



# Predicting Fuel Properties and Emissions for Advanced Biofuels for Diesel Engines

## Cooperative Research and Development Final Report

**CRADA Number: CRD-18-00765: Project 5**

NREL Technical Contact: Robert McCormick

**NREL is a national laboratory of the U.S. Department of Energy  
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**Technical Report  
NREL/TP-2A00-94890  
July 2025**

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**Cooperative Research and Development Final Report**

**Report Date:** April 11, 2025

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the CRADA final report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

**Parties to the Agreement:** ExxonMobil Technology & Engineering Co. (formerly ExxonMobil Research & Engineering)

**CRADA Number:** CRD-18-00765 Project 5, Modification 4; Exxon Ref: EM11699

**CRADA Title:** Predicting Fuel Properties and Emissions for Advanced Biofuels for Diesel Engines

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**Sponsoring DOE Program Office(s):**

Office of Energy Efficiency and Renewable Energy (EERE), Vehicle Technologies Office)

**Joint Work Statement Funding Table showing DOE commitment:**

<b>Estimated Costs</b>	<b>NREL Shared Resources a/k/a Government In-Kind</b>
Years 1-3	\$0.00
TOTALS	\$0.00

**Executive Summary of CRADA Work:**

The project will investigate variations in biofuel composition and optimize performance in combustion for conventional and future compression ignition engines. It will evaluate a variety of bio-derived molecules in the diesel range that can be produced using technology in ExxonMobil’s portfolio as well as fuels that cover the range of potential molecular structures for robust model development. Changes in fuel/air premixing and stratification in advanced engines could alter the relationship between fuel properties and performance in comparison to current-generation spray combustion approaches. NREL’s experience in fuel and combustion modeling will enable the development of general rules for predicting the performance of a wide range of biofuel options.

## **Summary of Research Results:**

Multi-Project CRADA Field of Study:

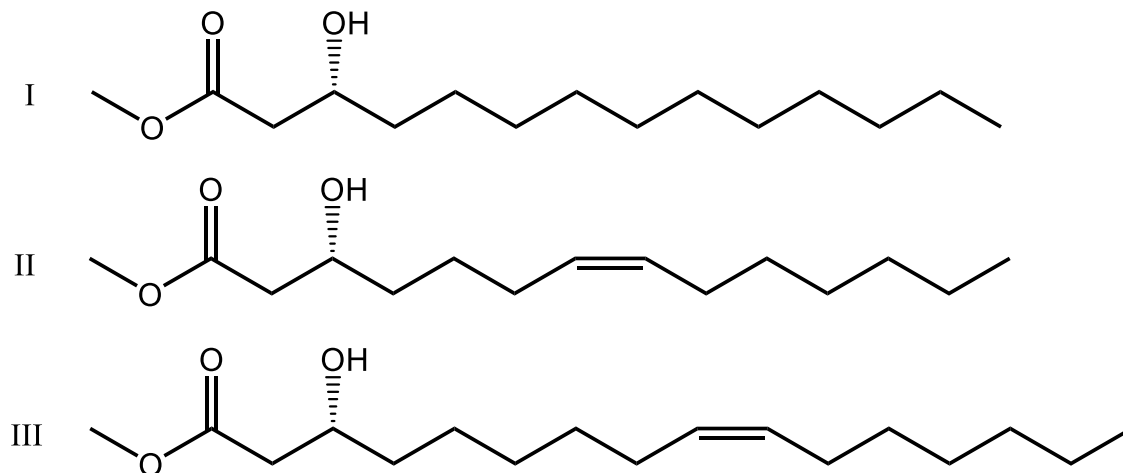
Project 5 is discussed in this final report. Other project final reports under this CRADA number are unrelated and will be published separately. Note: The partner NETL listed on the agreement was not involved in this project.

### **Task 1: Evaluate bench scale autoignition and soot precursor formation for advanced biofuels.**

This task focused on measurement of properties, autoignition, and soot formation for two prototype biofuels supplied by ExxonMobil.

