Fuel Properties of Oxymethylene Ethers with Terminating Groups from Methyl to Butyl

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Abstract

Oxymethylene ethers (OMEs) have been studied as possible additives or replacements for diesel fuels. Typically, studies have considered only methyl-terminated OMEs. Recent structure-property relationship models suggest that extended-alkyl OMEs may provide improvements to many of the properties of methyl-terminated OMEs that make them less suitable as diesel fuel blendstocks. In this work, we describe the synthesis and characterization of 16 different OMEs with methyl, ethyl, propyl, butyl, isopropyl, and isobutyl terminating alkyl groups with varying oxymethylene chain length. Indicated Cetane Number, Lower Heating Value, Flash Point, Density, Viscosity, Vapor Pressure, and Oxidative Stability are tested via ASTM standard methods. Additionally, Water Solubility, Boiling Point, seal material compatibility, and sooting propensity (via the Yield Sooting Index) are measured for these fuels. For diesel compatibility, all tested OMEs except smaller methyl and ethyl OMEs, and the branched isopropyl OME, meet cetane number requirements. Extending the alkyl end group increases the heating value, but all OMEs, due to their oxygen content, have heating values less than diesel; despite this, all OMEs show significant reductions in soot production per unit heating value. Only the heaviest OMEs meet diesel viscosity requirements, and most are higher density than diesel. OMEs with larger alkyl groups show the highest stability under accelerated auto-oxidation conditions. Increases in alkyl group length cause order of magnitude reduction in water solubility, from hundreds of g/L for methyl terminated OMEs to hundreds of mg/L for butyl terminated OMEs. Limited seal material testing indicates that PEEK polymers are unaffected by OMEs; while extended alkyl groups may improve compatibility with FKM (Viton), other common elastomers (NBR, silicone) remain incompatible with all tested OMEs. Overall, it is found that methyl-terminated OMEs exhibit the most potential for soot reduction, but OMEs with larger propyl and butyl terminating alkyl groups show improved compatibility with existing diesel systems.

Introduction

Compression ignition (diesel) engines are currently the most common prime mover for medium and heavy duty vehicles in the United States and around the world. Road freight accounts for roughly half of diesel consumption globally,[1] with concurrent environmental costs. In the US alone, medium and heavy duty vehicles account for approximately a quarter of greenhouse gas (GHG) emissions, and more than half of nitrogen oxide (NO_x) and particulate matter (PM) emissions.[2] As a result, there have been a number of attempts to reduce various emissions from diesel engines; of note are US 2007 on-road and Tier 4 off-road, and European Tier 1-6/I-VI, emissions regulations. US EPA on-road standards require model year 2007 and newer vehicles produce less than 0.2 g/bhp-hr NOx and 0.01 g/bhp-hr PM emissions, while EU Tier 6/VI, which targets PM and NOx emissions below 0.01 and 0.46 g/km respectively,[3] has been adopted throughout the European Union (EU) and India, and various other tiers have been adopted by other nations in Asia and Latin America.[3] While the increasingly stringent regulations typically lead to equipment manufacturers making improvements to engines and exhaust treatment systems, there are significant opportunities to reduce criteria pollutants and life cycle GHG emissions through development of new fit-for-purpose sustainably derived fuels and blendstocks.

Sustainably derived ethers have previously been studied as blendstocks for diesel to reduce many of these emissions. Around the turn of the millennium, focus was given to dimethyl ether as a diesel additive,[4] and later, to oxymethylene ethers.[5–8] Oxymethylene ethers (OMEs), typically of the form R-O-$(CH_2O)_n$-R', have shown promise specifically in the area of reduction of PM emissions, with some OME fuels exhibiting as much as 90% reduction in PM compared to traditional diesel fuel.[7,8] Most studies have investigated OMEs where R and R' are both methyl (CH_3) groups and n, or the number of oxymetheylene units, is either 1 or a range from 3-6 (often referred to polyoxymethylene dimethyl ethers). Despite the significant reduction of PM, these methyl-terminated OMEs suffer from several inferior properties to diesel fuel, including heating value, viscosity, seal compatibility,

and, for shorter oligomers, reactivity. For example, the simplest methyl-terminated OME, dimethoxymethane (with only a single oxymethylene unit), has a Cetane Number (CN) of 28,[6] well below diesel requirements, which range from as low as 40 in the United States to 51 in the European Union.[9,10] Most methyl-terminated OMEs have kinematic viscosities less than 2 mm^2/s, the minimum standard for diesel, and dimethoxymethane has the highest Lower Heating Value (LHV) of traditional OMEs at 23.3 MJ/kg, only slightly higher than half that of typical diesel fuel.[6] Several recent works have considered the effects of methyl-terminated OMEs on various common seal materials, concluding that many common elastomers used in fuel systems exhibit significantly higher OME absorption in comparison to diesel fuel.[8,11,12] Additionally, one recent work has included dibutoxymethane blended with diesel in an exposure test of various thermoplastics and thermosets to diesel/additive blends,[13] and it was shown that as a blend with these hard polymers, there was little effect.

Recent work by Bartholet et al.[14] developed models of various OME structures and suggested that OMEs with non-methyl terminating alkyl groups may have superior properties for blending with diesel, without sacrificing too much of the soot-reduction potential observed for methyl-terminated OMEs. While the modeling results point to significant promise for these OME variations as diesel fuel blendstocks, limited measured property data exists in the literature for these molecules. Ethyl-terminated OMEs have received the most attention of these possible variations, with studies considering such details as physico-chemical properties,[6] engine performance,[15] and even chemical kinetics.[16–18] These works agree with the trends found in Bartholet,[14] wherein ethyl-terminated OMEs have improved heating values, higher viscosity, and continue to have acceptable autoignition properties. Additionally, recent work by Drexler et al.[19] has synthesized and characterized a number of symmetric and asymmetric OMEs with extended and branched terminating alkyl groups, all with only one oxymethylene unit. These OMEs are found to have comparable densities to diesel, and improved diesel-relevant properties such as CN, flash point, and viscosity, when compared to dimethoxymethane. In particular, Drexler shows that freeze points of extended-alkyl OMEs

are extremely low, in some cases below -100°C.[19] These values indicate that for extended-alkyl OMEs blended with diesel fuel, cold flow properties will be driven primarily by the diesel components and are of minimal concern for blendstock selection, so we do not address them further here. A past work by Murphy has shown that B-1-B has acceptable miscibility with diesel.[20] Additional work by Arellano-Treviño et al.[21] and An et al.[22] has considered the synthesis of, and measured some properties of, mixtures of butyl-terminated OMEs, but neither made any attempt to isolate and characterize individual components of their synthesis products. While these previous works demonstrate potential for improving the suitability of OMEs for fuel use by altering the alkyl terminations, there has not been a systematic study which varies both end group and oxymethylene chain length simultaneously to isolate influences of each alteration on the fuel properties.

