U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Co-Optimization of Fuels & Engines

Functional Group Analysis for Diesel-like Mixing-Controlled Compression Ignition Combustion Blendstocks

DISCLAIMER

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161
ph: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

This document was printed on recycled paper.
(9/2003)

About the Co-Optimization of Fuels & Engines Project

This is one of a series of reports produced as a result of the Co-Optimization of Fuels & Engines (Co-Optima) project, a Department of Energy (DOE)-sponsored multi-agency project initiated to accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission vehicle engines. The simultaneous fuels and vehicles research and development is designed to deliver maximum energy savings, emissions reduction, and on-road performance.

Co-Optima brings together two DOE Office of Energy Efficiency & Renewable Energy (EERE) research offices, nine national laboratories, and numerous industry and academic partners to make improvements to the types of fuels and engines found in most vehicles currently on the road, as well as to develop revolutionary engine technologies for a longer-term, higher-impact series of solutions. This first-of-its-kind project will provide industry with the scientific underpinnings required to move new biofuels and advanced engine systems to market faster while identifying and addressing barriers to commercialization.

In addition to the EERE Vehicle Technologies and Bioenergy Technologies Offices, the Co-Optima project team includes representatives from the National Renewable Energy Laboratory and Argonne, Idaho, Lawrence Berkeley, Lawrence Livermore, Los Alamos, Oak Ridge, Pacific Northwest, and Sandia National Laboratories. More detail on the project, as well as the full series of reports, can be found at www.energy.gov/fuel-engine-co-optimization.

Availability

This report is available electronically at no cost from http://www.osti.gov/bridge.

Citation

Please cite as follows:

Gaspar, Daniel J., Robert L. McCormick, Eugene Polikarpov, Gina M. Fioroni, Anthe George, and Karl O. Albrecht. *Functional Group Analysis for Diesel-like Mixing-Controlled Compression Ignition Combustion Blendstocks* (Technical Report) Pacific Northwest National Laboratory, 2016. osti link

Note

Report Contributors and Roles

Lead Author(s)

Lead author

Daniel J. Gaspar, Pacific Northwest National Laboratory

Co-lead author

Robert L. McCormick, National Renewable Energy Laboratory

Co-Author(s)

Evgueni Polikarpov, Pacific Northwest National Laboratory

Gina M. Fioroni, National Renewable Energy Laboratory

Anthe George, Sandia National Laboratories

Karl O. Albrecht, Pacific Northwest National Laboratory

Acknowledgments

This report and the work described were sponsored by the U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) and Vehicle Technologies Office (VTO) under the DOE Co-Optimization of Fuels and Engines Initiative. The authors gratefully acknowledge the support and direction of Alicia Lindauer at BETO, Kevin Stork at VTO, and the Co-Optima leadership team.

The following U.S. Department of Energy Office of Energy Efficiency and Renewable Energy (EERE) officials and managers played important roles in establishing the project concept, advancing implementation, and providing ongoing guidance:

Reuben Sarkar, Deputy Assistant Secretary for Transportation

Bioenergy Technologies Office
Jonathan Male, Director
Alicia Lindauer, Technology Manager
Borka Kostova, Technology Manager

Vehicle Technologies Office
Michael Berube, Director
Gurpreet Singh, Program Manager, Advanced Combustion Engines Program
Kevin Stork, Technology Manager, Fuel Technologies and Deployment
Leo Breton, Technology Development Manager
Mike Weismiller, Technology Development Manager

The national laboratory project management team consisted of:

John Farrell (Technical Monitor), National Renewable Energy Laboratory (NREL)
John Holladay, Pacific Northwest National Laboratory (PNNL)
Robert Wagner, Oak Ridge National Laboratory (ORNL)

Table of Contents

List of Tables ..... **v**

Abbreviations and Acronyms ..... **vi**

Executive Summary ..... **vii**

1 Introduction **1**

1.1 Purpose 1

1.2 Background 1

1.3 Research Methodology and Approach 1

1.4 Overview of Content 2

2 Diesel Fuel Property Requirements **3**

2.1 Discussion of Diesel-Like Fuel Properties 3

2.2 Fuel Property and Chemistry Effects on Emissions and Fuel Economy 5

3 Functional Groups **7**

4 Conclusions **11**

References **12**

List of Tables

Table 2-1. Fuel property specifications for diesel fuel……...…….3
Table 3-1. Functional Groups for Diesel-Like Thrust II Bio-Blendstocks……...……..…….7

Abbreviations and Acronyms

ACI	Advanced compression ignition
CN	Cetane number

Executive Summary

Purpose

This report addresses the suitability of hydrocarbon and oxygenate functional groups for use as a diesel-like fuel blending component in an advanced, mixing-controlled, compression ignition combustion engine. The functional groups are chosen from those that could be derived from a biomass feedstock, and represent a full range of chemistries. This first systematic analysis of functional groups will be of value to all who are pursuing new bio-blendstocks for diesel-like fuels.