#### **Fuel Property Evaluation of Unique Fatty Acid Methyl Esters Containing $\beta$ -Hydroxy Esters from Engineered Microorganisms**

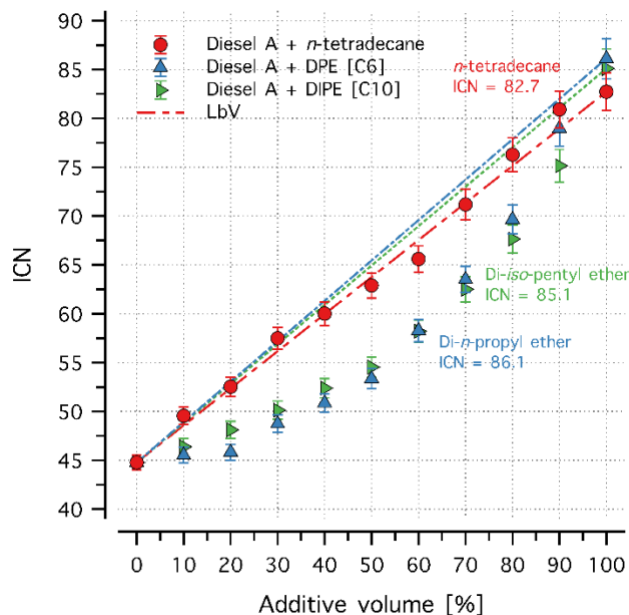
Fatty acid methyl esters (FAME) containing unique  $\beta$ -hydroxy esters were produced using an engineered microorganism by glucose fermentation. This study investigated the properties of the unique FAME mixture both neat and in blends with conventional diesel, as well as properties of  $\beta$ -hydroxy esters. The unique FAME blend contained relatively shorter-chain FAME (average fatty acid chain carbon number 14.6) with 58% monounsaturated fatty acids and 9% saturated and monounsaturated  $\beta$ -hydroxy acid chains. The unique FAME had a significantly lower distillation T90 (321°C versus 352°C) and higher cetane number (56.7 versus 52) compared to soy biodiesel. The cloud points of the unique FAME and soy biodiesel were within method repeatability. Unexpectedly (because of the lack of methylene-interrupted double bonds), the unique FAME had low oxidation stability (1.5 h) as determined by Rancimat induction period. Stability could be improved through the addition of commonly used antioxidants. We speculate that monounsaturated  $\beta$ -hydroxy FAME may be the source of this instability. Blends with conventional diesel up to 50 vol % showed similar kinematic viscosity (within method repeatability) as blends of conventional FAME. The unique FAME had no effect on distillation T90 even at the 80% blend level. A 30 vol% blend into conventional diesel had a Rancimat induction period of only 2 h, very nearly the same as the neat, unique FAME sample. The addition of antioxidants produced blends of acceptable stability. Based on an assessment of the properties of individual  $\beta$ -hydroxy FAME molecules, they have a higher boiling point, higher cloud point, lower cetane number, and potentially lower storage stability than analogous FAME not having the  $\beta$ -hydroxy group. Removing them from the fuel product in the production process may result in a biodiesel product with superior properties to what is on the market today. These results have been published in an open-access journal article (McCormick, et al., 2024).



**Figure 1. Examples of diesel-boiling-range  $\beta$ -hydroxy methyl esters.**

### Properties and Autoignition Reactivity of Diesel Boiling Range Ethers Produced from Guerbet Alcohols

We examine the properties of diesel boiling range ethers made from coupling of alcohols produced by oligomerization of ethanol (Guerbet alcohols) for their utility as low-carbon liquid fuel blendstocks for diesel engines. Basic properties of boiling point, flash point, freezing point, density, and viscosity are well suited for blending into diesel fuels. For the mixture of ethers, the lightest component, di-n-butyl ether, can be present at up to 20 vol% while still having an adequately high flashpoint for safe handling. Soot formation tendency (as yield sooting index) is well below that of conventional diesel. The ethers have similar compatibility with elastomers as conventional diesel, based on Hansen solubility parameter analysis. Oxidation stability was assessed for 30 vol% blends of individual ethers in a conventional diesel fuel using a long-term storage test. Over 6 weeks we observed no formation of peroxides or degradation. n-alkyl ethers with a carbon number of 8 or higher have a cetane number over 100, which is outside the defined range of cetane number, while branched ethers are over 70. The ethers also blend antagonistically into conventional diesel for cetane number, meaning that the blend's cetane value is lower than predicted based on a linear by volume, mass, or mole model. We show that aromatics and naphthenes present in the petroleum diesel are likely to act as radical scavengers to slow or shut down autoignition of the highly reactive ethers at low to medium blend levels. Overall, diesel boiling range ethers show significant promise as high-quality, low-net carbon diesel blendstocks. This research was published in an open access journal article (McCormick, et al., 2025).



