I.1 Diesel-like Fuels, Combustion, and Emissions

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Project Introduction

The need to reduce the carbon footprint from medium- and heavy-duty diesel engines is clear; low-carbon biofuels are a powerful means to achieve this. Liquid fuels are rapidly deployed because existing infrastructure can be utilized for their production, transport, and distribution. Their impact is unique as they can decrease the greenhouse gas (GHG) emissions of existing vehicles and in applications resistant to electrification. However, introducing new diesel-like bio-blends into the market is very challenging. At a minimum, it requires a comprehensive understanding of the life-cycle GHG emissions of the fuels, the implications for refinery optimization and economics, the fuel's impact on the infrastructure, the effect on the combustion performance of current and future vehicle fleets, and finally the implications for exhaust aftertreatment systems and compliance with emissions regulations. Such understanding is sought within the Co-Optima project.

Objectives

Efforts within the Co-Optima projects discussed in this report provide industry with the fundamental scientific understanding necessary to commercialize new diesel-like biofuels and advanced engine technologies.

Overall Objective

- Identify technically and economically attractive diesel-like bio-blendstocks with the potential to reduce GHG emissions by 60% or more compared to fossil-derived diesel fuel.
- Demonstrate abilities to overcome barriers to commercialization of otherwise-attractive bio-blendstocks.
- Quantify benefits of bio-blendstocks on performance and emissions of current and future diesel engines.

Fiscal Year 2021 Objectives

- Summarize efforts to analyze and evaluate diesel-like bio-blendstocks and their production pathways; identify the most attractive options to-date in a detailed, publicly available technical report.
- Quantify benefits of oxygenated bio-blendstocks in advanced diesel combustion regimes, including low-temperature, premixed compression-ignition combustion and mixing controlled, compression-ignition combustion with ducted fuel injection.

Approach

The Co-Optimization of Fuels & Engines (Co-Optima) project is sponsored by the U.S. Department of Energy through the Vehicle Technologies and Bioenergy Technologies Offices of the Office of Energy Efficiency and Renewable Energy. The large, multidisciplinary project team includes researchers at National Renewable Energy Laboratory, as well as Argonne, Idaho, Lawrence Berkeley, Lawrence Livermore, Los Alamos, Oak

Ridge, Pacific Northwest, and Sandia National Laboratories. Additionally, research staff from many universities and industrial partners contribute to this first-of-its-kind collaboration.

A three-tiered screening approach guides the work of multiple teams to identify attractive diesel-like bio-blendstocks and rank them according to their benefits. Tier 1 screening involves quantitative characterization of thousands of candidates through computational methods and testing of small quantities as needed to provide information about their suitability as diesel-like fuels. Blends of attractive candidates with fossil diesel fuel are evaluated in tier 2 screening to determine if the blends can meet ASTM D975 specifications for diesel fuels. Research efforts are devoted to overcoming barriers to commercialization for otherwise attractive candidates. Finally, the most attractive candidates are comprehensively evaluated in tier 3 screening. These evaluations include techno-economic analyses (TEA), life-cycle analyses (LCA) for a full range of production pathways, refinery blending analyses, and experiments in a variety of research engines and operating conditions.

Results

Key accomplishments for this fiscal year include:

- Publication of 13 low-carbon bio-blendstocks and associated production pathways with potential for reduced pollutant emissions and improved engine operability.
- Quantification of the benefits bio-blendstocks for advanced low-temperature premixed combustion to enable low-NOx combustion at low loads with low exhaust temperatures.
- Demonstration of synergies between ducted fuel injection and oxygenated, low-net-CO_2 fuels for significant, simultaneous reductions in engine-out soot, NO_x, and CO2 emissions.