We have analyzed the suitability of various functional groups that may be obtained by conversion of biomass, and report their suitability for use as a blendstock in a diesel-like fuel for Co-Optima Thrust II (advanced compression ignition, or ACI) engine. We used the diesel fuel ASTM specifications as the basis for this analysis, along with the potential to improve efficiency and/or emissions performance in an advanced ACI engine. Seven functional groups were analyzed in detail (and another two – aldehydes and carboxylic acids – excluded *a priori* based on our Thrust I analysis), including seventeen variants. Of these seventeen variants, thirteen were determined to have at least fair potential, or were completely unknown as diesel-like blendstocks or fuels in an ACI engine. The results of this analysis will help focus efforts to identify diesel-like Thrust II blendstocks and fuels which can be used with modified combustion strategies to improve system efficiency and reduce harmful emissions within the Co-Optimization of Fuels and Engines program.

Results Highlights

This report details the systematic analysis of diesel boiling range bio-blendstock molecular functionality effects on fuel properties that are desirable for this type of fuel.

By evaluating the fuel properties of a large, and aspirationally all-inclusive list of functional groups comprising the entirety of diesel boiling range fuel molecules, we have identified those with the most promising properties for improving diesel engine-emission control system efficiency. Additionally, we learn about the full range of fuel properties available and observe the extent to which they fall outside the range accessible with conventional petroleum-derived fuels. Fuels with unusual properties may provide opportunities for innovative engine designs and operational strategies. The results of this analysis point the Co-Optima program in potentially fruitful directions.

Key Conclusions

Our analysis indicates that many biomass-derived chemistries may be suitable for use as mixing-controlled ACI combustion fuel or blendstocks. Among those materials worthy of further investigation, we find:

- Ethers, including glymes derived from propylene glycol, acetals and other polyethers
- Ketones, including polyketides
- Alkanes, including n-alkanes and iso-alkanes

- Alkenes, including mono-alkenes and possibly some di-alkenes
- Esters, including saturated and some unsaturated esters, and lactones (cyclic esters)
- Alcohols, especially with little or no branching and chain lengths of at least nine carbons

This rich set of chemistries has the potential to produce blendstocks that improve engine performance, primarily through reduced emissions and resulting in improved system efficiency, to meet the goals of the Co-Optima program. These results for the basis for Tier 2 screening, and will guide near-term research activities for the High Performance Fuels team, along with the rest of the Co-Optima program.

1 Introduction

1.1 Purpose

The Co-Optimization of Fuels and Engines (Co-Optima) project is focused on the co-development of advanced fuels and engines to improve the overall system performance, including both efficiency and emissions. One research thrust within Co-Optima is focused on the development of engine-fuel combinations which offer improved performance for advanced compression ignition (ACI) engines which use a mixing-controlled combustion strategy, such as modern diesel engines. This analysis is intended to inform the development of new bio-blendstocks for use in these engines by bounding the search space for biomass conversion experts. The development of biomass-derived fuel molecules and mixtures will benefit from a systematic and comprehensive approach to understand the suitability of the full range of functional groups for use in diesel-like ACI engines. This approach will narrow the search space for Co-Optima researchers by reducing the number of target functional groups, and by providing some general guidelines as to the structure of potential materials within a functional group class.

1.2 Background

Co-Optima builds upon a rich history of research and development focused on the generation of new fuels and blendstocks for diesel-like engines. This history includes the development and approval of biodiesel, primarily consisting of fatty acid methyl esters, or FAMEs, at levels up to 20%. Petroleum-based diesel fuels consist primarily of alkanes (also known as paraffins), with some aromatic hydrocarbons present as well. In addition to the wide range of hydrocarbons that are present in petroleum-based diesel fuels, many other molecules have been evaluated for use in diesel engines in terms of autoignition requirements (cetane number). The results of many of these measurements are found in the literature, and tabulated in the NREL cetane number compendium (NREL 2014).