**Figure 2. Indicated cetane number (ICN) of Diesel A (petroleum diesel) blended with linear ether (di-n-propyl ether), branched ether (di-iso-pentyl ether), and linear hydrocarbon (n-tetradecane) with similar ICN.**

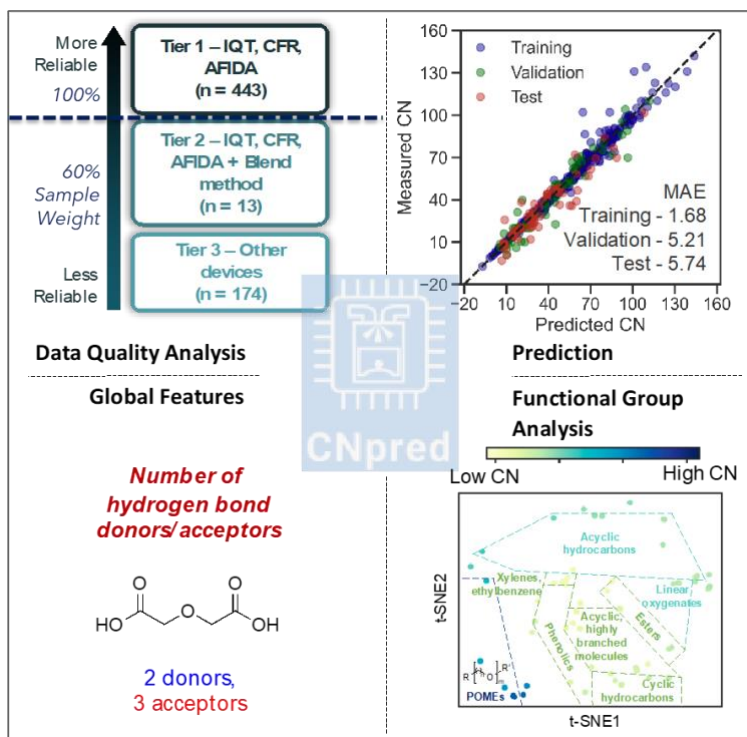
## **Task 2: Extend fuel property prediction and classification, kinetic, and emission models to advanced biofuels and mixtures.**

This task focused on the development of prediction models for cetane number of pure compounds and simple mixtures, as well as vaporization properties of fuel relevant compounds. Additionally, combustion chemical kinetics models were developed for  $\beta$ -hydroxy methyl esters and for diesel boiling range ethers.

### Models for Cetane Number Prediction – Pure Compounds

Designing alternative fuels for advanced compression ignition engines is enabled by having a predictive model for cetane number (CN). Here we introduce physics-informed graph neural networks for reliable CN prediction that considers molecular features pertinent to the physical properties of molecules that affect CN. The reliability (or precision) of CN data was also considered for improving the CN predictive model. Various instruments for measuring CN exist, including standard and non-standard methods. A systematic data quality analysis was carried out for 630 measured CN values collected from the literature and new measurements acquired in this study using the Advanced Fuel Ignition Delay Analyzer (AFIDA). The model imposed lower sample weights on the data coming from less precise measurement methods. This approach effectively maximized prediction accuracy while incorporating data from the wide variety of available sources. Using sample weights based on measurement precision decreased the mean absolute error (MAE) up to 0.8 CN units. Accuracy was also improved by including CN-related physical properties such as the number of hydrogen bond donors and acceptors. The test set MAE is 5.74 and 7.01 for the model with and without inclusion of these properties, respectively. Investigating molecular structural effects on CN was carried out to gain chemical insights for the design of new fuel candidates. Dimensionality reduction analysis of feature vectors showed a

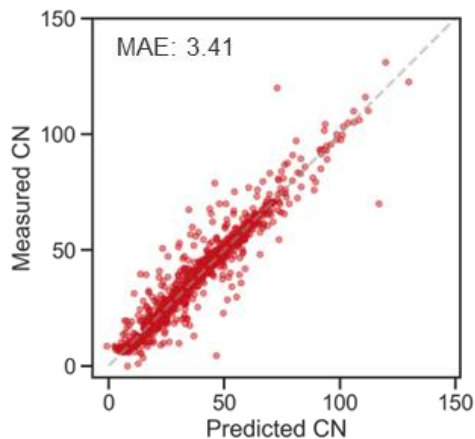
clear clustering of functional groups and CN, and the structural effects derived from the model were consistent with the physicochemical insights. These results were published in a peer-reviewed conference paper (Kim, et al., 2023a).



