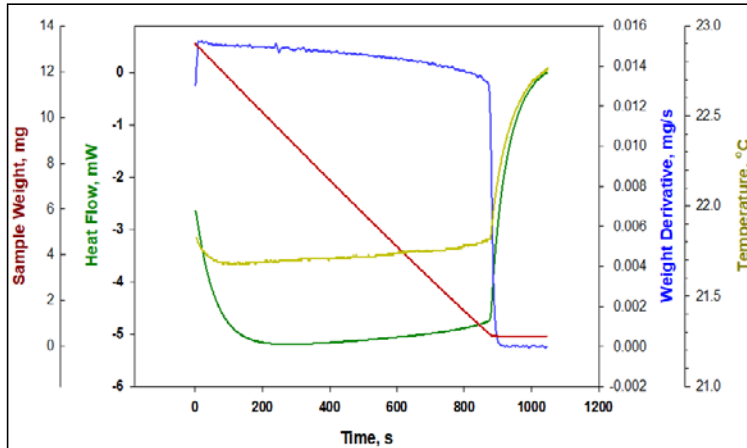
- **Increased compression ratio**
 - Greater thermodynamic efficiency
- **Engine downsizing/downspeeding**
 - Smaller engines operating at low speed/higher load are more efficient
 - Optimized with 6- to 9-speed transmission
- **Turbocharging**
 - Recovering energy from the engine exhaust
 - Required for engine downsizing
- **Direct injection**
 - Fuel evaporates in the combustion cylinder, cooling the air-fuel mixture
 - Also required for engine downsizing

All of these strategies can take advantage of more highly knock-resistant fuels:

- *Higher octane number*
- *Higher heat of vaporization (HOV)*

Background: Simultaneous Differential Scanning Calorimetry/ Thermogravimetric Analysis (DSC/TGA) to Directly Measure HOV

- HOV is a key fuel property that can affect a fuel's knock resistance
- In previous work, we developed a DSC/TGA method that simultaneously measures the heat flow and weight loss of a sample versus an empty reference pan
- Sample introduced via a gas-tight syringe and allowed to evaporate under a stream of nitrogen (50 mL/min) at ambient lab conditions
- The area under the curve is calculated to get the total heat due to sample evaporation and is divided by the sample mass to get the total HOV in kJ/kg

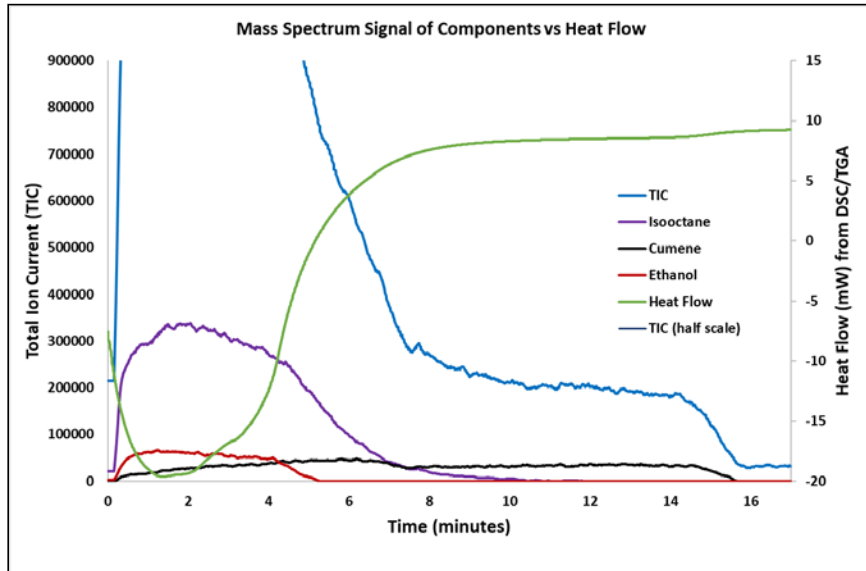


Thermogram of n-hexane evaporation

- Chupka (Fioroni), G., et al., "Heat of Vaporization Measurements for Ethanol Blends Up To 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines," *SAE Int. J. Fuels Lubr.* 8, no. 2: 251–263, 2015, <https://doi.org/10.4271/2015-01-0763>
- Fioroni, G., et al., "Measurement of Heat of Vaporization for Research Gasolines and Ethanol Blends by DSC/TGA," *Energy Fuels*, 2018. <https://pubs.acs.org/doi/10.1021/acs.energyfuels.8b03369>