Despite the history of research into the effects of new blendstocks and fuels on diesel engine performance, there persists a pressing need to systematically evaluate the suitability of the full range of materials that could be generated from alternative feedstocks with the potential to reduce harmful emissions and improve overall system performance (whether by increases in engine efficiency or by reducing the energy penalty associated with the emissions control system on the vehicle). This is a necessary first step toward co-optimizing the performance of this engine-fuel combination.

1.3 Research Methodology and Approach

This analysis was performed in three steps to ensure a comprehensive but manageable approach. First, the specifications for diesel fuel were analyzed in the context of new bio-blendstocks. These specifications were used as a starting point for establishing a minimum set of requirements for Co-Optima blendstocks. Where appropriate, more stringent requirements are suggested as a starting point for future discussions with the rest of the Co-Optima program.

Second, the range of hydrocarbon and oxygenate chemistries were examined for their suitability as diesel-like bio-blendstocks in the context of the diesel requirements and what is known about their properties, as a class. Of course, individual molecules possess properties which may vary widely from the general properties of a group, and individual molecules may or may not be

suitable from any functional group class. Nonetheless, this analysis should reduce the search space considerably by focusing our efforts on those classes of molecules most likely to be suitable.

Finally, the physical and chemical properties of candidate molecules from those classes considered most promising were examined, and compared to the specifications established in Section 2. The results of this analysis were used to confirm the suitability of these classes of molecules.

1.4 Overview of Content

The rest of the report consists of three additional sections. In Section 2, we detail the fuel properties that are most relevant to efficiency and emissions performance. In Section 3, we describe our systematic assessment of the functional groups, which have been demonstrated or hypothesized to be generated from biomass. In Section 4, we provide examples of candidate molecules which we believe meet the requirements detailed in Section 2, and will be assessed in future Tasks.

2 Diesel Fuel Property Requirements

While we do not presuppose the combustion conditions and requirements pending a detailed development of a merit function with well-justified terms and values, we propose that diesel fuel specifications provide a solid starting point for analysis. In particular, the suite of physical properties is likely to be the same, subject to adjustment or modification as the merit function is established. The analysis requires that we bound the molecular structure by factors such as number of carbons, carbon connectivity and branching, type and chemical state of heteroatoms such as O or N, and which heteroatoms may be permissible. This can be done by reference to the structure-property relationships established for hydrocarbons and many simple oxygenates. Less common chemistries will require additional property measurement.

Combustion properties, especially autoignition as embodied in cetane number, have been measured for many potential candidates and serve as a very useful basis for evaluation of classes of molecules, even if specific candidates have not been measured. We also note that reducing criteria emissions has the potential to improve overall system efficiency losses associated with emissions control technology energy consumption and system trade-offs. This is discussed in more detail below.

Finally, key properties such as toxicity (acute toxicity, teratogenicity, etc.), biodegradability, and water solubility play key roles in determining whether a particular material is appropriate for widespread use. These are also evaluated for each functional group, with the caveat that each individual material (molecule or mixture) should be no more toxic than our existing fuels. Furthermore, criteria emissions – particulate matter, carbon monoxide, nitrogen oxides and non-methane hydrocarbons – should be improved by the inclusion of the Co-Optima ACI bio-blendstock.

2.1 Discussion of Diesel-Like Fuel Properties

Table 2.1 list important properties for diesel fuels, taken from ASTM D975 Standard Specification for Diesel Fuel Oils and other industry specifications. Probably the most critical properties for defining a diesel-like fuel are boiling point (or distillation curve), cetane number (CN), and flashpoint. The T90 of a mixture blendstock should meet the maximum T90 requirement for diesel fuels and a single component blendstock should have a boiling point well below the maximum allowable T90 of 338°C. Diesel fuels are highly reactive – they ignite readily upon injection into the engine. The property that ensures adequate reactivity is a minimum CN of 40. Within certain bounds defined by economics, cetane improver additives such as 2-ethylhexylnitrate can be used to increase CN, so potentially a bio-blendstock with a lower CN could be used if it was low-cost and had other significant fuel property advantages. A minimum flashpoint is required for safe handling of the fuel and ensures that the vapor space above the fuel in a retail or vehicle fuel tank is not flammable.

