Model-based compositional predictions for a Differential Scanning Calorimetry/Thermogravimetric Analysis-Mass Spectrometry system used for Heat of Vaporization measurements

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Abstract

A Differential Scanning Calorimetry/Thermogravimetric Analysis (DSC/TGA) procedure for determination of Heat of Vaporization (HOV) of fuel and surrogate fuel mixtures has been previously utilized for evaluation of oxygenate impacts on spark ignition fuels. This analysis has been further leveraged with mass spectrometry (MS) to elucidate vapor phase compositional changes during evaporation. In this article we focus on a simple system of three compounds (ethanol, n-hexane, and n-octane) to provide a model-based understanding of the evaporation process under these experimental conditions. An Aspen Plus model was set up to provide liquid and vapor phase concentration predictions during mixture evaporation using the initial mixture composition, and measured temperature and mass loss profiles from DSC/TGA experiments. Agreements between the trends of the MS ion count profiles and model composition predictions provide a degree of validation of this modeling approach that can allow the interpretation and extrapolation of DSC/TGA measurements for more complex fuel mixtures.

1. Introduction

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Heat of Vaporization (HOV) can affect anti-knock properties of a fuel in gasoline direct injection engines [1,2]. Specifically, oxygenated fuel species (predominantly ethanol for current commercial fuel formulations) that have higher HOVs compared to hydrocarbons, provide enhanced evaporative cooling which leads to reduced engine knocking tendency of the fuel. This allows gasoline spark ignition engine designs with higher compression ratio, which translate directly into higher engine thermal efficiency [1,3]. The non-ideal evaporation behavior from the introduction of polar oxygenated molecules into hydrocarbon mixtures has been measured [4,5] and can be well-predicted [6], especially when binary interaction model parameters are available for the species, and those parameters are based on experimental vapor-liquid equilibrium (VLE) measurements. The system (ethanol, n-hexane, and n-octane) used for illustration in this article is well-studied for binary interaction behavior [7,8]. Activity coefficient models, such as NRTL [9], are usually property methods of choice for capturing non-idealities in the liquid phase when interaction parameters regressed from experimental data are available; Aspen Plus [10] provides built-in binary parameters for interactions among all three species. Multicomponent system behavior (ternary system in our case) can be predicted accurately when binary interaction parameters are available for constituents; this is allowed by the mathematical formulation of activity coefficient models like NRTL, where no additional parameters are necessary for multicomponent systems, and cumulative effect of interactions on the activity coefficient of each component can be accounted by its binary interaction with each of the other components in the mixture [9]. The liquid phase modeling can be easily extended to more complex mixtures using experimentally derived binary interaction parameters if available, or otherwise using predictive activity coefficient models such as UNIFAC [6,11,12] when experimental data is not available. This approach can help predict compositional and thermal changes during droplet evaporation in

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an engine and benefit engine performance and design, including the modeling of potential improvements in key metrics such as engine knocking and soot formation [1,6,13,14,15]. We used the Redlich-Kwong (RK) equation of state [16] for the vapor phase model, by specifying the built-in property method NRTL-RK in Aspen Plus; in this case the experimental data was at atmospheric pressure conditions and the use of ideal gas instead of RK in the vapor phase would work equally well; our choice of RK for the vapor phase model was solely based on the consideration that our model framework should continue to provide good predictions at higher pressure conditions.

2. Methods

Experimental methods for the DSC/TGA-MS system have been previously published [17,18]. Briefly, a Q600 series DSC/TGA from TA Instruments (New Castle, DE) was coupled to a JEOL JMS-GC Mate II double focusing mass selective detector. The detector was set to scan from m/z 33-200 with unit mass resolution and ionization source at 20 eV to minimize fragmentation while producing adequate signal. The experiments were conducted under ambient laboratory conditions with no temperature control utilized by the instrument. Standard aluminum DSC pans were used for the analysis. To avoid any evaporation prior to initiation of the experiment, samples were transferred to the tared aluminum pan while inside the instrument via a gas-tight syringe and the experiment was started as soon as the instrument furnace door was closed. No lid was utilized on top of the pan as adequate evaporation is necessary to obtain satisfactory signal in the mass spectrometer. The volume of sample used was 15 μL for each experiment. Heat flow varied during the evaporation process because of the system's natural tendency towards thermal equilibrium within the instrument; temperature reduction due to evaporation was thus compensated by additional heat flow from surroundings to help bring the sample pan back