Synthesis of OMEs is a well-studied process and thus there is a strong basis of literature for methods to synthesize new OMEs for study and consideration as future fuel blendstocks. In general, OMEs are synthesized through the formation of dimethoxymethane from methanol via various methods such as acetalization,[5] conversion of dimethyl ether,[23,24] and recently through dehydrogenation,[25] followed by elongation (i.e. increasing of the number of oxymethylene units) via a formaldehyde source such as paraformaldehyde or trioxane, as reviewed by Baranowski.[26] Methanol and higher alcohols can be produced from biological sources,[27,28] and formaldehyde production from methanol is well documented[29] and one of the most common industrial production methods – thus, it is reasonable to conclude that processes to formulate these OMEs using bio-sourced materials are possible with current technologies.

In this work, 16 different OMEs with methyl, ethyl, propyl, butyl, isopropyl, and isobutyl terminating alkyl groups are synthesized and characterized, in order to provide a broad reference of relevant properties so that future combustion and engine studies may more easily select a particular OME (or mix thereof) based upon the desired balance of properties important in fuel handling, engine performance, and emissions, including improved soot

reduction. Of these 16, 10 have been studied before for fuel properties,[6,19,30,31] although not all tests performed here (e.g. water solubility, oxidative stability) have been performed for all of these. The remaining six OMEs have not, to our knowledge, been studied for fuel properties. Recommendations are provided based upon these results for the ideal OME for various goals such as maximal soot reduction or best overall compatibility with diesel fuel.

Nomenclature and Structures

Numerous abbreviations for OMEs have been used in literature, such as OME, POME, PODE, OMDME, etc. Given the variety of OMEs tested here, this work uses a shorthand method to highlight the specifics of each molecule, referring to the OMEs using the abbreviation *X*-*n*-*Y*, where *X* and *Y* refer to the terminating alkyl groups – *M*=Methyl, *E*=Ethyl, *P*=Propyl, *B*=Butyl, *iP*=isoPropyl, and *iB*=isoButyl – and *n* refers to the number of oxymethylene units in the central chain. Note that the total number of oxygen atoms in these OMEs is *n+1* as there is always one additional oxygen which is not a member of an oxymethylene unit.

As an example of this nomenclature, Fig. 1 shows butoxymethoxymethoxybutane, which is here termed B-2-B. It is possible to produce non-symmetric OMEs where *X* and *Y* are not the same; indeed, some of these molecules arise from the trans-acetalization reactions used in Arellano-Treviño's recent work[21] and make up part of the resultant tested mixture. However, this work focuses on symmetric OMEs to highlight the trends in properties from either alkyl group effects or chain length effects; asymmetric OMEs are beyond the intended scope of this work. Specifically for the iso-OMEs, iP-1-iP and iB-1-iB, the oxygen is attached at the same location as the hydroxyl group of the corresponding alcohol; for clarity, these structures are provided below in Figs. 2 and 3.

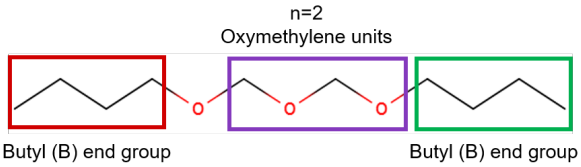

Figure 1: Example OME structure – B-2-B

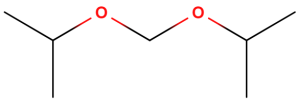

Figure 2: iP-1-iP

Methods

Fuels Used

The OMEs tested in this work are a combination of commercially available and synthesized in-house. All methyl-terminated OMEs were acquired commercially. M-1-M was purchased from Fisher Scientific and Sigma Aldrich, purity >98%. M-2-M was purchased from AstaTech Inc., purity >97%. M-3-M through M-5-M were acquired as a mixture from ASG Analytik-Service GmbH, and was distilled in-house to purities >95%. E-1-E was purchased from Fisher Scientific and Sigma Aldrich, purity >98%. P-1-P was provided as a sample by Lambiotte & Cie, purity >97%. B-1-B was purchased from Fisher Scientific and Sigma Aldrich, purity >98%. E-2-E, E-3-E, P-2-P, P-3-P, B-2-B, and B-3-B were synthesized via elongation of the appropriate X-1-X with trioxane over Amberlyst 15 catalyst [26] and distilled to purity >95%. iP-1-iP and iB-1-iB were synthesized from trioxane and the corresponding iso-alcohol over Amberlyst 15 catalyst and distilled to purity >95%. For the extended OMEs, typical impurities consisted of small amounts of the oligomers with one more and one fewer

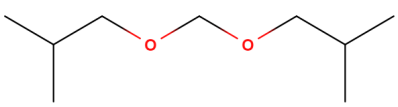

Figure 3: iB-1-iB

oxymethylene units.

Table 1 is provided below for CAS numbers of OMEs where these have been registered; additionally, basic properties such as molecular weight (MW) and oxygen content by mass are provided.

Table 1: CAS Number, Molecular Weight, and Oxygen Content of Tested OMEs

OME	CAS #	MW	Oxygen Mass%
M-1-M	109-87-5	76.09	42.05
M-2-M	628-90-0	106.12	45.23
M-3-M	13353-03-2	136.15	47.01
M-4-M	13352-75-5	166.17	48.14
M-5-M	13352-76-6	196.2	48.93
E-1-E	462-95-3	104.15	30.72
E-2-E	5648-29-3	134.17	35.77
E-3-E	4431-82-7	164.2	38.98
P-1-P	505-84-0	132.2	24.21
P-2-P	Not registered	162.23	29.59
P-3-P	4478-22-2	192.25	33.29
B-1-B	2568-90-3	160.25	19.97
B-2-B	Not registered	190.28	25.23
B-3-B	Not registered	220.31	29.05
iP-1-iP	2568-89-0	132.2	24.21
iB-1-iB	2568-91-4	160.25	19.97

Testing Methods

In this work, several properties were measured for the matrix of OME variations. For some properties, ASTM standard methods were available, however, a number did not have ASTM

standard methods available, or the available methods were not designed to handle the range of values encountered in the testing. As much as possible, each test was attempted to be performed on all of the desired molecules; however, due to limited quantities of some of the more difficult molecules to isolate, some tests were performed only on a subset in order to show the likely trends.