Background: Simultaneous Differential Scanning Calorimetry/ Thermogravimetric Analysis (DSC/TGA) to Directly Measure HOV

- HOV method was further expanded by adding a high-resolution mass spectrometer (MS) to the system to identify and track the evolution of key species, such as ethanol and aromatics from gasoline/ethanol blends
- Heat flow signal can be overlaid with component evolution from MS



- Note large change in the heat flow signal overlaid from the DSC/TGA with the end of evaporation of ethanol
- Demonstrates the intensity of the cooling effect of ethanol on the sample and how it affects the DSC/TGA heat flow and mass loss signals (mass loss not shown for clarity)

Results: Properties of Alcohols and Gasolines Used in This Study

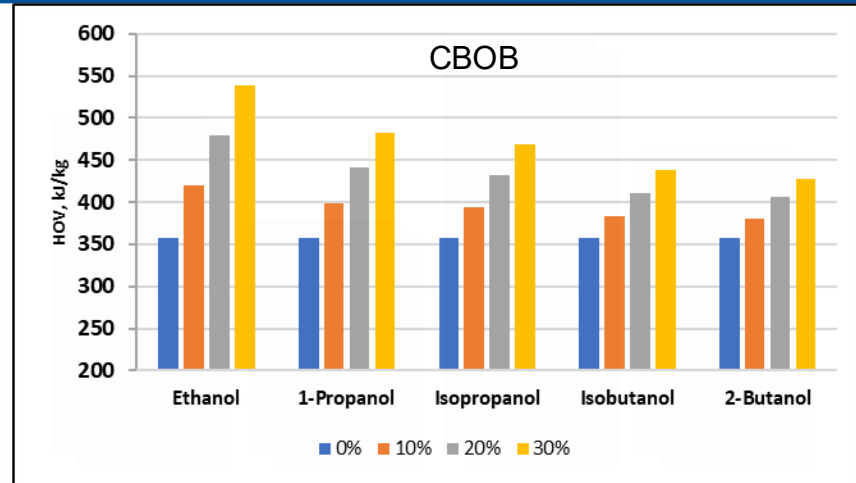
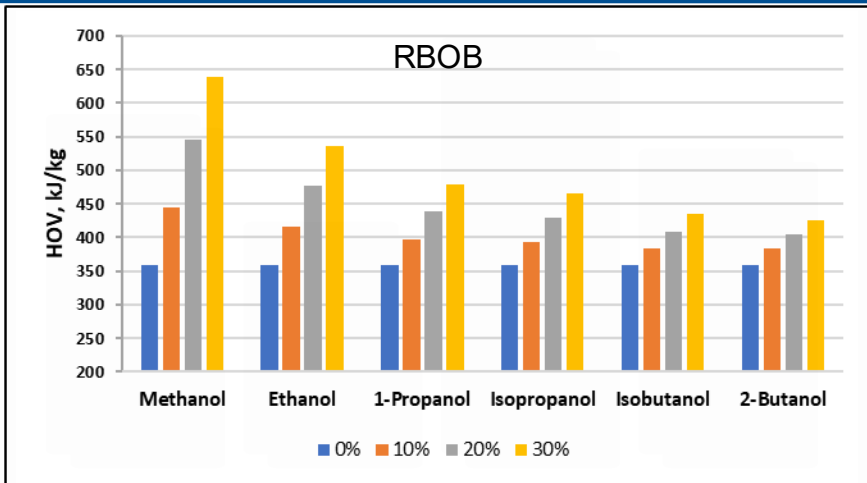
Property	RBOB	CBOB	FACE B
Research octane number	87.5	86.8	95.8
Motor octane number	80.6	81.1	92.4
Density (g/cm ³)	0.7438	0.7078	0.6970
Reid vapor pressure (kPa)	36.40	80.05	50.3
HOV (DSC/TGA) (kJ/kg)	359	358	341
DHA (vol.-%)			
n-Paraffins	11.6	23.2	8.0
i-Paraffins	40.9	41.6	86.9
Cycloparaffins	6.0	7.1	0.1
Aromatics	33.7	20.4	5.8
Olefins	7.06	7.5	0.02

Alcohol	HOV (kJ/kg)	Boiling Point (° C)
Methanol	1173.5	65
Ethanol	918.6	78
1-Propanol	788.7	97
Isopropanol	743.8	83
Isobutanol	685.4	108
2-Butanol	670.5	100