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towards ambient conditions. The difference in heat flow measured for the reference and sample pans in the instrument provides heat flow information; while we have used that information in other internal models, we specifically chose not to use the measured heat flow for the current modeling because of higher noise and uncertainties compared to the measurements of temperature and mass loss. An Aspen Plus modeling approach related to these experiments is described here since that has not been reported previously. The focus is on vapor phase concentration predictions from the Aspen Plus model during the evaporation process and comparison with MS ion counts using a representative m/z for each species (n-hexane: 86, n-octane: 85, and ethanol: 45) from experimental DSC/TGA-MS data for two different initial molar concentrations (A) 25%/25%/50% n-hexane/n-octane/ethanol and (B) 40%/40%/20% n-hexane/n-octane/ethanol. The concentrations of ethanol are relevant for allowable ranges of ethanol blends with gasoline, although gasoline is made up of a significantly more diverse set of hydrocarbons. These two systems are referred to as Case A and Case B in the remainder of this article. The only input data linking the model with the experimental measurements were the mass loss and temperature measurements, along with initial liquid compositions. All other model outputs were predicted. Experimental data used as model inputs are shown in Figure 1.

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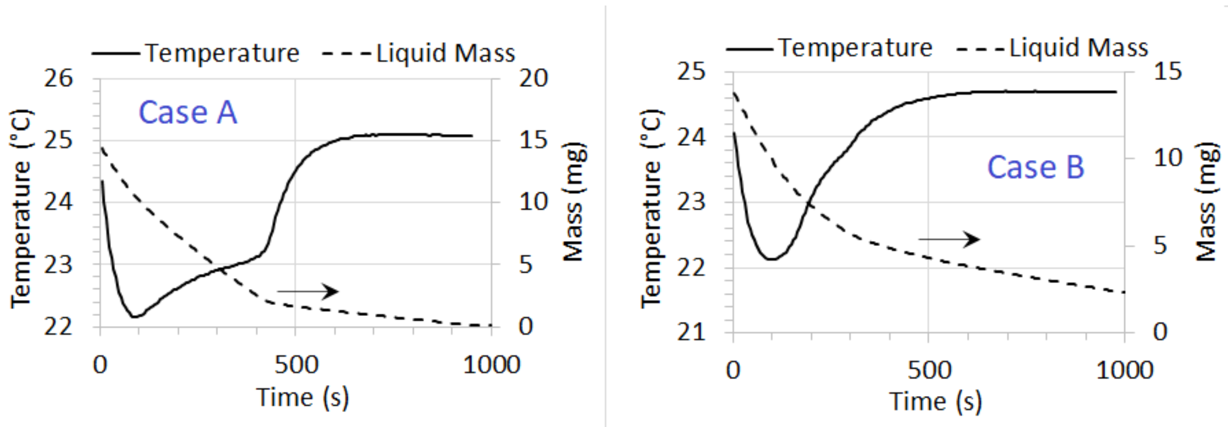

Figure 1: Experimental data used as inputs for the Aspen Plus model. Case A had an initial molar concentration of 25%/25%/50% n-hexane/n-octane/ethanol, while Case B had 40%/40%/20% n-hexane/n-octane/ethanol. The initial concentrations, temperature and mass loss data from experiments were used as model inputs for predicting vapor compositions. DSC/TGA data was exported every 5 seconds.

The Aspen Plus flash block (FLASH2) was used in the model for phase equilibrium (VLE) predictions since this system does not exhibit liquid-liquid phase separation. Flash calculations use the specified property method for phase equilibrium calculations to predict vapor and liquid phase compositions for a specified feed composition of the mixture of interest; calculations use two specified inputs (e.g., among temperature, pressure, molar vapor fraction, or duty) to estimate the necessary unspecified state variables and simultaneously satisfy phase equilibrium criteria predicted by the property method at those conditions. Chemical thermodynamics textbooks provide further details; both NRTL and UNIFAC models and algorithms for coding flash calculations can be found in chemical thermodynamics textbooks [19,20]. In our case, temperature and evolved molar vapor fraction for each measurement in time were specified as flash calculation inputs. The temperature was specified based on the experimental measurements and the specified molar vapor fraction was calculated based on the mass loss in each DSC/TGA