To date, 13 technically and economically viable bio-blendstocks have been identified that have significant potential to reduce GHG emissions. These are summarized in Figure I.1-1 and are classified by molecule type. Eight of the blendstocks meet fuel property requirements and have minimal barriers to adoption; some are already commercially available, such as biodiesel and renewable diesel. The remaining five bio-blendstock candidates – an ester and all of the ethers – show significant potential to reduce emissions, but present at least one barrier to adoption and use. These barriers are typically associated with one or more of the following: feedstock costs and availability; insufficient or incompatible properties; and excessive GHG emissions in currently available production pathways.
Co-Optima researchers have previously demonstrated their ability to address barriers to commercialization. For example, polyoxymethylene ethers (POMEs) exhibit high (undesirable) water solubility and insufficient

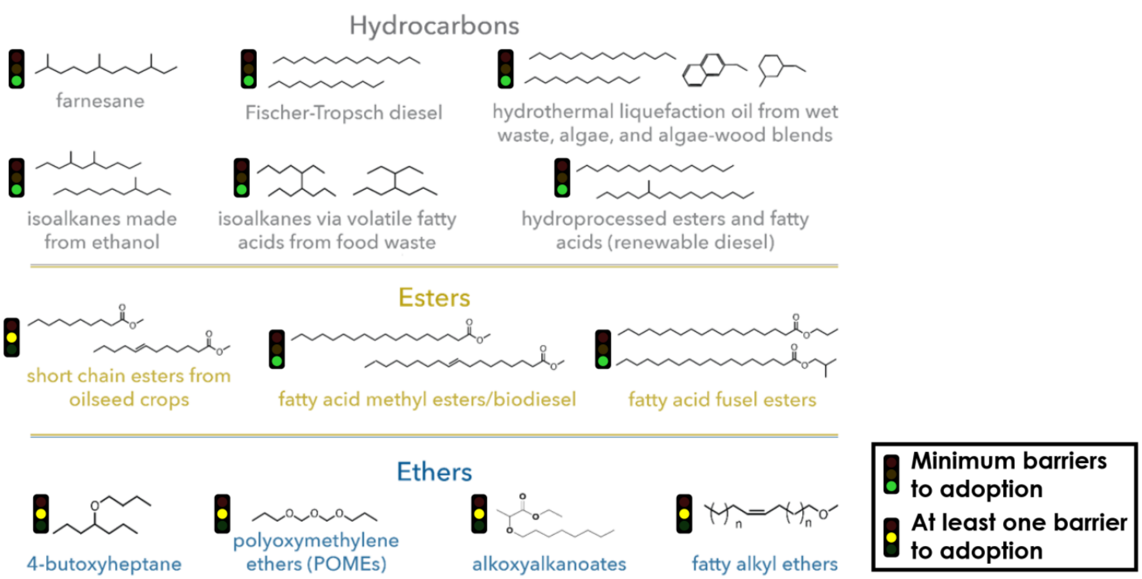
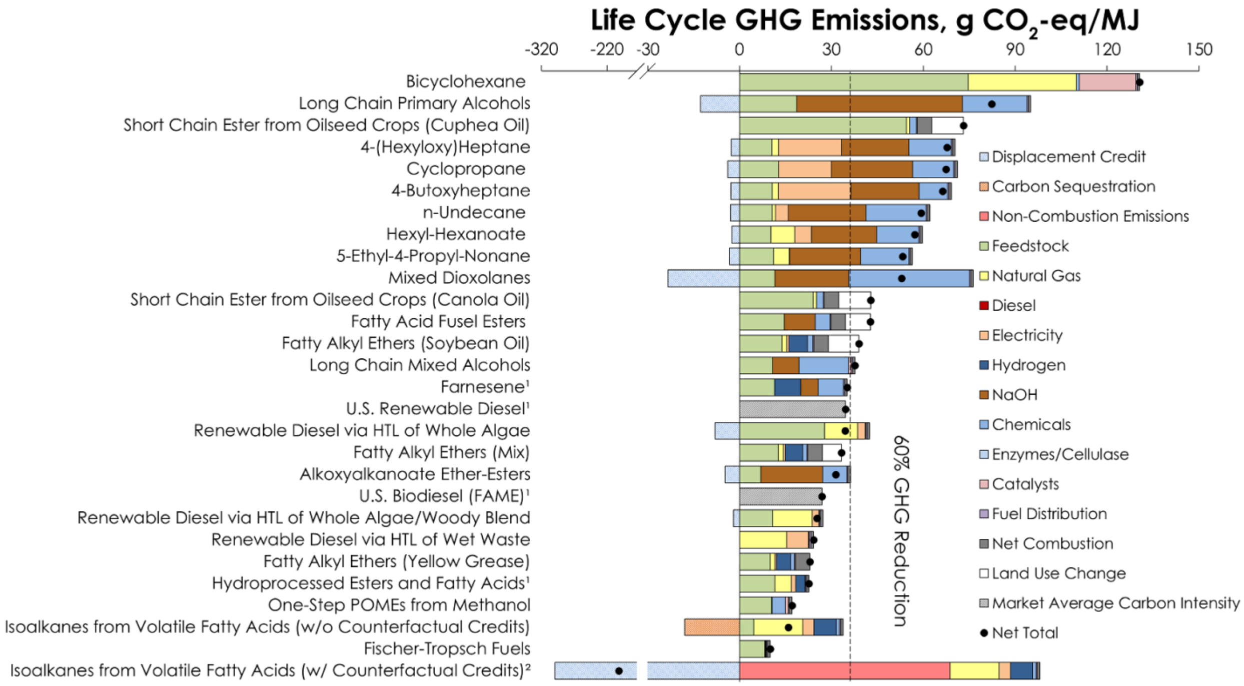