CBOB: conventional blendstock for oxygenate blending
 DHA: detailed hydrocarbon analysis
 FACE: Fuels for Advanced Combustion Engines
 RBOB: reformulated blendstock for oxygenate blending
 RVP: Reid vapor pressure

- Alcohol blends were prepared volumetrically by hand blending at 10%, 20%, and 30% in both RBOB and CBOB (FACE B blends were prepared at 30% alcohol and 20% cumene only)
- D86 and RVP were measured on RBOB and CBOB blends; DSC/TGA/MS was measured on all blends

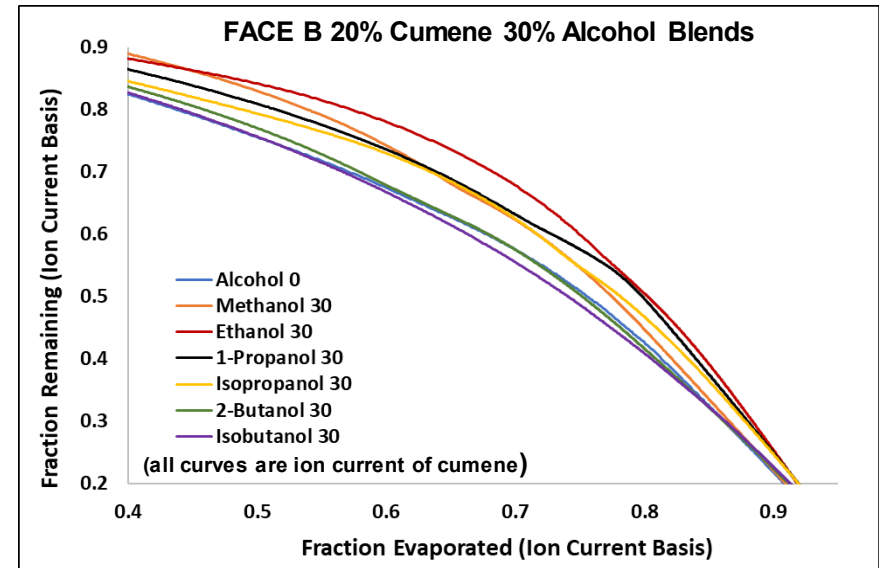
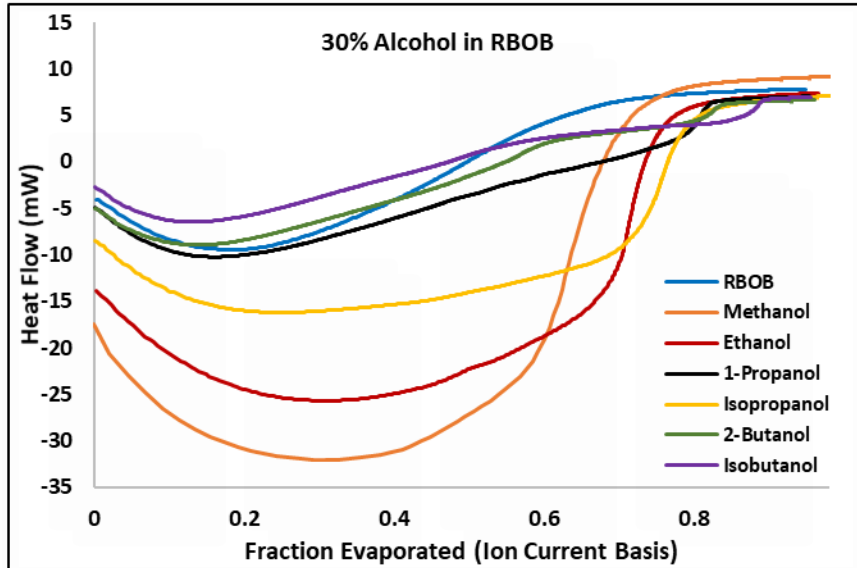
Results: FACE B, RBOB, and CBOB: HOV of Blends



30% Alcohol in FACE B	HOV (kJ/kg)
A0 (FACE B + 20% Cumene)	335.6
Methanol	656.6
Ethanol	560.9
1-Propanol	508.4
Isopropanol	495.0
Isobutanol	470.0
2-Butanol	463.8