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measurement step (Figure 1). The model-predicted output composition of the liquid after each flash step was used as the input feed mixture composition for the next step. The initial composition for the first flash calculation was specified based on experimental mixture compositions for Case A and Case B respectively. Initial liquid mass of 14.160 mg (Case A) and 13.626 mg (Case B) were chosen in the model to match the experiments; matching the initial mass in the model is important to allow proper correction for nitrogen dilution (N_2 flow of 50 mL/min), as described later. The NRTL-RK property method built into Aspen Plus was used for these calculations. Figure 2 is a simple depiction of the model workflow.

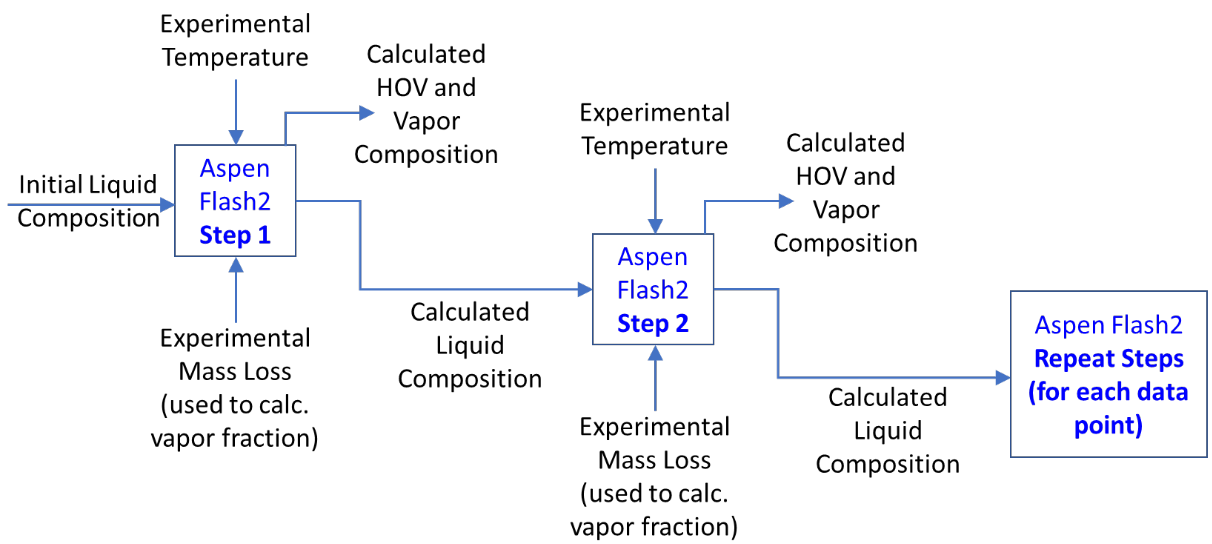

Figure 2: Simple schematic showing steps in Aspen Plus model

3. Results and Discussion

Since the MS response was not calibrated to compound concentrations for the available experimental data, only ion counts were reported – total ion counts (TIC) and extracted ion counts (EIC) for each individual component. A few additional steps were taken before comparing the modeled molar flow rates with the ion counts. The adjustments included time

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shifts of 75s and 30s respectively for Case A and Case B, which were necessary adjustments due to the experimental design. The shifts were determined based on noticeable and identically trending changes in both the MS data and modeled predictions. This relative delay in MS signal in these experiments is due to the amount of time required for analytes to reach the detector; start of evaporation occurring immediately after sample introduction generating heat flow and mass loss at the DSC/TGA, while beginning of MS signal is slightly delayed by time required for analytes to traverse the transfer line (0.1 µm ID x 3 m inert capillary). Note the model inputs were based on DSC/TGA recorded mass and temperature data, while the ion counts were measured by independent recording of the MS data. No attempts were made to match any of the data before 100s because the DSC/TGA-MS system was going through the dynamics of pushing out existing gas holdup within the system, and thus experiencing an initial higher dilution of vapors in the transfer line as the sample reached the MS ion source; the initial climb of experimentally measured ion counts corroborate the idea that the ion count measurements were suppressed by dilution. This may be further addressed in future modeling by careful quantification of system volumes, associated initial gas holdups, and the dynamics of how the initial vapors travel through the system.