**Figure 3. Cetane number prediction approach and results for pure compounds.**

### Models for Cetane Number Prediction – Multicomponent Surrogates

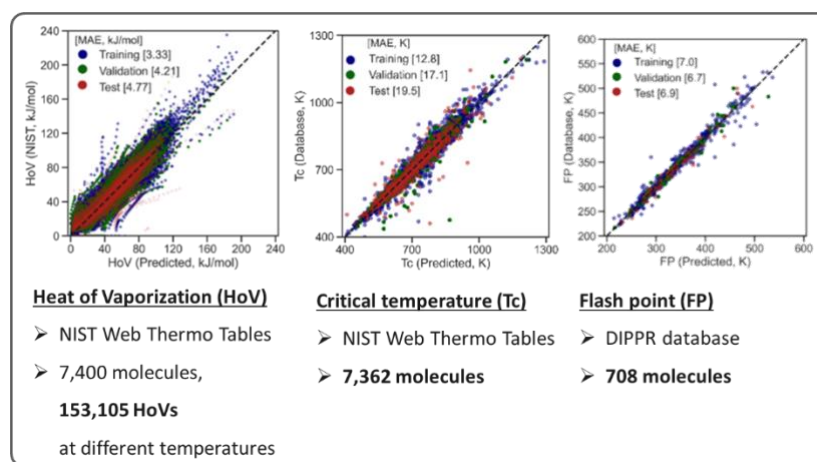
Cetane number (CN) is an important fuel property in designing fuels for conventional and advanced compression ignition engines. In this study we used graph neural networks (GNNs) that predict CNs of multicomponent surrogate mixtures with 2D structures and mole fractions of molecules given as model inputs. The GNN considers the influences of mixing multiple components and their chemical structures on CN and was shown to reproduce the non-linear blending behavior observed for certain mixtures. The GNNs were trained using the CNs of 1,143 mixtures, and reliable accuracy was achieved with mean absolute errors of 3.4-3.8 from the cross-validation. The results were published in a peer-reviewed conference paper (Kim, et al., 2023b).



**Figure 4. Plot showing accuracy of blend CN prediction model.**

### Prediction of Fuel Vaporization Properties

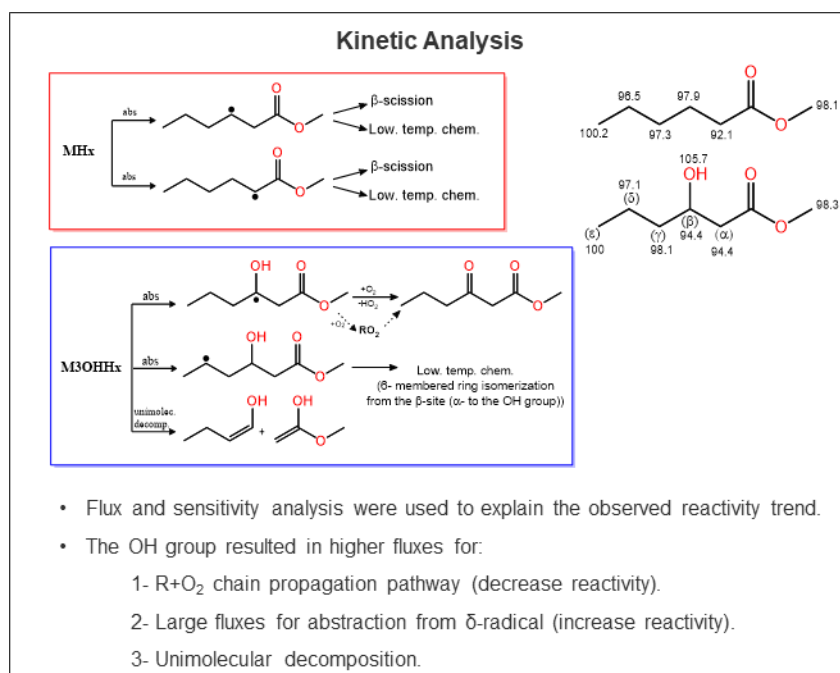
Computational predictions of vaporization properties can support the design of alternative fuels. This research developed chemically explainable graph attention networks to predict five physical properties related to fuel vaporization: heat of vaporization (HoV), critical temperature, flash point, boiling point, and liquid heat capacity. The predictive model for HoV was trained using ~150,000 data points and considered measurement uncertainties and temperature dependence. This model was expanded to the other properties of interest through transfer learning, overcoming limitations due to fewer data points (700–7500). Investigation of the chemical interpretability of the model demonstrated that the model explains molecular structural effects on vaporization properties. Finally, the predictive models were applied to design fuels that have desirable properties. The results were published in a peer-reviewed journal article (Kim, et al., 2024).