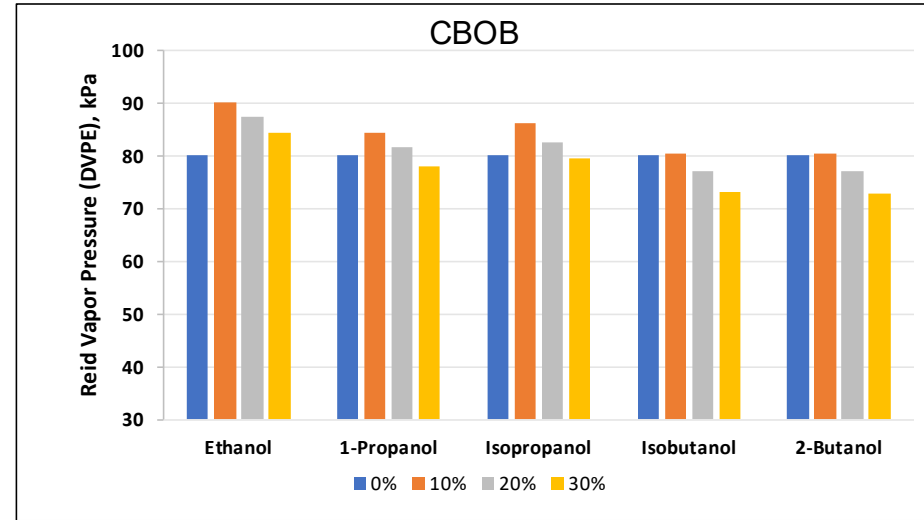
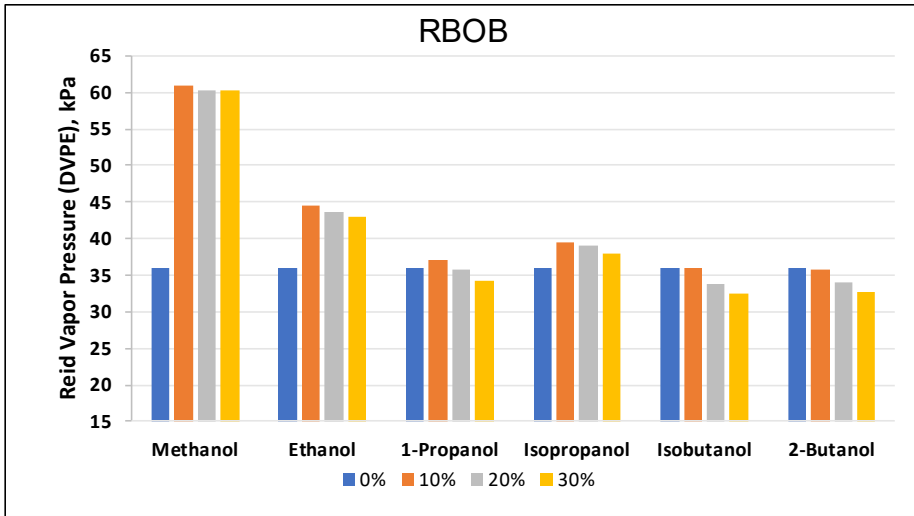
- HOV was calculated at 25°C by DHA
- HOV of blends follows the trend of the pure component HOV as expected, with methanol having the largest increase in HOV of the blend and 2-butanol showing the least effect

Results: Heat Flow Effect of Alcohols in RBOB and Cumene Evolution in FACE B Blends