Table 2-1. Fuel property specifications for diesel fuel.

Property	Value	Test method
Cetane number[1]	>40 (minimum)	ASTM D613, D6890, D7170
Viscosity[1]	1.9-4.1 cSt at 40ºC	ASTM D445

Distillation properties[1]	50% Report 90% min. 282 max. 338ºC End Point 366ºC	ASTM D86
	50% Report 90% min. 300ºC max. 356ºC End Point 421ºC	SimDis ASTM2887
Cloud point (mixtures)	*depends on location; propose -10ºC for screening mixtures	ASTM2500 (cloud point)
Flash point[1]	52ºC (minimum)	ASTM D93
Corrosion[2]	"1", 3 hrs. @ 122ºF	ASTM D130
Biodegradability	Not defined	
Toxicity	Equivalent or lower than currently compliant diesel fuel.	

[1]Colonial Pipeline Company, Specifications For Fungible 15 ppm Sulfur Diesel Fuel
[2]Fungible Product Grade Specifications, Buckeye Pipe Line Company, L.P. buckeye pipe line transportation, LLC Laurel Pipe Line Company, L.P. norco pipe line company, LLC Wood River Pipe Lines, LLC, Shipping Information Notebook, March 3, 2015

Flow properties are also important for diesel boiling range materials, and these are controlled by specifying limits on viscosity and cloud point. A minimum viscosity is required to prevent injection pump and injector leakage in some engine designs. A maximum viscosity must be met for fuel injection system design and to limit the pressure and size of pump required to inject the fuel. In cold ambient conditions, diesel may partially solidify, plugging fuel lines. ASTM D975 requires reporting of the most commonly used cold flow property, which is determination of the cloud point (ASTM D2500). The cloud point is the temperature at which the solution turns cloudy due to formation of solid particles composed of components that become insoluble at the cloud point. This corresponds to the earliest point of wax precipitation that may result in the plugging of the fuel lines or filters. The use of cold flow improver additives, design of engine and fuel transfer system design and operating conditions all may result in the successful use of the fuel in ambient conditions below the cloud point. The Low Temperature Flow Test (LTFT) (ASTM D4539) and the Cold Filter Plugging Point Test (CFPP) (ASTM D6371) are useful when determining the suitability of diesel fuel for cold temperatures in vehicles and heavy trucks when flow improver additives are utilized. Currently, distributors, producers and end users in the United States use cloud point, CFPP and LTFT to estimate vehicle low temperature operability limits for diesel fuel as no single test has been found adequately describe the performance of all fuels in all vehicles. Due to the variety of regional and seasonal temperatures across the United States, ASTM D975 does not specify a single suitable cloud point, LTFT or CFPP temperature. Instead, the specification provides guidance that fuel suppliers and purchasers agree on acceptable properties utilizing the 10^{th} percentile minimum air temperatures for the U.S as guidance. The minimum air temperature specifications are generally provided by state, although some additional regional resolution within states is provided. January is among the most extreme winter months, with the range in the continental U.S. of -34°C in Minnesota to 3°C in the southern region of Florida. Temperatures in Alaska in January range from -19°C in the southern region to -49°C in the northern region. We propose to limit freezing point for pure component bio-blendstocks to a maximum of 0°C given that soy-derived biodiesel is widely used

and has this cloud point. For mixture bio-blendstocks we propose a maximum cloud point of -10°C for initial screening purposes, recognizing that complex thermochemical process-derived mixtures would likely be tailored for local seasonal and market requirements similar to the situation with conventional diesel fuels today.

Ultimately the solubility of a bio-blendstock in conventional diesel at low temperatures is the critical performance property. Assessment of blend properties will occur in the second phase of this Co-Optima project on diesel blendstocks.

Other properties are also specified by ASTM and similar industry standards. These include conductivity and lubricity, which are typically met through the use of fuel additives and thus do not need to be specified for bio-blendstocks. Bio-blendstocks that impart conductivity and lubricity to the fuel would eliminate the need for these additives which would provide a small economic advantage, however these are fuel blend properties that will be assessed at a later stage of the Co-Optima program. Corrosion is specified by the ASTM D130 Copper Corrosion Test. For pure component blendstocks any corrosion would be caused by impurities remaining in the fuel from the production process, and for mixtures control of acids to below 0.5 mg KOH/g would likely be adequate to prevent corrosion.