**Figure 5. Results of fuel vaporization property prediction models.**

## Combustion Kinetics of $\beta$ -hydroxy Methyl Esters

Biodiesel, composed of fatty acid methyl esters, is one of the major biofuels used today. The fats and oils feedstocks used to make biodiesel are in relatively short supply, leading to research on engineered microorganisms for conversion of sugar to fatty acid esters that contain unique  $\beta$ -hydroxy-esters. This study investigated the effect of the  $\beta$ -hydroxyl group on the combustion chemical kinetics of methyl esters by comparing methyl hexanoate (MHx – a commonly used surrogate for biodiesel) and methyl 3-hydroxyhexanoate (M3OHHx – as a comparable surrogate for diesel boiling range hydroxy esters). The combustion chemical reactions were studied experimentally in a laminar flow reactor at 0.84 and 10 bar, 600 to 1,100 K, and stoichiometric conditions; and in a constant volume combustion chamber (CVCC) at 5 and 10 bar, 600 to 900 K, and equivalence ratios of 0.3 and 0.6. MHx was more reactive in the CVCC at temperatures below 800 K at 10 bar and an equivalence ratio of 0.6. MHx also had a higher indicated cetane number (16.4) than M3OHHx (8.1). These reactivity differences were investigated using the MHx kinetic model (updated in this work) and a new M3OHHx model. The kinetic models predict that radicals formed from MHx are consumed by low-temperature autoignition chemistry reactions, whereas the M3OHHx reactivity was significantly governed by the  $\beta$ -radical (on the same carbon as the OH group) chemistry, which mainly terminated via a less reactive chain propagation pathway to methyl-3-oxohexanoate + HO<sub>2</sub>. The results are presented in a peer-reviewed journal article (Mohamed, et al., 2023).

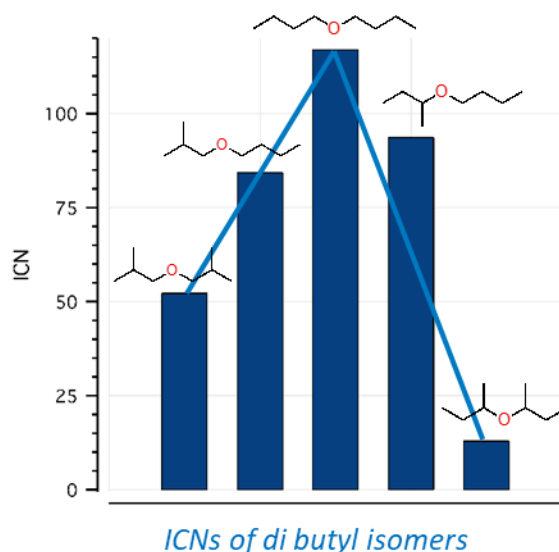


**Figure 6. Results of kinetic analysis for methyl hexanoate (MHx) and methyl 3-hydroxy hexanoate (M3OHHx).**

## Diesel Boiling-Range Ether Combustion Kinetics

While combustion of gasoline ethers such as methyl-tert-butyl ether is well studied, the mechanism and kinetics of diesel boiling-range ethers are not well understood. We investigated the combustion kinetics for three di-butyl ether isomers as surrogates for the range of ethers being studied as diesel blendstocks. We also calculated critical isomerization reaction rates for ether autoignition from theory.

The combustion chemistry and kinetics of three diesel boiling-range butyl ether isomers were investigated using a plug flow reactor. The isomers were di-n-butyl ether (DNBE), diisobutyl ether (DIBE), and di-sec-butyl ether (DSBE) – covering the range of ether structures seen in large diesel boiling range ethers. These ethers showed different degrees of negative temperature coefficient (NTC) behavior and autoignition reactivity. Speciation results from the laminar flow reactor GC analysis were compared to simulations using existing chemical kinetics models and new models developed in this work. The chemical kinetic analysis shows that the combustion behaviors of the three isomers are influenced by the key species formed in the low-temperature reaction regime. The key species identified for DNBE, DIBE, and DSBE at atmospheric pressure are n-butanal, isobutanal, and sec-butanol, respectively. These results were published in a peer-reviewed journal article (Naser, et al., 2024).