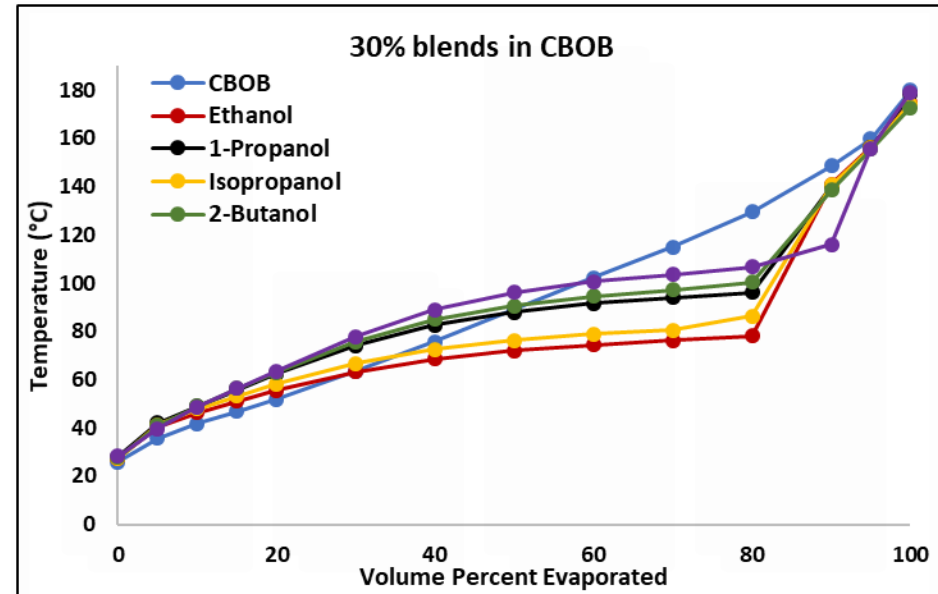
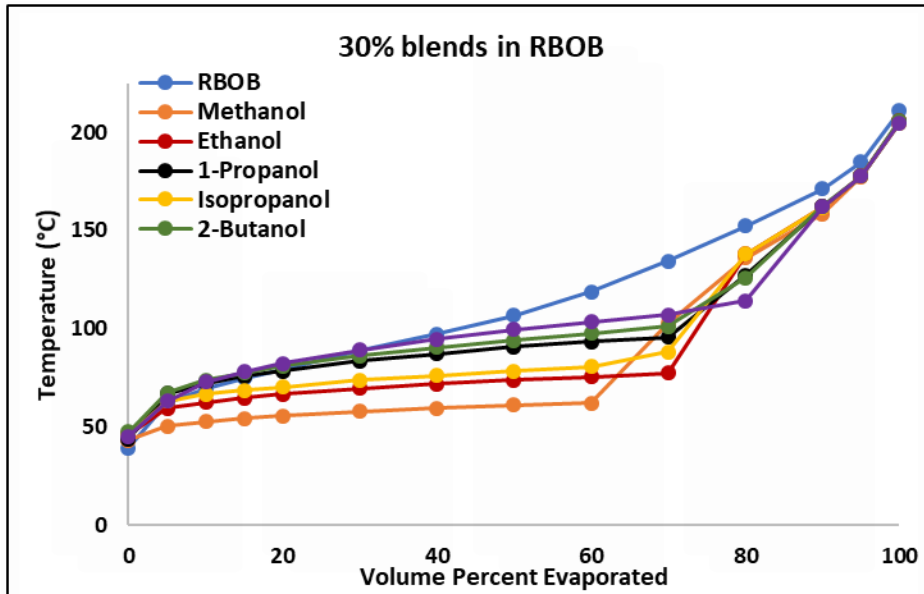
- The lower the boiling point of the alcohol (OH), the higher its heat flow signal, and the more rapid its evaporation from the sample
- Examination of cumene evaporation with different OHs shows that cumene evaporation is delayed with higher-volatility, lower-boiling OHs, suggesting that cumene evaporation is suppressed until later in the sample evaporation process due to the cooling effect of the OH

Results: Reid Vapor Pressure in RBOB and CBOB



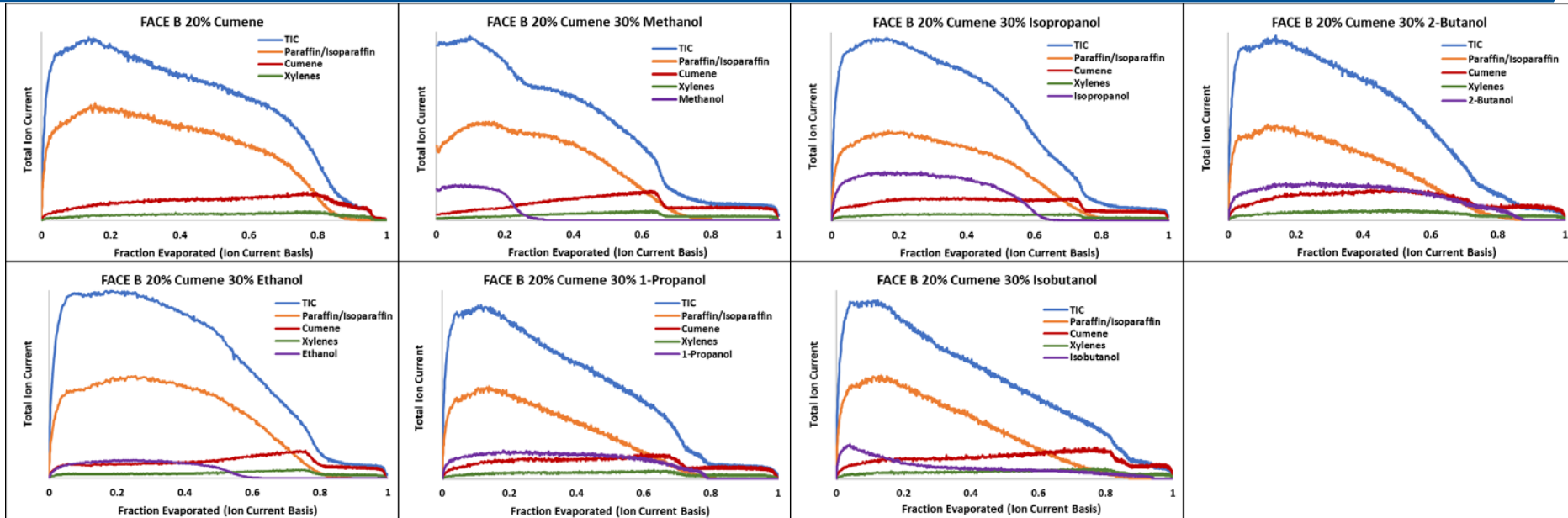
- Methanol and ethanol increased RVP significantly
- Isopropanol also increased RVP, especially in the low-vapor-pressure RBOB
- The effect of 1-propanol was marginal
- 2-Butanol and isobutanol showed reductions in the RVP