For the ASTM standard methods, the following tests were performed:

- Indicated Cetane Number (ICN), ASTM D8183.[32] This method is certified in the range of $35 < ICN < 85$, and while it can measure results outside this range, the accuracy is not guaranteed in the standard. Work by Abel et al. has shown that this method has good agreement with other CN measurement standards in normal diesel ranges, and that only for extremely high or low reactivity fuels do the several common methods start to diverge.[33] These tests were performed in a Seta Analytics Advanced Fuel Ignition Delay Analyzer (AFIDA).

- Lower Heating Value (LHV), ASTM D240.[34] Note that this method directly measures the higher heating value; LHV can be calculated via stoichiometry and the known heat of vaporization of water. These tests were performed in an IKA C200 calorimeter.

- Flash Point (FP), ASTM D93A.[35] These tests were performed in an Anton-Paar PMA4 closed-cup flash point tester. This method was not able to process flash points below ambient conditions, and so some lighter OMEs could not be safely tested.

- Density and Viscosity (ρ and ν), ASTM D7042.[36] Measurements were conducted over a range of temperatures from 20-100°C where possible. These tests were performed in an Anton-Paar SVM-3000 viscometer.

- Vapor Pressure, ASTM D6378.[37] From this data, a curve-fit was applied to calculate Antoine equation coefficients. These tests were performed in a Grabner Instruments VPXpert-L vapor pressure tester.

- Oxidative Stability, ASTM D7545.[38] These tests were performed in a Petrotest PetroOXY device as 20 vol.% blends in tridecane to simulate likely blending conditions.

For non-ASTM test methods, the following tests were performed:

- Yield Sooting Index (YSI)
- Water Solubility (WS)
- Boiling Point (BP)
- Seal material compatibility

YSI characterizes the sooting propensity of a fuel based on the amount of soot formed when the test compound is doped into the fuel of a methane/air nonpremixed flame.[39,40] The raw soot concentrations are rescaled relative to two endpoint species to produce an index analogous to an octane number or a cetane number. For the B-n-B OMEs, the standard methodology was used: dopant mole fraction = 1000 ppm, upper endpoint = toluene (YSI $\equiv$ 170.9), and lower endpoint = n-heptane (YSI $\equiv$ 36.0).[41] However, these parameters were changed for the other OMEs to accommodate their very low sooting tendencies.[42] In particular, the dopant mole fraction was raised to 3000 ppm to increase the absolute soot concentrations, n-heptane was switched to the upper endpoint, and water (YSI $\equiv$ 0.0) was adopted as the lower endpoint to minimize extrapolation of the measured YSIs outside of the endpoint range.

Water solubility was measured in a HP 5890 Series II gas chromatograph with a flame ionization detector (GC-FID) in a 30 m Restek Rtx-Wax column, 0.25 mm diameter with 0.25 µm film. As water cannot be accurately measured in a GC-FID device, a relative response ratio (RRR) method was used. The target OME was blended with 99% ethanol (n-propanol was used for the iP-1-iP case due to simultaneous elution of ethanol and iP-1-iP) at known masses after drying over MS4Å molecular sieves, and the responses recorded:

$$RRR = \frac{area_{ethanol}/mass_{ethanol}}{area_{OME}/mass_{OME}} \quad (1)$$

From here, the OMEs were blended with Type I deionized water in individual vials (five samples per OME), shaken vigorously, and left to diffuse to equilibrium for 72 hours. The water layer was extracted, added to clean vials and the mass recorded, then a known mass of ethanol added. This mixture was tested in the GC-FID, and from the known mass of ethanol and measured response areas, the mass of OME can be calculated. From here, the mass of water is the remainder of the measured mass of OME/water blend, and water solubility in g/g is calculated:

$$mass_{OME} = RRR * \frac{area_{OME}}{area_{ethanol}/mass_{ethanol}} \tag{2}$$

This method provides good coefficient of variance (CoV, <5% for most samples), but the very low solubility of butyl-terminated OMEs resulted in higher CoV (approximately 15%) as the samples used masses of OME and ethanol only one order of magnitude higher than the resolution of the balance used.

Boiling points were not measured directly, but calculated from reduced pressure boiling points during purification. The reduced pressures were converted to atmospheric equivalents using the Atmospheric Equivalent Temperature calculation described in ASTM D1160.[43]

Material compatibility was tested on small (approximately 1 mm x 10 mm x 25 mm) coupons of the selected materials submerged in the OME fuels. Four representative materials were tested – silicone rubber, nitrile rubber (NBR), and flouroelastomer (FKM), which represent a number of common flexible seal materials, and poly-ether ether ketone (PEEK), a hard polymer sometimes used as a valve seat material. Polytetrafluoroethylene (PTFE) is one of the most common chemical-resistant hard sealing and valve seat materials, but it has been shown in literature to be resistant to OMEs[8] and so PEEK was selected as an interesting alternate material. Two coupons of each material had the mass taken before immersion, then at 24, 48, 72, and 144 hours of exposure to test for fuel absorption, and then again after drying in a fume hood for 24 and 48 hours to test for any permanent damage. When possible, the OME sample was unchanged, but some of the volatile OMEs required replenishing during the measurements to ensure the samples remained fully submerged.

Results and Discussion

Indicated Cetane Number

ICN was measured as the average of two tests due to the larger quantity of fuel required (approximately 40 mL per test). For all fuels, 2000 ppm of Infineum R655, a lubricity additive, was mixed with the fuel to ensure proper injector operation. Tests with P-1-P and B-1-B without the lubricity additive showed negligible (<0.3) change in ICN due to this additive. The average deviation from the mean is 0.55%, with iP-1-iP having the highest difference between its two measurements at 1.5%. The measured values are presented in Table 2. On-road diesel fuels in the US are typically ICN>40, with Texas requiring ICN>48 and California requiring ICN>53. The EU requires ICN>51.