**Figure 7. Indicated cetane numbers (ICN) of di-butyl ether isomers.**

The first isomerization reaction of alkylperoxy (RO<sub>2</sub>) radicals is the key step in low-temperature oxidation – the process underlying autoignition reactivity for diesel fuels. The first isomerization governs the competition between chain-propagation and chain-branching reactions – with chain-branching reactions leading to much higher reactivity. We systematically calculated high-pressure rate rules for the RO<sub>2</sub> isomerization reaction of generic mono-ethers, exploring 5-, 6-, 7-, and 8-membered ring transition states. The analysis considered primary, secondary, and tertiary carbon sites, where both the abstracting peroxy group and the abstracted hydrogen are located, with emphasis on distinguishing between secondary carbon atoms adjacent and nonadjacent to the ether functional group. Using the G4//B3LYP/6-311++G(2df,2pd) level of theory and transition state theory, we calculated rate constants and the Arrhenius coefficient for over 120 isomerization reactions. We examined the effect of ring atom count, revealing that 6- and 7-membered ring isomerizations were generally faster and therefore more likely to dominate combustion chemistry. The impact of the ether functional group on the transition states was investigated by comparing reactions with identical ring size, peroxy, and radical positions but with the ether functional group positioned either outside or inside the transition state ring. Compared to analogous alkane rate constants, differences of up to an order of magnitude were observed. We applied the new rate constants in the di-iso-butyl ether kinetic model and evaluated their influence on low-temperature autoignition chemistry and found that they altered the chain-propagation/chain-branching ratios by up to a factor of 9. The results of this foundational work were published in a peer-reviewed journal article (Mohamed, et al., 2024).

### **References:**

- Kim, Y., Cho, J., Naser, N., Kumar, S., Jeong, K., McCormick, R.L., St John, P.C., Kim, S. “Physics-informed graph neural networks for predicting cetane number with systematic data quality analysis” Proc Comb Inst doi.org/10.1016/j.proci.2022.09.059 (2023a). <https://www.osti.gov/biblio/1905807>.
- Kim, Y., Kumar, S., Cho, J., Naser, N., Ko, W., St. John, P.C., McCormick, R.L., Kim, S. “Designing high-performance fuels through graph neural networks for predicting cetane number of multicomponent surrogate mixtures” SAE Technical Paper No. 2023-32-0052 (2023b).
- Kim, Y., Cho, J., Jung, H., Meyer, L.E., Fioroni, G.M., Jeong, K., McCormick, R.L., St. John, P.C., Kim, S. “Design Green Chemicals by Predicting Vaporization Properties Using Explainable Graph Attention Networks” Green Chemistry doi.org/10.1039/D4GC01994F (2024).
- McCormick, R.L., Fioroni, G.M. Mohamed, S.Y., Naser, N., Alleman, T.L., Kim, S., Kar, K.C.H., Wang, Z., Lin, Y., Ju, Y. “Fuel Property Evaluation of Biodiesel Containing  $\beta$ -hydroxy FAME from Engineered Microorganisms” Fuel Communications doi.org/10.1016/j.jfueco.2024.100120. (2024).
- McCormick, R.L., Luecke, J., Mohamed, S.Y., Fioroni, G.M., Naser, N., Alleman, T.L., Kim, S., Lanci, M., Kar, K. “Properties and autoignition reactivity of diesel boiling range ethers produced from Guerbet alcohols” Fuel Communications doi.org/10.1016/j.jfueco.2024.100131 (2025).

Mohamed, S.Y., Naser, N., Kim, Y., Fioroni, G.M., St. John, P.C., McCormick, R.L., Kim, S. “A comparison between methyl hexanoate and methyl 3-hydroxyhexanoate reactivity: flow reactor experiment and kinetic study” Combustion and Flame **258** 113071 (2023).

Mohamed, S.Y., Kim, Y., Fioroni, G.M., Kim, S., McCormick, R.L. “High-Pressure Rate Rules for Ether Alkylperoxy Radical Isomerization” J Phys Chem A doi.org/10.1021/acs.jpca.4c04840 (2024).

Naser, N., Mohamed, S.Y., Fioroni, G.M., Kim, S., McCormick, R.L. “Chemical kinetics investigation of dibutyl ether isomers oxidation in a laminar flow reactor” Energy Fuels doi:10.1021/acs.energyfuels.4c03432 (2024).

**Subject Inventions Listing:**

None.

**ROI #:**

None.