Figure I.1-1: The 13 most promising blendstocks with potential to reduce GHG and other pollutant emissions. There are six hydrocarbons, three esters, and four ethers; five candidates have significant potential to reduce emissions but have at least one significant barrier to adoption and use.

heating values. Researchers identified a modified structure of these molecules to mitigate these barriers, as well as a process to produce the altered POME blend from biomass [1]. Thus, further research and development efforts may be expected to improve the viability of some of these candidates. Details about the discovery, production, and screening processes, as well as the analyses and engine-based research that supported the selection of these 13 bio-blendstock candidates are documented in a comprehensive report [2]. Complete life-cycle analyses have been performed on more than two dozen bio-blendstock candidates and production pathways. To date, over a dozen solutions have been identified that meet or exceed the target of 60% reduction of GHG emissions, when compared to fossil diesel fuel (see Figure I.1-2). This level of



¹ *GHG emissions of these pathways are from either an earlier study or average of market fuels.*

² *The negative GHG emissions from the "Isoalkanes from Volatile Fatty Acids" pathway is because of the credits of avoided emissions from landfill of the food waste feedstock.*

Figure I.1-2: Life cycle GHG emissions for diesel-like bio-blendstock candidates by GHT source. Black dots denote net GHG emissions. SO: soybean oil; YG: yellow grease; Mix: 60:40 mix of SO and YG.

reduction is compared to a 2005 baseline and is the EPA requirement for a renewable cellulosic biofuel. More details of this analysis may be found in reference [2]. Indeed, GHG emissions can be significantly reduced with a multitude of feedstocks, bio-blendstocks, and production pathways. GHG-negative fuels are possible by utilizing food waste that would otherwise emit GHGs while decomposing in a landfill.

Beneficial effects of bio-blendstocks on engine-out pollutant emissions have previously been shown by engine testing with multiple candidates for conventional diesel combustion (CDC) [3]. Current research at Oak Ridge National Laboratory focuses on the impact of oxygenated biofuels on advanced compression ignition combustion at low engine loads, when exhaust temperatures may not be hot enough to maintain NO_x-aftertreatment catalysts above their light-down temperature. For these experiments, hexyl hexanoate (HH), a short-chain ester, and dibutoxymethane (DBM), a surrogate for the altered POME blend described above, are blended with certification diesel fuel at 25 vol%. A low-load, premixed charge compression ignition (PCCI) combustion strategy is developed with a late fuel injection to achieve autoignition of a highly premixed fuel-air mixture. The key advantage of this combustion regime is that the high degree of premixing reduces local equivalence ratios so that nitrogen oxide (NO_x) formation is suppressed. Indeed, Figure I.1-3 shows that both NO_x and unburned hydrocarbon (HC) emissions are reduced by 94% and 49%, respectively. However, these benefits come at the expense of increased carbon monoxide (CO) emissions. Both the HH and DBM blends act to further reduce engine-out NO_x and HC emissions, and the DBM blend helps mitigate the penalty in CO emissions. Similar findings have also been observed in transient tests while switching between conventional