Table 2: Indicated Cetane Number of various OMEs

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	25.6	56.1	64.0	71.1	85.2
Ethyl	41.1	60.3	59.4		
Propyl	53.2	59.3	66.1		
Butyl	76.3	76.9	76.0		
Isopropyl	11.2				
Isobutyl	53.2				
Typical Diesel	>40				

Based upon these criteria, it is found that M-2-M and longer methyl OMEs, and all ethyl, propyl (except iP-1-iP), and butyl OMEs meet the minimum US requirements, and for maximum compatibility, M-2-M and higher, E-2-E and E-3-E, and all propyl (except iP-1-iP) and butyl OMEs are the best candidates. Larger alkyl groups are less sensitive to the length of the oxymethylene chain on ICN, up to the point where the ICN of butyl-terminated

OMEs appears entirely independent of the number of oxymethylene units. The kinetics of extended-alkyl OMEs are a new frontier in combustion chemistry; some recent works by Kroger et al.,[16] Jacobs et al.,[18] and Li et al.[17] have considered the kinetics of E-1-E, but no detailed chemical studies of larger extended-alkyl OMEs have been published. Recent work by the authors[44] considers ignition behavior of E-1-E, E-2-E, P-1-P, and iP-1-iP in a rapid compression machine, wherein it is hypothesized that the additional sites available for RO_2 pathways on the longer alkyl groups such as propyl have significant effects on ignition, which may cause the decreased effect of chain length as alkyl groups are extended. Understanding the full causes of these ignition behaviors will require significant future study in fundamental theory and experiments.

Of particular note are the behaviors of the iso-OMEs, iP-1-iP and iB-1-iB. These have significantly lower ICN than their linear counterparts P-1-P and B-1-B, by 79% and 30% respectively. This is not an entirely unexpected result; for example, *n*-octane has a CN of approximately 65 (depending on the exact measurement method), while its branched counterpart iso-octane has CN approximately 17.[45] While detailed chemical mechanisms have not been developed for any propyl- or butyl-terminated OMEs, work on methyl- and ethyl-terminated OMEs indicates that RO_2 chemistry remains an important step in the ignition of these fuels,[16–18,44] and thus similar effects on inhibition of RO_2 pathways via branched structures are to be expected and warrant further investigation. While ICN cannot be directly converted to either form of octane number (RON or MON), it is clear that many fuels with high octane numbers have low cetane numbers; the ICN of iP-1-iP is similar to that of iso-octane, and this may warrant investigation of iP-1-iP as a potential gasoline, rather than diesel, additive.

In the corrigendum to their 2016 analysis of M-n-M and E-n-E OMEs, Lautenschütz et al. review cetane numbers, also using an AFIDA device.[6] We find lower ICN for all comparable OMEs than Lautenschütz, with an average difference of 13% lower ICN; the least difference is in the E-2-E measurement (4.5% lower) and the highest in M-2-M (21% lower). Drexler

et. al.[19] tested E-1-E, P-1-P, and B-1-B in an AFIDA; we find similar results to this work, where the highest difference is a 3.2% higher ICN for P-1-P. In either case, the conclusions are similar – most OMEs other than M-1-M, and in some jurisdictions E-1-E, meet diesel requirements for reactivity.

In the literature, neat OMEs as well as OMEs blended with diesel fuel have been tested.[7] Here ICNs were measured for a representative high-ICN OME, B-1-B, blended volumetrically with a certified diesel, ICN=40.7, in increments of 10 volume % (Fig. 4). Due to the similar densities of B-1-B and diesel, this is essentially equivalent to a mass ratio blend as well. It is observed that the ICN of the mixture is nonlinear with volumetric blending; the presence of B-1-B shows an antagonistic effect on mixture ICN resulting in a lower ICN than would be predicted by linear blending rules; this is in agreement with existing literature on ether blending effects in distillate fuels.[46] The maximum deviation from the linear blending rule is 6.3%, indicating that while the presence of the ether has some negative effect, it is insufficient to overcome the ICN benefit of the high-reactivity OME.

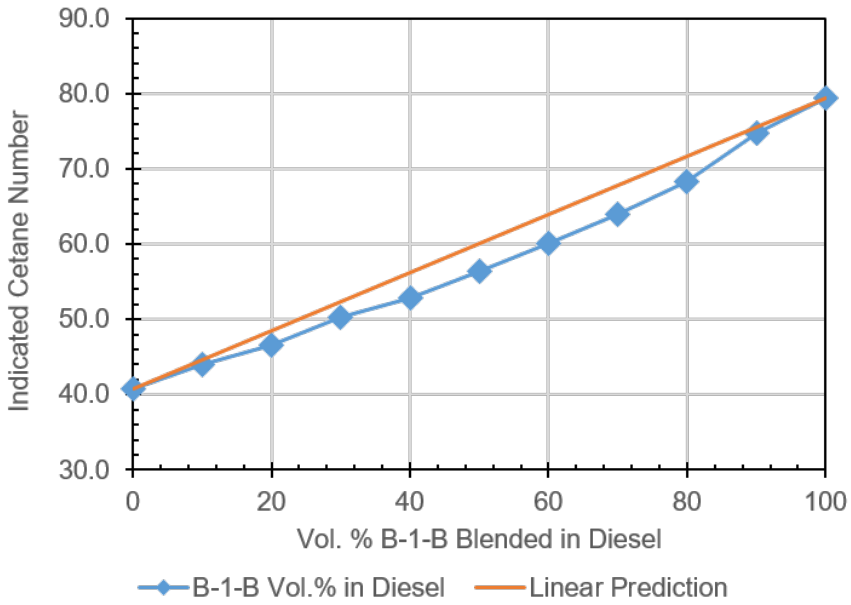

Figure 4: Effect of varying B-1-B blending ratio in diesel (ICN=40.7) on ICN of mixture, compared with a linear blending assumption.

Lower Heating Value

LHV was not measured directly; the calorimeter used (IKA C200) combusts a known mass fuel sample in an oxygen environment and measures the change in temperature of a water bath to determine energy released. As the water formed from combustion will condense when cooled, this method measures the higher heating value (HHV). For engine operation, LHV is the more applicable measurement as the combustion chamber is maintained at high temperature with very short dwell times, so under typical operation none of the latent heat of the water vapor will be released. Thus, HHV is converted to LHV via the assumption of complete combustion and subtraction of the latent heat of the produced water mass; the results of this analysis are presented in Table 3.

ASTM D975 and EN590 diesel standards do not specify a minimum acceptable value for LHV or HHV of diesel; however, typical diesels have LHV>42 MJ/kg,[47] and while biodiesel LHV will depend in part on the oxygen content, some traditional biodiesels have been found to have LHV between 37 and 40 MJ/kg.[47,48] Synthetic diesels from processes such as Fischer-Tropsch or hydrotreatment of bio-oils may have much higher LHVs, up to 49 MJ/kg.[49] The high oxygen content of OMEs results in significantly lower LHVs than traditional diesels, a weakness noted in prior work.[6] OMEs with extended alkyl groups reduce the oxygen:carbon ratio and thus should produce higher LHVs, and one would further expect longer oxymethylene chain OMEs to produce lower LHV than their shorter counterparts.