Oxidation stability is also important for storage and handling, and for protection of the engine's high temperature/high pressure fuel injection system. There is no widely accepted test for conventional diesel fuel oxidation stability. However, McCormick and co-workers (McCormick 2015) have utilized the Rapid Small Scale Oxidation Test (RSSOT) method ASTM D7545 to assess stability of diesel-oxygenate blends. This is essentially a finished fuel blend property and will be assessed in the next phase of the Co-Optima program.

Bio-blendstock toxicity and biodegradability are properties that should be considered for the bio-blendstocks. Toxicity should be no greater than that of conventional diesel, and known human carcinogens and reproductive toxins should be excluded. Biodegradability should be no worse than that of conventional diesel.

2.2 Fuel Property and Chemistry Effects on Emissions and Fuel Economy

Historically diesel vehicles have contributed a large fraction of transportation-derived NO_x and PM emission inventories yet very little to CO and unburned hydrocarbon emission inventories. Hence the focus for diesel engine development over the past few decades has been on meeting the increasingly stringent NO_x and PM emission standards while preserving high fuel economy characteristics. Today modern diesel engines and their emission control systems are a tightly integrated system. The emission control system will typically consist of a secondary fuel injector (in the exhaust), a diesel oxidation catalyst (DOC), a diesel particle filter (DPF), a urea solution injection system, a urea NO_x Selective Catalytic Reduction (SCR) catalyst, and an ammonia slip catalyst. Thermocouples, pressure sensors, and NO_x and ammonia sensors provide signals to a sophisticated engine control system. While the catalyst components can operate continuously, the DPF requires periodic heating to high temperatures to burn off accumulated soot. While actual system impacts on fuel economy are complex, the need to inject fuel into the exhaust – which is burned over the DOC to increase the DPF temperature – has a negative impact on overall fuel economy. Additionally, the buildup of ash, primarily from the engine

lubricant, on the DPF increases pressure drop over time which can also negatively impact fuel economy.

Dramatically reducing or eliminating soot formation from diesel combustion, and hence also eliminating the requirement for a DPF, would result in a significant improvement in fuel economy and potentially also a reduction in engine cost. From a fuel property perspective fuels with known routes to PM precursors (aromatics, alkenes) will produce more PM than fuels without direct reaction routes (alkanes, and many oxygenates). Oxygenates in general are well known to reduce diesel PM (engine-out), although not all functional groups are equivalent. In particular, functional groups that can react directly to form CO_2 (such as the ester group) are less effective at PM reduction [http://papers.sae.org/2004-01-1849/] compared to other molecules that also contain two oxygen atoms. However for diesel combustion there does not appear to be a predictive fuel property metric like particulate matter index in spark-ignition combustion. Soot formation tendency metrics such as oxygen extended sooting index (Barrientos 2013) or yield sooting index (McEnally 2011) may provide some guidance.

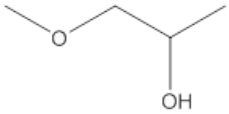
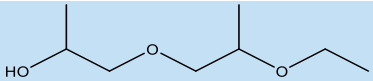
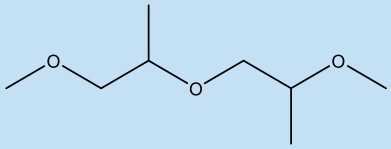
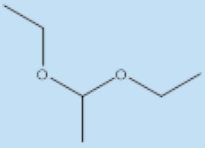
Sootless diesel combustion has been shown to be possible. In particular, Gemlich and coworkers at Sandia National Laboratory have reported a sootless leaner lifted-flame combustion using an oxygenated fuel (Gehmlich 2016). More recently the same group has shown that injecting the fuel through a duct allows leaner lifted-flame combustion to be achieved with a hydrocarbon fuel (Gehmlich 2016). Very little is known about how fuel properties and chemistry (other than oxygen content) impact or enable sootless combustion, but it seems logical that the same considerations that apply to conventional diesel combustion would also apply in this case.