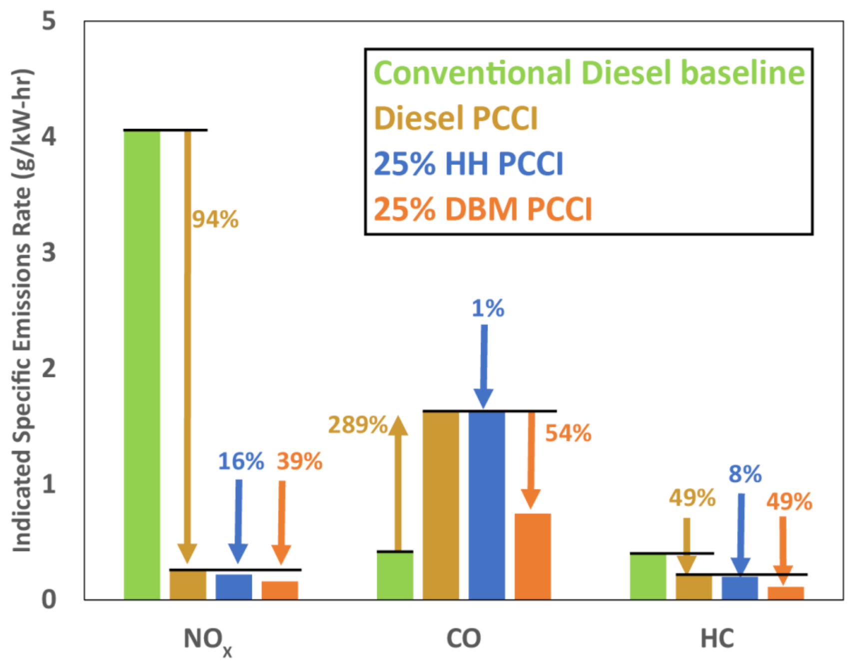


Figure I.1-3: The effects of a PCCI combustion strategy and the use of oxygenated fuel blends on emissions of NOx, CO, and HCs. Some oxygenated compounds may help mitigate penalties in CO emissions that result from PCCI combustion.

diesel combustion and PCCI combustion Thus, the combination of advanced compression ignition and bio-blendstocks may help achieve compliance with upcoming ultra-low NO_x emissions standards.

A study conducted at Sandia National Laboratories quantifies the potential reductions in engine-out soot, NO_x, and net carbon dioxide (CO_2) emissions that can be obtained by using ducted fuel injection (DFI) in combination with dilution (i.e., lower intake-oxygen mole fractions) and sustainable fuels with varying levels of oxygenation in a heavy-duty application. A set of four fuels is used: CFC, HEA00, HEA33, and HEA67. "CFC" denotes a No. 2 petroleum diesel certification fuel. "HE" denotes a 50/50 blend by volume of low-net-CO_2 diesel fuels produced by hydrothermal liquefaction and the ethanol-to-diesel process, respectively, provided by Pacific Northwest National Laboratory. The "Axx" after "HE" denotes the volumetric content of a low-net-CO2 alkoxyalkanoate (AOA) blendstock in the HE base fuel, which in the current experiments is isopentyl 2-isopentyloxy propanoate provided by Sandia National Laboratories' biofuels production group. Different AOA fractions are tested to explore the effects of increasing the oxygen content of the fuel. Experiments are conducted for all four fuels, for CDC and DFI, at moderate load (1200 rpm, 10 bar gross indicated mean effective pressure [IMEPg]) and idle (700 rpm, 1.0 bar IMEPg), and at two different dilution levels for CDC and DFI (18% and 16% oxygen for CDC, 16% and 14% for DFI). A total of 32 experimental conditions are tested in the 1.72-liter, optical, single-cylinder engine.