Table 3: Lower Heating Value of various OMEs [MJ/kg]

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	23.2	21.0	20.0	19.3	18.8
Ethyl	28.8	25.9	24.1		
Propyl	32.0	29.0	27.0		
Butyl	34.1	31.2	29.2		

Isopropyl	31.4
Isobutyl	33.7
Typical Diesel	>42

These results are consistent with expectations; higher alkyl groups produce higher LHV, and longer oxymethylene chains produce lower LHV. There is a diminishing effect on the reduction in LHV per oxymethylene unit as the ratio of oxygen:carbon approaches unity with longer chains. The iso-OMEs diverge again from their linear counterparts, but only slightly. This is also consistent with alkane behavior, where LHV of branched molecules is slightly reduced in comparison to linear variants.[50] The reported values here for M-n-M, E-n-E, P-1-P, and B-1-B are in good agreement with literature,[6,19,30,31] with a maximum difference of 4.9% higher LHV reported here for E-1-E compared to measurements from Drexler et al.[19] In our data, an average coefficient of variance (CoV) of 1.2% is found, with M-1-M showing the highest CoV of 4.6%.

None of the tested OMEs show what could be considered "high" LHV; even the highest tested value, for B-1-B, is still approximately 3 MJ/kg less than many typical biodiesels.[47] For maximizing energy content, we recommend usage of OMEs with as long of terminating alkyl groups as other requirements may permit.

Yield Sooting Index

Smoke point measurements by Tan et al.[51] show that methyl-terminated OMEs, which contain no carbon-carbon bonds, have negligible sooting tendencies compared to conventional diesel fuel. In contrast, extended alkyl OMEs do contain carbon-carbon bonds, so they would be expected to have higher sooting tendencies, which diminishes one of the most important attributes of OMEs as alternative diesel fuels. One of the main objectives of this work is to quantify the trade-off between sooting tendency and the desirable properties of extended alkyl OMEs (e.g., higher LHV, lower water solubility). The smoke points of the OMEs are

outside the measurement limits of the ASTM D1322 standard and cannot be determined directly.[52] However, the YSI approach used in this study has a much wider dynamic range and values could be measured for all the neat OMEs.

Table 4: Yield Sooting Index of various OMEs

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	6.6	5.2	0.5	-2.5	-4.8
Ethyl	15.5	13.8	11.9		
Propyl	30.8	25.5	21.3		
Butyl	46.0	42.7	37.8		
Isopropyl	38.4				
Isobutyl	52.2				
Typical Diesel	>200				

Table 5: YSI/LHV of various OMEs [1/(MJ/kg)]

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	0.284	0.248	0.025	-0.130	-0.255
Ethyl	0.538	0.533	0.494		
Propyl	0.963	0.879	0.789		
Butyl	1.35	1.37	1.29		
Isopropyl	1.22				
Isobutyl	1.55				
Typical Diesel	∼4.8				

Table 4 lists the measured YSIs and Table 5 lists the ratios of the YSIs to the LHVs reported in the prior section. YSI uncertainty is +/- 7%. YSI quantifies the amount of

soot formed per mole of fuel, whereas YSI/LHV indicates the amount of soot produced per unit of fuel energy, which is the more engine-relevant quantity. The YSIs demonstrate that all the OMEs significantly reduce soot compared to diesel fuel: the sootiest OME, iB-1-iB, decreases it by a factor of 3.8 while the least sooty OMEs, M-4-M and M-5-M, decrease it by an effectively infinite ratio since they have negative YSIs. These negative YSIs are discussed in more detail elsewhere;[42] in short, they occur because M-4-M and M-5-M produce virtually no soot and instead decompose to large quantities of formaldehyde (CH_2O), which suppresses soot formation from the methane background fuel in the YSI flames to a total soot fraction below that observed in the zero YSI case. The results in Table 5 show that the reductions in YSI/LHV are smaller, but still significant. For example, whereas iB-1-iB reduces YSI by a factor of 3.8, it reduces YSI/LHV by a factor of 3.1. This observation demonstrates that the OMEs reduce soot even when accounting for the larger amount of fuel required to produce a given amount of energy.

Flash Point

Flash point (FP) is an important factor in the safety of handling fuels; while gasolines typically have FP well below ambient and are treated as flammable liquids, diesel fuels typically have FP >52°C (>55°C in the EU) and are classified as combustible liquids.[53] As documented by Härtl et al. and Lautenschütz et al.,[6,30] smaller OMEs such as M-1-M and E-1-E have FP below or close to this requirement, but the most commonly studied OMEs (M-3-M and higher) will meet this requirement.

Table 6: Flash Point of various OMEs [°C]

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	<20[a]	<20[a]	56.4	85.6	116
Ethyl	<20[a]	35.5	69.4		

Propyl	31.7	66.5	91.0
Butyl	58.6	89.6	114
Isopropyl	21.3		
Isobutyl	49.4		
Typical Diesel	>52		

[a]Flash point too low to safely test in PMA4

As shown in Table 6, FP appears to be a significant weakness in compatibility of OMEs with diesel; about half (M-3-M and higher, E-3-E, P-2-P and higher, and B-1-B and higher) meet this requirement, while others do not. Our measurements have an average coefficient of variance (CoV) of 0.98%, with B-1-B showing the highest CoV of 1.8%, for five tests performed for each fuel. The reported values for M-n-M and E-n-E are in good agreement with Lautenschütz's work, with a maximum deviation of <1% higher for M-3-M.[6] We also find comparable FP to Drexler et al.[19] for P-1-P and B-1-B, with <1% difference. Some of these fuels had FP too low to safely test in the PMA4 device, which is not natively equipped to test FP below ambient temperatures, and while some cooling of the test cup is possible, a different device with native cooling capability may be required for testing of low-FP OMEs; we note that Lautenschütz et al. report FP values for M-1-M and E-1-E of -32°C and -5°C respectively[6] and Deutsch et al. report a FP of 16°C for M-2-M,[31] below the safe testing limits of the methods used here.

Density and Viscosity

Physical properties of the liquid fuel will have significant effects on the behavior of the spray in the fuel injector for a CI engine; the influential work of Lefebvre on sprays indicate that ρ and ν are of high importance for spray development.[54] The effect of biodiesels on the performance of CI engine injectors has been a matter of concern due to typically higher ρ and ν; as reviewed by Algayyim et al., many studies have been conducted which find

that typical biodiesels produce sprays with greater penetration and larger diameter droplets, hindering evaporation due to lower area:volume ratios.[55] Further, some work suggests that larger droplets may increase soot formation.[56] CI engines are designed around combustion of a particular ideal fuel spray, so rather than preferring some minimum (e.g. YSI) or maximum (e.g. LHV), the ideal OME for diesel blending will match as closely as possible to typical diesel values. We present density of the OMEs at 20°C in Table 7, and the viscosity at 40°C in Table 8 below.