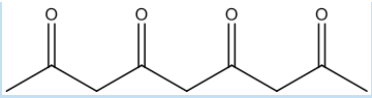
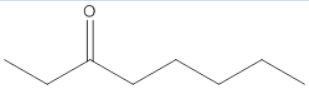
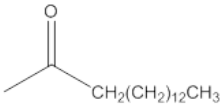
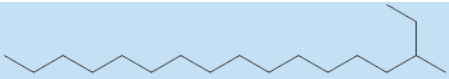
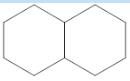
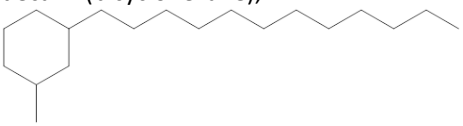
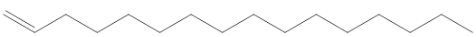
3 Functional Groups

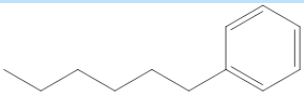
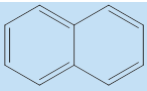
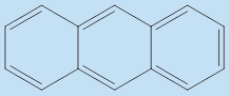
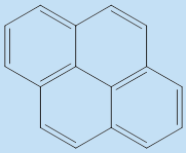
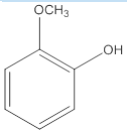
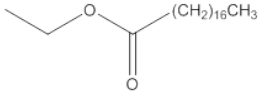
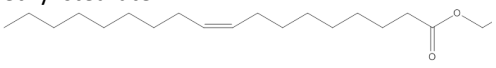
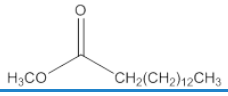
We have examined the full range of chemistries which we believe can be derived from biomass and used as a blendstocks or fuels for mixing in controlled compression ignition combustion. We have searched the literature for these materials to obtain physical properties and combustion properties, where available. We are building on the large body of work for hydrocarbons, and reasonably extensive body of work for some materials (FAMEs, other long-chain esters, ethers, alcohols) and have identified some new materials as well such as the polyketides.

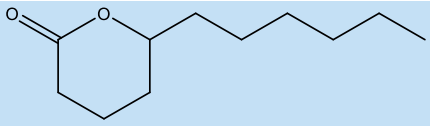
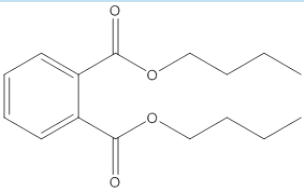
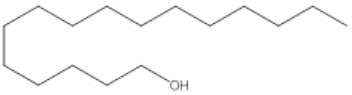
We have taken what is known regarding mixing-controlled compression ignition and used that to inform our analysis of the suitability of these materials for mixing-controlled compression ignition combustion. From the combination of these sources of information, filtered by the diesel fuel requirements detailed in Table 2-1, we have determined which functional group classes are expected to be suitable for this purpose. We describe the results of this analysis in Table 3-1. This table contains our best assessment of the suitability of each class, along with perceived potential benefits and shortcomings. We also provide examples so that the structural motifs can be compared. Note that these are only representative molecules, and it remains to identify the full suite of candidate molecules, and perform retrosynthetic analyses to ensure we have pathways to production. Finally, many processes will generate mixtures of materials, so it is important to understand the full range of potential chemistries to understand when co-products are compatible and when separations or further conversions are required.

Table 3-1. Functional Groups for Diesel-Like Thrust II Bio-Blendstocks

Functional Group	Suitability	Potential advantages/ shortcomings	Examples
Ethers			
mono-ethers R-O-R'	Very good	Pros: Very high autoignitability. CN depends upon branching. Cons: Stability; peroxide forming; materials compatibility.	 hexyl methyl ether  propylene glycol methyl ether (PGME)
polyethers, including acetals and glymes R-(O-R')n-R''	Very good	Pros: Very high autoignition propensity. Potential for reduced emissions. CN depends upon branching. Cons: Possible hydrolysis under mild aqueous acid conditions. Cost. Glymes from ethylene glycol are toxic.	 1-(2-ethoxypropoxy)-2-propanol  2-methoxy-1-(2-methoxy-1-methylethoxy)propane  n-butylal