Another adjustment was made to put the ion counts and modeled mole flows on the same basis. There was a constant nitrogen purge flow of 50 mL/min in the DSC/TGA cell throughout the experiment. However, the molar evaporation rate kept changing during the duration of the experiment (as reflected by changes in mass loss rate, in addition to compositional changes). The ion counts are based on an approximately constant volumetric flow of nitrogen plus sample vapors into the MS (flow rate dictated by the vacuum of the MS interface and volume of the capillary). When the evaporation rate decreases there is a lower ion count of the vapor species

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because of higher nitrogen dilution. Since the model predicts the molar vapor flow rate for each DSC/TGA data point (based on mass loss, as mentioned earlier), it was a simple calculation to factor in a proportional dilution effect of the constant nitrogen flow rate (50 mL/min). The results shown in Figure 3 reflect these adjustments. Similar plots are included in the Supplementary Information (Figure SI-1) with the additional data from the MS that was truncated prior to time zero (in Figure 3) because offsets of negative 75 s and 30 s were included for the MS data to account for transfer line delays; Figure SI-1 shows the buildup of ion concentrations during the initial stages, as discussed above.

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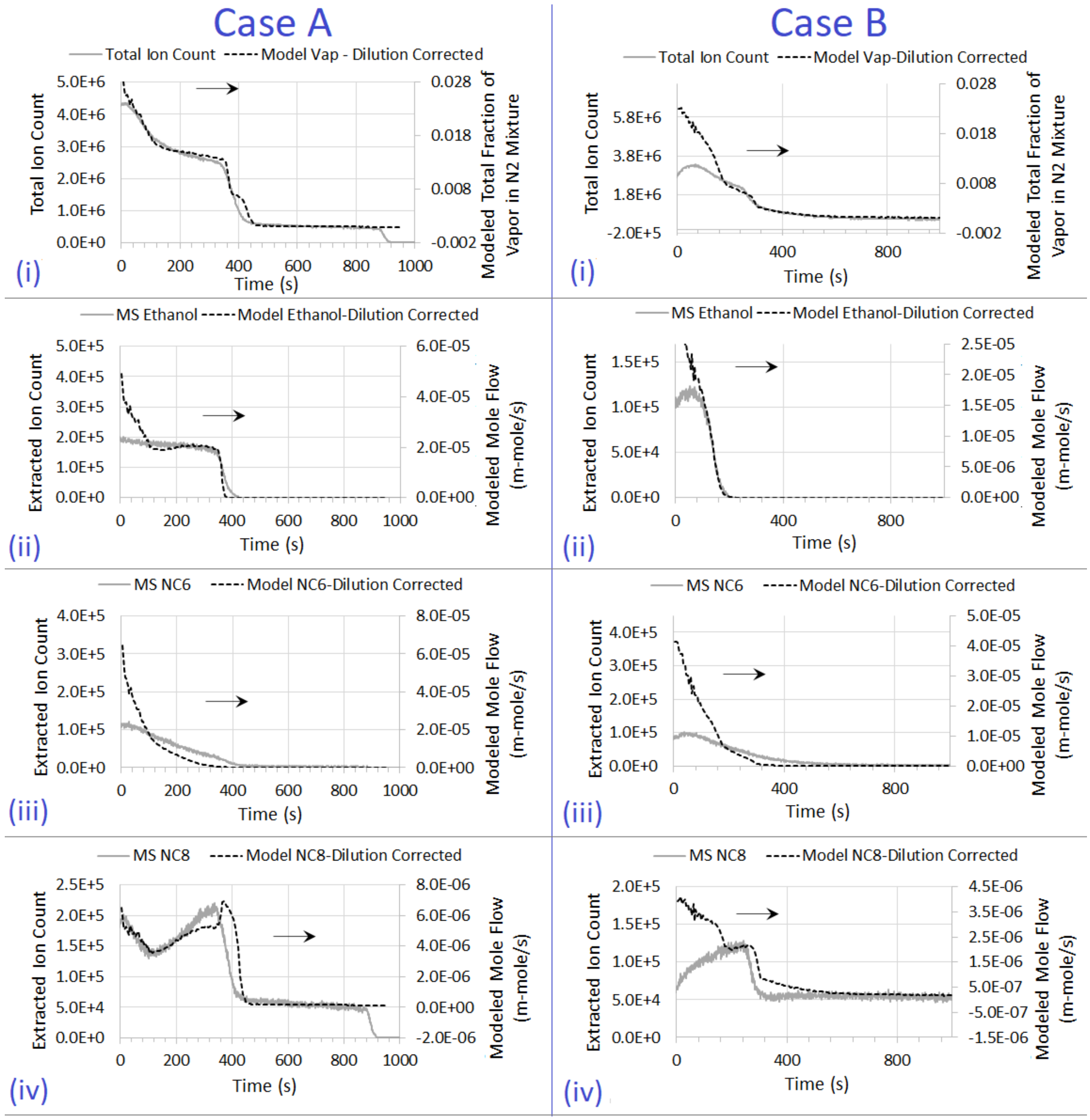