Table 7: Density at 20°C of various OMEs [g/mL]

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	0.860	0.992	1.03	1.07	1.10
Ethyl	0.829	0.912	0.971		
Propyl	0.834	0.900	0.948		
Butyl	0.837	0.888	0.931		
Isopropyl	0.818				
Isobutyl	0.824				
Typical Diesel	0.84-0.87				

Table 8: Kinematic Viscosity at 40°C of various OMEs [mm^2/s]

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	n/a[b]	0.617	0.876	1.32	1.98
Ethyl	0.346	0.652	0.963		
Propyl	0.644	0.949	1.39		
Butyl	0.945	1.32	1.85		
Isopropyl	0.515				

Isobutyl	0.904
Typical Diesel	2.0-3.2

[b]At lab ambient pressure (84 kPa), M-1-M will boil at approximately 37°C, so no density or viscosity at 40°C can be measured without a device to maintain the viscometer above ambient pressure

None of the OMEs tested match perfectly with typical diesel for ρ except M-1-M; however, all of the n=1 and n=2 OMEs are very close to diesel and may be good substitutes in this respect. Longer oxymethylene chains produce higher ρ due to higher oxygen content, which helps offset some LHV losses by allowing for more fuel mass per unit volume. Only two tested OMEs, M-5-M and B-3-B, even approached the ν values typically seen in diesels, with most being less than half that of the minimum diesel ν. The average CoV for ρ and ν measurements was less than 0.1% for 3 tests per fuel.

In comparison with literature, we find nearly identical ρ measurements to Lautenschütz[6] and Drexler,[19] with the largest observed difference as a 1.5% higher ρ for M-2-M.[6] For ν, Lautenschütz et al. measure ν at 25 °C and Drexler et al. measure at 20 °C, while Deutsch et al. measure at 40 °C, as reported in Table 8 above. We find good agreement with Deutsch et al. for all values except M-2-M, where we observe a 9.2% higher ν. A temperature sweep was performed for ρ and ν (Figs. 5-8) with a step of 10°C, so to compare with Lautenschütz et al. we take an average of our 20°C and 30°C values. Acknowledging that ν is nonlinear with temperature, and thus some small error is to be expected from this approximation, we nonetheless find good agreement except for M-1-M and E-1-E, where we observed significantly (16% and 19% respectively) lower ν than Lautenschütz et al. For E-1-E, P-1-P, and B-1-B, we find a 15% lower ν for E-1-E than Drexler et al.,[19] but find good agreement (within 5%) for the remaining fuels.