Results: D86 Distillation Curves for 30% Blends in RBOB and CBOB



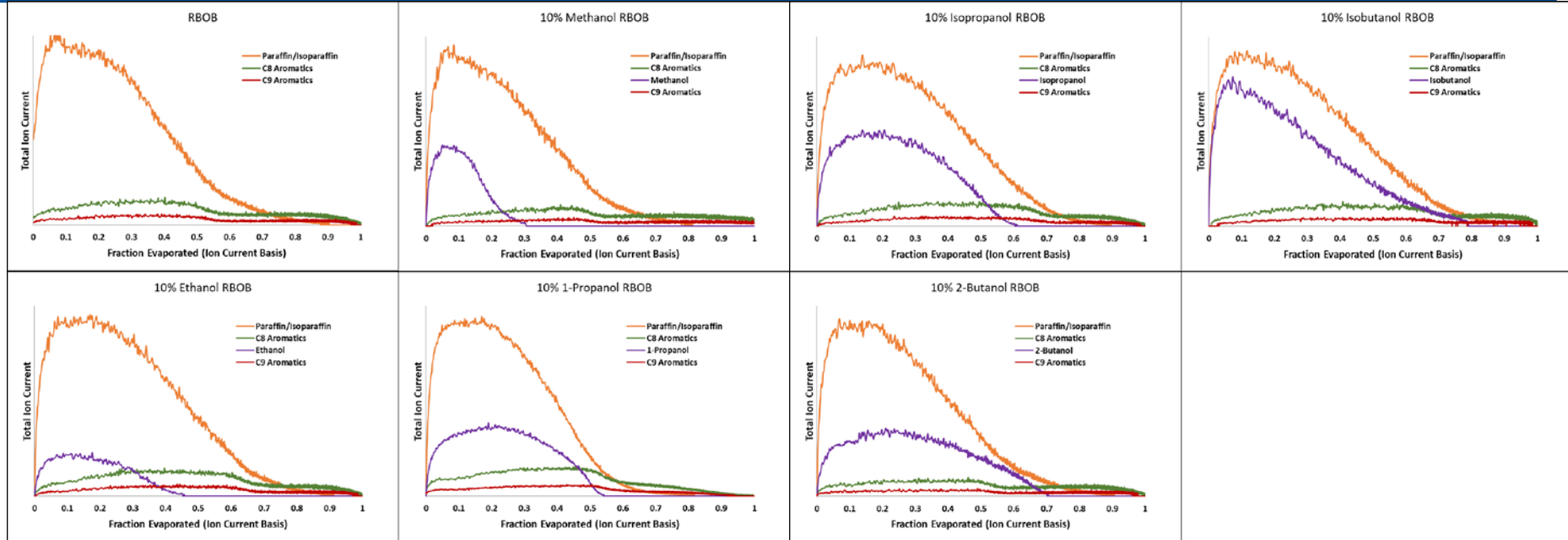
- Methanol, ethanol, and isopropanol show the greatest impact on boiling point depression. (Note, methanol was not blended into CBOB)
- 2-butanol, isobutanol, and 1-propanol all show a similar depression