Ketones			
Polyketides R(C=OR')nR''	Unknown	Pros: Potential for reduced emissions, similar properties as FAME, higher cetane number, lower density. Cons: Physical properties may not be appropriate (i.e., mostly solids at RT, very high BP). Many contain acidic groups and require upgrading. Limited performance data. Cost.	 Poly-beta-keto-acyl-CoA derivative
Ketones R-C(=O)-R'	Unknown	Pros: Potential for reduced emissions. May act like the longer of the carbon chains; methyl ketones may be especially interesting. Cons: Potential materials compatibility issue.	 3-octanone  2-hexadecanone
Alkanes (saturated aliphatic hydrocarbons)			
n-alkanes CH3-(CH2)n-CH3	Excellent	Pros: Outstanding diesel with increasing C#, e.g., hexadecane CN=100. Cons: Potential cost of bio-derived alkanes. No emissions benefit relative to petroleum-derived material, other than potentially diluting aromatics. High freezing point.	 hexadecane
iso-alkanes R-CH-R'R''	Excellent	Pros: Branching may improve cold flow properties. Cons: Increasing branching reduces cetane number	 2-ethylhexadecane
cyclic alkanes/ naphthenes C_nH2_n (saturated); C_nH2_n-2 (unsaturated)	Fair	Pros: Substituted napthenes may exhibit good cetane (1-methyl-3-dodecylcyclohexane ~ 70) Cons: Low cetane for unsubstituted naphthenes (decalin ~ 36). Increased sooting tendencies.	 decalin (bicyclohexane);  1-methyl-3-dodecylcyclohexane
Alkenes (unsaturated aliphatic hydrocarbons)			
alkene	Very good	Pros: Good cetane number with increasing C# and less branching, e.g., n-alkenes above C9 have CN>=50. Cons: Lower cetane number than	 1-hexadecene

		comparable alkanes. Potential stability issues.	
dienes	Fair	Pros: May be tolerable as part of mixture. Minimize content to boost CN. Cons: Lower cetane compared to mono-alkenes. Oxidative stability and gum formation may be issues.	$H_2C{=}CH(CH_2)_6CH{=}CH_2$ 1,9-decadiene
conjugated dienes/ polyenes	Poor	Pros: None Cons: Low CN. No benefit. Potential gum and/or soot formers.	
Aromatics (phenyl derivatives and polyaromatic hydrocarbons)			
mono-aromatics R-Ph	Poor	Pros: Necessary for seal swelling. Cons: Limited by regulation; soot former. Low CN: need to get to n-nonylbenzene before CN reaches 50.	 1-phenylhexane
poly-aromatics	Poor	Pros: Helps swell seals. Cons: Limited by regulation; soot former. Very low CN	 napthalene  anthracene  pyrene
oxygenated aromatics **(also see specific oxygenate functional groups)**	Poor	Pros: As a small fraction of larger mixture, may be tolerable. May help swell seals. Cons: Soot forming. Low CN.	 hydroxyanisole/guaiacol
Esters			
methyl and ethyl esters of fatty acids	Excellent	Pros: Good cetane for larger C#. Improve lubricity. Saturated and mono-unsaturated desirable. Currently used as biodiesel. Good and currently part of fuel mix up to B20. CN depends upon branching. Cons: Potential cold flow	 ethyl stearate  ethyl oleate 

		problems. Poly-unsaturated have lower CN and oxidation stability issues. Water solubility/ hygroscopicity can limit infrastructure compatibility.	n-pentadecanoic acid ester
lactones (cyclic esters)	Good/ Very good	Pros: Longer chain alkyl substituted may be good. More hydrophobic than alcohols, especially alkyl-substituted. Cons: Low MW lactones have high octane number and low CN. Higher MW may be suitable.	 δ-undecalactone
esters with aromatic groups	Poor	Pros: Longer alkyl chain substituted may show better CN Cons: aromatic moiety leads to increased particulate emissions	 dibutyl phthalate
Alcohols			
mono-functional alcohols R-OH	Good	Pros: Good CN for n-alcohols with ~C8 and higher; longer chains behave more like alkanes. CN depends upon branching. Cons: Water solubility/ hygroscopicity is high and cetane low for shorter chain length; reduced infrastructure compatibility. Melting point may pose issues with n-alcohols (iso-alcohols have lower mp).	 1-nonanol  1-hexadecanol

References consulted include but are not limited to the following and references therein: Gomez-Cuenca 2013′ Nord 2005, Santana 2006; NREL 2014, Serdari 1999, Freedman 1990, Knothe 2003, Horvath 2008, Hilden 2001, de Menezes 2005.

4 Conclusions

Previous evaluations, including the successful use of biodiesel, have demonstrated the potential of bio-blendstocks to perform adequately in diesel engines. Our analysis of available data indicates a number of functional groups may be valuable in decreasing emissions while maintaining engine efficiency, leading to overall system efficiency gains.