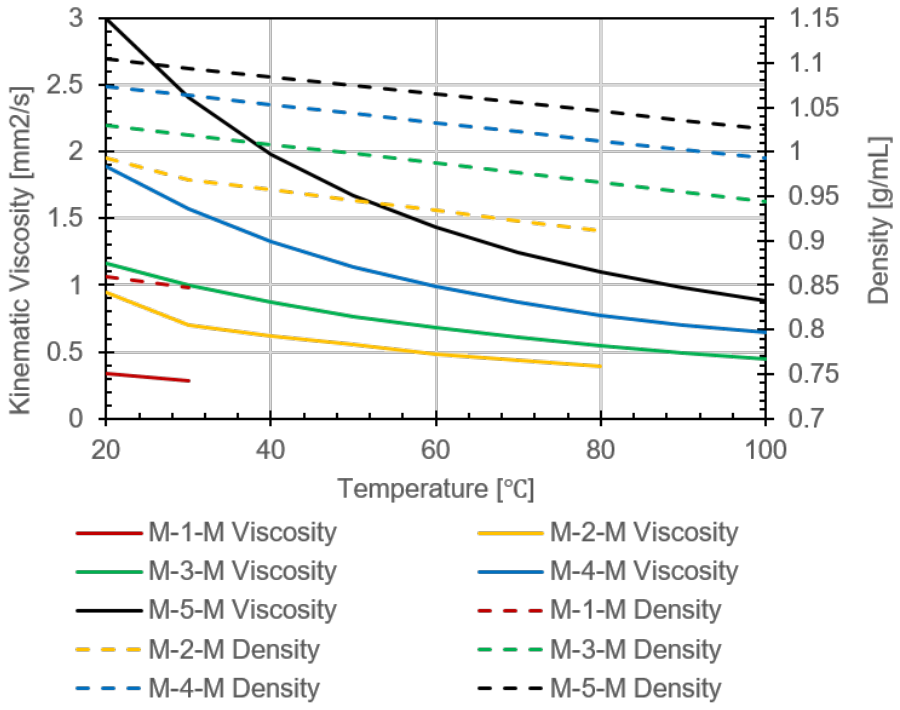

Figure 5: Viscosity and density curves of M-n-M OMEs between 20°C and 100°C

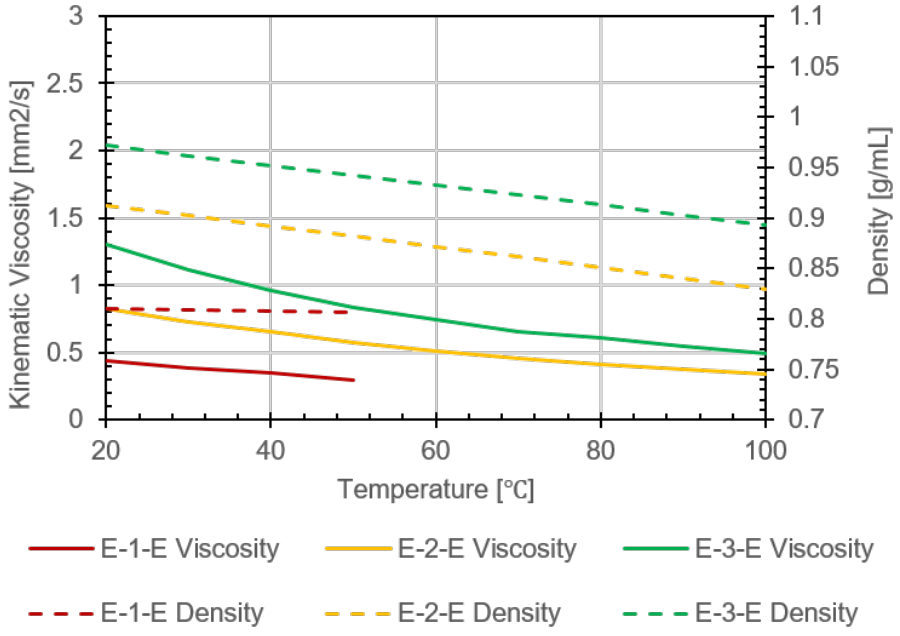

Figure 6: Viscosity and density curves of E-n-E OMEs between 20°C and 100°C

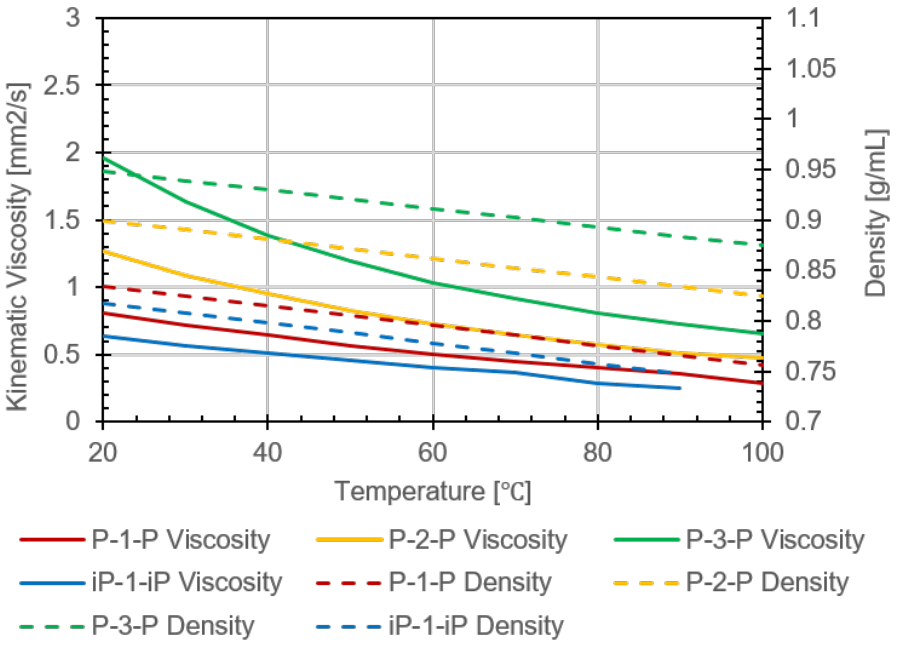

Figure 7: Viscosity and density curves of P-n-P and iP-1-iP OMEs between 20°C and 100°C

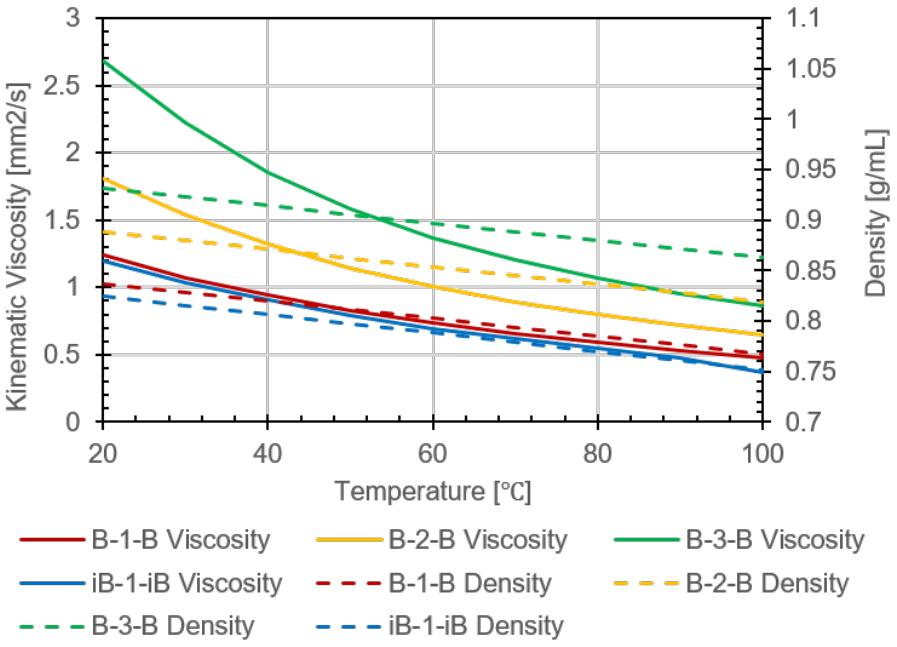

Figure 8: Viscosity and density curves of B-n-B and iB-1-iB OMEs between 20°C and 100°C

Vapor Pressure

A subset of the OMEs were tested for vapor pressure, however, due to high fuel volume requirements not all were tested. The tested OMEs were M-1-M, M-3-M, M-4-M, M-5-M, E-1-E, P-1-P, and B-1-B. Antoine equation (Eq. 3) parameters were calculated for these OMEs and are presented below; M-1-M and E-1-E have Antoine coefficients provided in the NIST Webbook[57,58] and produce curves within 5% of our calculated values. The average CoV for five tests per fuel was 5.5%, driven primarily by exceptionally high CoV (29%) for M-5-M (the average CoV for the other tests, excluding M-5-M, was a more reasonable 1.8%). Generally, CoV increased with decreasing volatility. Due to limits of the testing device and the fuels, different temperature ranges were tested, up to either just below the boiling temperature or the device maximum temperature (120°C), and starting at 0°C or a temperature providing above 5 mbar vapor pressure (to prevent damage to the machine due to low vacuum). Coefficients are reported as calculated from the curve fit, but we note that the measured values from which these are produced are accurate to 3 significant figures and calculated values from these should be treated as such.

$$log_{10}(P_{vap}) = A - \frac{B}{C+T} \tag{3}$$

Table 9: Antoine equation coefficients for some OMEs [bar, K]

Fuel	Temp Range Tested [°C]	A	B	C
M-1-M	0-35	3.881	991.89	-59.23
E-1-E	0-80	3.995	1201.2	-59.07
P-1-P	20-120	4.762	1920.2	1.598
B-1-B	30-120	3.911	1882.5	32.66
M-3-M	20-120	4.246	1629.4	-24.69

M-4-M	30-120	4.309	2130.2	39.43
M-5-M	50-120	4.142	2301.4	49.54

The vapor pressure of diesel will vary with the various volatile components, so several common alkanes are shown on the plot below (Fig. 9) using Antoine parameters from NIST[59–61] to provide a point of reference.