Results: MS Ion Current versus Fraction Evaporated: FACE B Blends



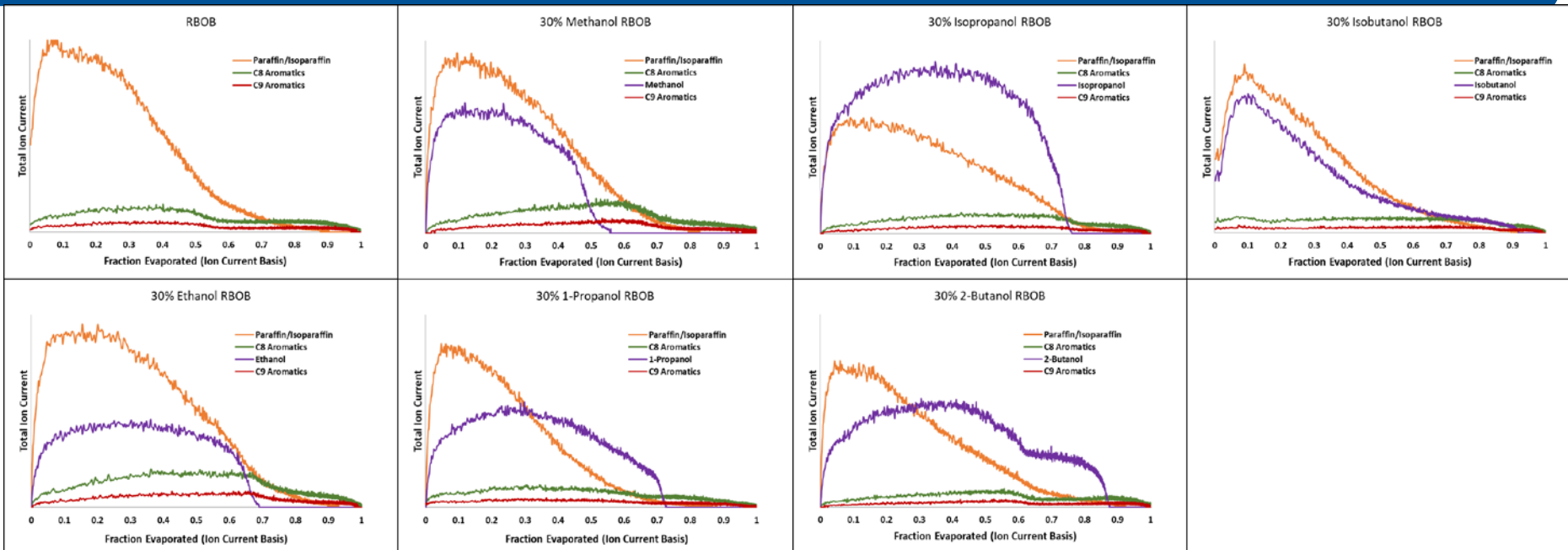
- Methanol evaporates very early in the sample evaporation process (30% fraction evaporated). Ethanol and isopropanol are double that of methanol (~60% evaporated)
- 1-Propanol, 2-butanol, and isobutanol take the longest (>80% of fraction evaporated)
- The lower-molecular-weight, lower-boiling-point alcohols (methanol and ethanol) evaporate off at a lower fraction evaporated even though they are at a higher molar concentration