Figure 3: Comparison of MS ion counts with modeled vapor molar flows for Case A (50% ethanol) and Case B (20% ethanol). Ion counts and modeled total vapor fraction in N_2 for (i) the total mixture; extracted ion counts and modeled molar flows for (ii) ethanol, (iii) NC6 or n-hexane, and (iv) NC8 or n-octane.

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4. Conclusion

The compounds in this system behave non-ideally, with known binary azeotropes for both n-hexane and n-octane with ethanol [21]; some of the non-idealities are exhibited in the behavior of n-octane shown in Figure 3. The figure shows that while the compositions at the start of experiment are not matched because of the build-up of ions and corresponding experimental signals during that phase, there is good agreement in the trends of the ion counts with the modeled molar flow rate predictions during the later phase where the dilution effects during vapor transfer can be accounted with reasonable certainty. This indicates that the simple equilibrium model in Aspen Plus quantitatively captures much of the evaporation phenomenon in the DSC/TGA-MS experimental system. Some of the unexplained deviations need further investigation through both experiments and additional modeling complexity. Future experiments should include calibration of mass/molar response of each component to improve modeling accuracy. Additionally, usage of higher resolution mass spectrometry would allow for better differentiation of m/z in the spectra derived from oxygenates vs hydrocarbons allowing for the analysis and prediction of more complex systems.

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Author Contributions

AD: modeling, initial draft, final editing; GMF: experiments, writing/review/edits, project lead; EDC: experiments, writing/review/edits; CKH & LF: experiments; SW: modeling guidance, thermodynamics review, editing; RLM: writing/review/edits, overall guidance.

Competing Interests

The authors declare no competing interests. Products or companies are named solely for descriptive clarity, and this neither constitutes nor implies endorsement by NREL or by the U.S. government.

References

[1] Ratcliff, M.A., Burton, J., Sindler, P., Christensen, E. et al., "Effects of Heat of Vaporization and Octane Sensitivity on Knock-Limited Spark Ignition Engine Performance," SAE Technical Paper 2018-01-0218, 2018, doi:10.4271/2018-01-0218.

[2] Chupka, G.M., Christensen, E., Fouts, L., Alleman, T.L., Ratcliff, M.A., McCormick, R.L., "Heat of Vaporization Measurements for Ethanol Blends Up to 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines," SAE Technical Paper 2015-01-0763, 2015, doi:10.4271/2015-01-0763.

Pursuant to the DOE Public Access Plan, this document represents the authors' peer-reviewed, accepted manuscript.
The published version of the article is available from the relevant publisher.

[3] Leone, T.; Anderson, J.; Davis, R.; Iqbal, A.; Reese, R.; Shelby, M.; Studzinski, W. The Effect of Compression Ratio, Fuel Octane Rating, and Ethanol Content on Spark-Ignition Engine Efficiency. Environmental Science and Technology 2015, 49, 10778-10789.

[4] Andersen, V. F., Anderson J. E., Wallington, T. J., Mueller S. A., and Nielsen O. J., "Vapor Pressures of Alcohol−Gasoline Blends," Energy Fuels 2010, 24, 6, 3647–3654, doi:10.1021/ef100254w.