The preliminary experimental results are shown in Figure I.1-4. At moderate load (Figure I.1-4a), moving from the orange-circled point on the right to the one on the left represents decreases in engine-out soot and NO_x emissions of 92% and 83%, respectively. The results at idle (Figure I.1-4b) are also quite compelling, with decreases in engine-out soot and NO_x emissions of 93% and 80%, respectively. Each line connects operating points whose only primary difference is in intake-oxygen mole fraction. For each condition, increasing the oxygen content of the fuel lowers soot emissions. Switching from CDC to DFI at constant dilution also yields lower soot emissions. These combined soot benefits enable the use of increased dilution to achieve the observed reductions in NO_x emissions. The net-CO_2 emissions for HEA00, HEA33, and HEA67 are 82%, 76%, and 70% lower, respectively, than for CF_C, due to the lower net-CO_2 contents of the sustainable fuels (Figure I.1-2, reference [2]). DFI with HEA33 or HEA67 fuel might enable the removal of the diesel

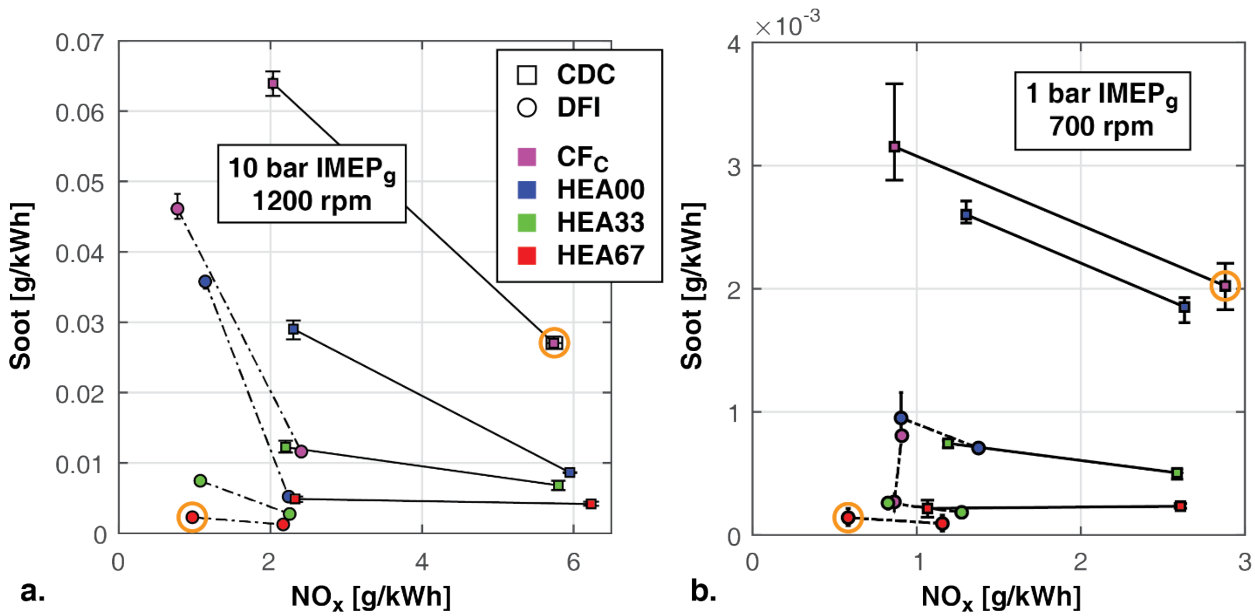


*Figure I.1-4: Trade-off plots showing engine-out soot and NOx emissions for CDC vs. DFI for four fuels and two dilution levels at (**a.**) moderate load and (**b.**) idle conditions. At least three replicate experiments are conducted at each operating condition.*

particulate filter (DPF), because the engine-out soot emissions are lower than the 0.02 g/kWh Tier 4 Final standard for off-road engines with power ratings of 130 – 560 kW. This would substantially reduce the aftertreatment-system cost and increase the engine efficiency via lower backpressure and obviation of DPF regenerations. Upgrades are currently underway to increase the peak cylinder pressure of the optical engine to 20 MPa, to determine whether the observed promising trends extend to full-load conditions.