Molecular structure influences autoignition and combustion properties in ways that are somewhat well understood. There is still an opportunity to improve this understanding, especially for oxygenates which have received little study, and for blends and mixtures outside of the existing biodiesel realm.

Defining improvements in key properties such as CN, etc., awaits the development of a merit function, with values and weightings specific for both conventional diesel combustion and related technologies such as leaner lifted flame with ducted fuel injection. Nonetheless, these results are the beginning of a set of Tier 2 screening criteria.

References

Barrientos 2013 Barrientos, E. J., M. Lapuerta, A. L. Boehman, Group additivity in soot formation for the example of C-5 oxygenated hydrocarbon fuels. Combust. Flame 2013, 160, 1484−1498.

de Menezes 2005 de Menezes, Eliana Weber, Rosangela da Silva, Renato Cataluna, Ricardo J. C. Ortega, Effect of ethers and ether/ethanol additives on the physicochemical properties of diesel fuel and on engine tests. Fuel, 2005, 85, 815-822.

Freedman 1990 Freedman, B. and M. O. Bagby, Predicting Cetane Numbers of n-Alcohols and Methyl Esters from their Physical Properties. J. Amer. Oil Chem. Soc. 1990, 67:565. doi:10.1007/BF02540768

Gehmlich 2016 https://crcao.org/workshops/2016AFEE/Final%20Presentations/Session%204/4-4_Gehmlich,%20Ryan.pdf

Gomez-Cuenca 2011 Gomez-Cuenca, F., M. Gomez-Marin, M. B. Folgueras-Diaz, Effects of ethylene glycol ethers on diesel fuel properties and emissions in a diesel engine. Energy Convers. Mgmt., 2011, 52, 3027-3033.

Gomez-Cuenca 2013 Gomez-Cuenca, F., M. Gomez-Marin, M. B. Folgueras-Diaz, The influence of propylene glycol ethers on base diesel properties and emissions from a diesel engine. Energy Convers. Mgmt., 2013, 75, 741-747.

Horvath 2008 Horvath, Istvan T., Hasan Mehdi, Viktoria Fabos, Laszlo Boda, Laszlo T. Mika, γ-Valerolactone–a sustainable liquid for energy and carbon-based chemicals. Green Chem., 2007, 10, 238-242. DOI: 10.1039/b712863k.

Knothe 2003 Knothe, Gerhard, Andrew C. Matheaus, Thomas W. Ryan III, Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester. Fuel, 2003, 82, 971-975.

McCormick 2015 McCormick, R.L., Matthew A. Ratcliff, Earl Christensen, Lisa Fouts, Jon Luecke, Gina M. Chupka, Janet Yanowitz, Miao Tian, and Michael Boot, Properties of oxygenates found in upgraded biomass pyrolysis oil as components of spark and compression ignition engine fuels. Energy Fuels 2015, 29, 2453−2461. DOI: 10.1021/ef502893g.

McEnally 2011 McEnally, Charles S., Lisa D. Pfefferle, Sooting Tendencies of Oxygenated Hydrocarbons in Laboratory Scale Flames. Environ. Sci. Technol., 2011, 45 (6), 2498–2503. DOI: 10.1021/es103733q

Nord 2005 Nord, Kent E. and Dan Haupt, Reducing the Emission of Particles from a Diesel Engine by Adding an Oxygenate to the Fuel. Environ. Sci. Technol., 2005, 39, 6260-6265.

NREL 2014 http://www.nrel.gov/docs/fy14osti/61693.pdf

Santana 2006 Santana, Roberto C., Phuong T. Do, Malee Santikunaporn, Walter E. Alvarez, Joshua D. Taylor, Edward L. Sughrue, Daniel E. Resasco,

Evaluation of different reaction strategies for the improvement of cetane number in diesel fuels. Fuel, 2006, 85, 643-656.

Serdari 1999 Serdari, Aikaterini, Euripides Lois, Stamoulis Stournas, Impact of Esters of Mono- and Dicarboxylic Acids on Diesel Fuels. Ind. Eng. Chem. Res. 1999, 38, 3543-3548.

U.S. DEPARTMENT OF ENERGY
Energy Efficiency & Renewable Energy

Prepared by the National Renewable Energy Laboratory, Sandia National Laboratories and Pacific Northwest National Laboratory for the U.S. Department of Energy.
DOE/GO-xxxxxx-xxxx • December 2016