[5] Christensen, E., Yanowitz, J., Ratcliff M., and McCormick, R.L., "Renewable Oxygenate Blending Effects on Gasoline Properties," Energy Fuels 2011, 25, 4723–4733, doi:10.1021/ef2010089.

[6] Burke S, Ratcliff M, McCormick R, Rhoads R, Windom B. Distillation-based droplet modeling of non-ideal oxygenated gasoline blends: investigating the role of droplet evaporation on PM emissions. SAE Int J Fuels Lubr 2017;10(1):69–81.

[7] Ortega, J.; Espiau, F. A New Correlation Method for Vapor-Liquid Equilibria and Excess Enthalpies for Nonideal Solutions Using a Genetic Algorithm. Application to Ethanol + an n-Alkane Mixtures. Ind. Eng. Chem. Res., 2003, 42, 4978-4992.

[8] Shen, W.; An, X. Q.; McElroy, P. J.; Williamson, A. G. (Vapour + liquid) equilibria of (n-hexane + n-octane + n-hexadecane). The Journal of Chemical Thermodynamics. Volume 22, Issue 9, September 1990, Pages 915-921.

[9] Renon H., Prausnitz J. M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", AIChE J., 14(1), S.135–144, 1968.

Pursuant to the DOE Public Access Plan, this document represents the authors' peer-reviewed, accepted manuscript.
The published version of the article is available from the relevant publisher.

[10] Aspen Plus Process Simulator Version 10, Aspen Technology, Inc. 20 Crosby Drive, Bedford, MA. USA.

[11] Aage Fredenslund, Russell L. Jones and John M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures", AIChE Journal, vol. 21 (1975), p. 1086.

[12] Gmehling,J., R.Wittig, J.Lohmann, R.Joh. A Modified UNIFAC (Dortmund) Model. 4. Revision and Extension. Ind. Eng. Chem. Res.2002,41,1678-1688.

[13] Szybist, J.P., Busch, S., McCormick, R.L., Pihl, J.A., Splitter, D.A., Ratcliff, M., Kolodziej, C.P., Storey, J.E., Moses-Debusk, M., Vuilleumier, D., Sjoberg, M., Sluder, C.S., Rockstroh, T., Miles, P.C. "What Fuel Properties Enable Higher Thermal Efficiency in Spark-Ignition Engines?" Prog Energy Comb Sci doi.org/10.1016/j.pecs.2020.100876 (2020).

[14] Burke, S., Rhoads, R., Ratcliff, M., McCormick, R.L., Windom, B., "Measured and Predicted Vapor Liquid Equilibrium of Ethanol-Gasoline Fuels with Insight on the Influence of Azeotrope Interactions on Aromatic Species Enrichment and Particulate Matter Formation in Spark Ignition Engines" SAE Technical Paper 2018-01-0361, doi:10.4271/2018-01-0361.

[15] Ratcliff, M., Fioroni, G.M., Windom, B., St. John, P., Burke, S., Burton, J., Christensen, E., Sindler, P., Kim, S., McCormick, R.L. "Impact of Ethanol Blending into Gasoline on Aromatic Compound Evaporation and Particle Emissions from a Gasoline Direct Injection Engine" Applied Energy 250 1618-1631 (2019).

[16] O. Redlich and J.N.S. Kwong, "On the Thermodynamics of Solutions V. An Equation-of-state. Fugacities of Gaseous Solutions," Chem. Rev., Vol. 44, (1949), pp. 223 – 244.

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[17] G. M. Fioroni, L. Fouts, E. Christensen, J. E. Anderson, and R. L. McCormick, "Measurement of Heat of Vaporization for Research Gasolines and Ethanol Blends by DSC/TGA," Energy Fuels 2018, 32, 12, 12607–12616.

[18] Fioroni, G.M., Christensen, E., Fouts, L., and McCormick, R., "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," SAE Technical Paper 2019-01-0014, 2019, doi:10.4271/2019-01-0014.

[19] J.M.Smith, H.Van Ness, M.Abbott, M.Swihart. Introduction to Chemical Engineering Thermodynamics, 8th Edition, McGraw Hill, 2017.

[20] S.I.Sandler. Chemical, Biochemical, and Engineering Thermodynamics 5th Edition, Wiley, 2017.

[21] Horsley, L.H., Azeotropic Data, III, American Chemical Society, Washington, D.C., 1973.

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