Conclusions

Co-Optima research has identified a multitude of technically viable, economically relevant bio-blendstocks and production pathways with strong potential for reduced, or even negative, GHG emissions. Beneficial effects of these blendstocks on advanced combustion strategies have been demonstrated:

- Oxygenated bio-blendstocks can help mitigate penalties in CO with low-temperature, advanced compression-ignition combustion strategies, which may enable compliance with future low-NO_x emissions regulations.
- Oxygenated, low-carbon biofuels work synergistically with ducted fuel injection to achieve significant reductions in soot, NO_x, and CO2 emissions, which may also help reduce exhaust aftertreatment costs.

Key Publications

1. Arellano-Treviño, M. A., Bartholet, D., To, A. T., Bartling, A. W., Baddour, F. G., Alleman, T. L., Christensen, E. D., Fioroni, G. M., Hays, C., Luecke, J., Zhu, J., McEnally, C. S., Pfefferle, L. D., Reardon, K. F., Foust, T. D. and Ruddy, D. A. 2021. "Synthesis of Butyl-Exchanged Polyoxymethylene Ethers as Renewable Diesel Blendstocks with Improved Fuel Properties." *ACS Sustainable Chemistry & Engineering* 9(18): 6266-6273. DOI: 10.1021/acssuschemeng.0c09216.

2. Bartholet, D. L., Arellano-Treviño, M. A., Chan, F. L., Lucas, S., Zhu, J., St. John, P. C., Alleman, T. L., McEnally, C. S., Pfefferle, L. D., Ruddy, D. A., Windom, B., Foust, T. D. and Reardon, K. F. 2021. "Property predictions demonstrate that structural diversity can improve the performance of polyoxymethylene ethers as potential bio-based diesel fuels." *Fuel* 295: 120509. DOI: https://doi.org/10.1016/j.fuel.2021.120509.

3. Mueller, C.J., Nilsen, C.W., Biles, D.E., and Yraguen, B. 2021. "Effects of fuel oxygenation and ducted fuel injection on the performance of a mixing-controlled compression-ignition optical engine

with a two-orifice fuel injector." *Applications in Energy and Combustion Science* (6): 100024. https://doi.org/10.1016/j.jaecs.2021.100024.

References

[1] U.S. Department of Energy Bioenergy Technologies Office. May 2021. "Co-Optima FY20 Year in Review report." *DOE/EE-2341*. Available online: https://www.energy.gov/eere/bioenergy/co-optima-fy20-year-review-report. Accessed 10/28/2021.

[2] Gaspar, D. J. 2021. "Top 13 Blendstocks Derived from Biomass for Mixing-Controlled Compression-Ignition (Diesel) Engines: Bioblendstocks with Potential for Lower Emissions and Increased Operability." PNNL-31421. Pacific Northwest National Laboratory, Richland, WA.

[3] Burton, J., Martin, J., Fioroni, G., Alleman, T. et al., "Fuel Property Effects of a Broad Range of Potential Biofuels on Mixing Control Compression Ignition Engine Performance and Emissions," *SAE Technical Paper* 2021-01-0505, 2021, https://doi.org/10.4271/2021-01-0505.

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Acronyms, Abbreviations, Symbols, and Units

AOA	Alkoxyalkanoate
ASTM	American Society for Testing and Materials (ASTM International)
CO	Carbon monoxide
CO_2	Carbon dioxide
DBM	Dibutoxymethane
DFI	Ducted fuel injection
DPF	Diesel particulate filter
EGR	Exhaust gas recirculation
GHG	Greenhouse gas
HC	Hydrocarbon
HH	Hexyl hexanoate
IMEPg	Gross indicated mean effective pressure
LCA	Life-cycle analysis/analyses
NO_x	Oxides of nitrogen
PCCI	Premixed-charge compression ignition
POME	Polyoxymethylene ether
TEA	Techno-economic analysis/analyses