Results: MS Ion Current versus Fraction Evaporated: 10% Blends in RBOB



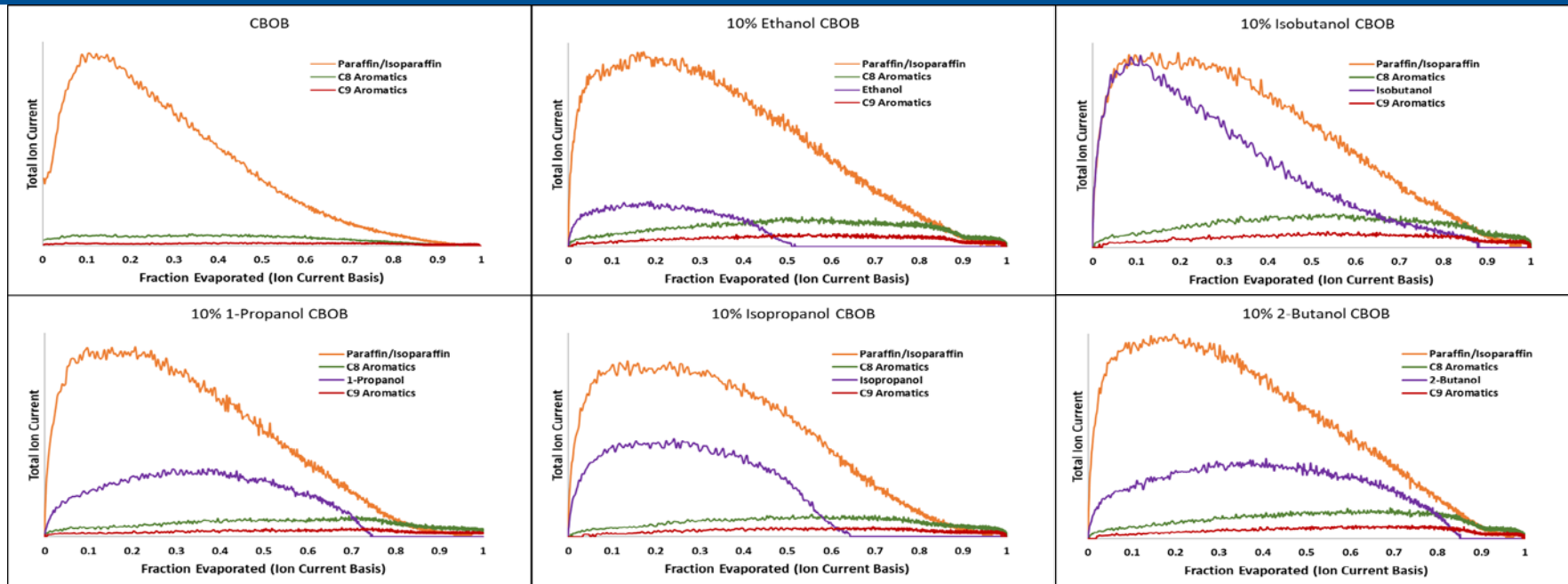
- As with the FACE B blends, the lower-molecular-weight and lower-boiling-point OHs evaporate from the sample more rapidly
- The alkanes appear to be unaffected by the alcohol evaporation despite the known azeotropes formed with alcohols and paraffins: 1-propanol may be an exception
- The aromatics curves all show a first phase evaporation with a dip to a second phase evaporation at a lower level

Results: MS Ion Current versus Fraction Evaporated: 30% Blends in RBOB



- As would be expected, the addition of more OH extends the evaporation of the OH to a higher fraction evaporated than with the 10% blends
- 2-butanol presents an unusual evaporation profile at this high blend level, demonstrating two stages of evaporation
- The aromatics behave similarly to the 10% blend case, exhibiting a first phase evaporation that corresponds to near the termination of alkane evaporation, followed by a second lower level evaporation

Results: MS Ion Current versus Fraction Evaporated: 10% Blends in CBOB



- In the CBOB vs. RBOB, ethanol finished evaporating at a similar fraction evaporated; however, the propanols persisted to about 10% later in fraction evaporated
- The isobutanol and 2-butanol also remained to about 10% higher fraction evaporated
- This is likely due to CBOB containing fewer heavy and higher-boiling components than the RBOB. (Note: T90 of CBOB was 150° C while T90 of the RBOB was 170° C)

Summary/Conclusions

- HOV of the blends followed the HOV of the pure component as expected, with the highest HOV component, methanol, showing the largest increase of HOV in the blends for FACE B, RBOB, and CBOB
- Methanol and ethanol significantly increased RVP, while the propanol isomers demonstrated a much smaller increase, and the butanol isomers decreased the RVP
- Methanol, ethanol, and isopropanol showed the largest boiling point depression in the D86 distillation curves, while 1-propanol, 2-butanol, and isopropanol had a smaller effect
- The lower the boiling point and the smaller the alcohol chain, the more rapid the evaporation of the alcohol was from the sample
- Evaporation of cumene was delayed by the presence of methanol, ethanol, or the propanol isomers but unaffected by the butanol isomers
- For all samples, the species evaporation profiles appeared strongly affected by interactions between the alcohols and hydrocarbon gasoline components

Summary/Future Work

- Effects of the alcohols on aromatic compound evaporation were more difficult to discern in RBOB and CBOB due to the complex nature of the full boiling range gasoline blendstocks
- With additional development of the DSC/TGA/MS method, it may prove possible to quantitatively examine evaporation of specific carbon number compounds within compound classes, especially C9 and larger aromatics
- Future work will examine specific azeotropic interactions using model systems consisting of an alcohol and a single hydrocarbon/aromatic component
- Experiments could examine evaporation of systems exhibiting a series of azeotropes with similar compounds or multiple azeotropic interactions with compounds of different classes

Acknowledgement

Thank you!!!

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