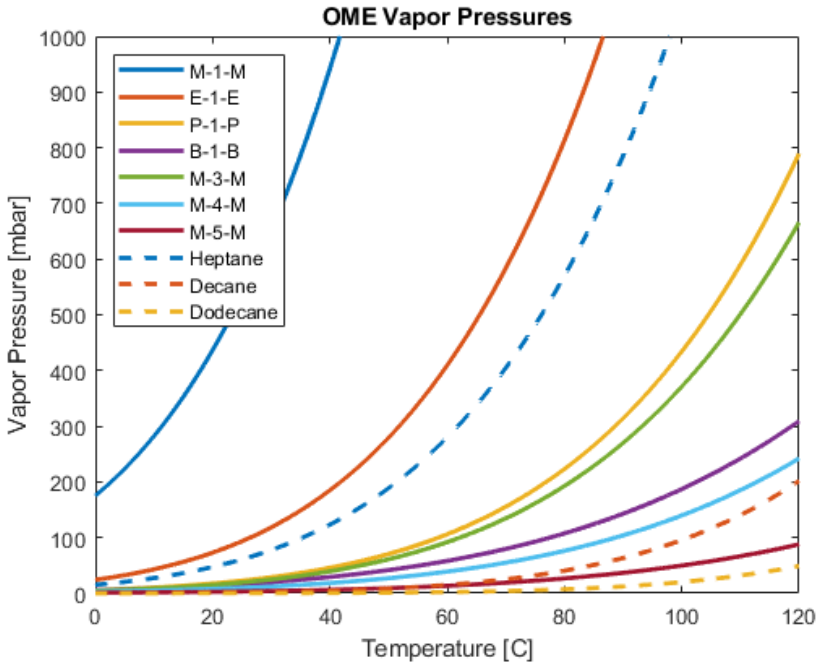

Figure 9: Antoine curves of OME vapor pressure, from calculated Antoine coefficients, compared to some typical alkanes (see Table 9)

Oxidative Stability

The most common test for oxidative stability of biodiesels is the Rancimat test (EN 15751). This test was attempted for oxidative stability, however, the nature of the method caused significant difficulties and was determined to be ineffective for testing OMEs. First and most relevant, the Rancimat test is by nature an open-system test. The oxidation is accelerated by pumping air through a heated fuel sample, and the volatiles (nominally acids) are collected

in water, with changes in the conductivity of the water indicating the presence of acids formed from auto-oxidation. As a result of heating to the test temperature of 110°C and simultaneously enforcing a gas flow, many of the OMEs will rapidly vaporize or even boil and be lost – further, as will be discussed in a later section, the water solubility of many OMEs is very high and vapors will contaminate the measuring water. The second problem is the nature of the test, which uses conductivity change of a water sample as a proxy for oxidation. This has been shown to work well for fatty-acid methyl ester biofuels,[62] but it was not clear prior to the tests whether the auto-oxidation products of an OME will necessarily ionize or otherwise change the conductivity of the measuring water.

As a result of these difficulties, a different test was used. The Petro-Oxy testing device is often used for gasoline and gasoline additives,[63] which makes it more suitable for the OMEs, some which have been shown to have higher volatility. Additionally, it is a closed-system measurement, preventing the vapor losses seen in some initial failed attempts to use the Rancimat method. The Petro-Oxy device subjects a small (5 mL) sample of the fuel to 140 °C under 7 bar of oxygen, and measures the induction time as defined by the time to a 10% reduction from the maximum pressure of the test.[38] Some past work has applied this method to biodiesels in comparison with the Rancimat method and determined minimum equivalent Petro-Oxy induction times,[64] proposing that the 8 hour Rancimat induction time required for European biodiesel is comparable to 27 minutes in a Petro-Oxy device, and the US standard of 3 hours is comparable to 17 minutes of Petro-Oxy testing, where longer induction times are indicative of higher oxidative stability. Due to limited equipment availability, only a subset of OMEs were tested in this device, focusing primarily on larger alkyl groups (E-1-E, P-1-P, P-2-P, B-1-B, B-2-B, B-3-B, iP-1-iP, and iB-1-iB). These were blended at 20 vol% in tridecane to simulate common blending ratios in diesel and allow for higher resolution due to lower concentrations of OME. The induction times for the tests are presented in Table 10. GC-MS testing was performed on the oxidized sample to determine the products of the auto-oxidation reaction. Common products included alkyl esters, carboxylic acids, and

alcohols. The presence of carboxylic acids indicates that Rancimat tests may be effective for heavier OMEs which can survive the heated open system environment without significant vapor loss.

Table 10: Induction times of select OMEs in Petro-Oxy test, 20 vol% in tridecane

End Group	Number of CH_2O Units		
	1	2	3
Ethyl	228 min		
Propyl	86 min	91 min	
Butyl	106 min	152 min	174 min
Isopropyl	38 min		
Isobutyl	88 min		
Tridecane	154 min		

A trend is observed with the oxymethylene chain length; longer chains lead to improved stability. However, no clear trend can be seen for alkyl groups – E-1-E is more stable than any of the propyl or butyl OMEs, however, all of the butyl OMEs are more stable than the propyl ones. The iso-alkyl OMEs do show significantly reduced stability in comparison to their linear counterparts. The mechanisms by which this is occurring are unclear and warrant further investigation. All of the tested OMEs, in 20% blends, exceed the biodiesel oxidative stability standards, but it is unclear whether these fuels will exhibit stability issues when tested neat. Single tests were performed for each fuel, and so we refer to the ASTM standard, section 14.1.5,[38] where the reproducibility R of this method can be calculated as $R = 0.0863X + 1.3772$, to estimate an average R of 10% of the measured values.

Water Solubility

Water interaction with fuels is important for a number of reasons, but most importantly, there are environmental and combustion concerns. A fuel which is highly soluble in water

poses risks in case of spillage; it will be significantly harder to separate from water sources due to lack of distinct phases, and there is a risk of fuel becoming dissolved into groundwater in high concentrations and being spread from the spill site. Further, a fuel which can carry high concentrations of water dissolved in the fuel itself, while less of an environmental concern, poses risks to engine and fuel system operation and can reduce the effective LHV of the fuel.

Table 11: Water solubility of various OMEs [g OME / kg water]

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	481	469	394	338	283
Ethyl	56.0	60.7	52.3		
Propyl	3.16	3.72	3.23		
Butyl	0.215	0.189	0.251		
Isopropyl	9.76				
Isobutyl	6.62				
Typical Diesel	<0.1				

As shown in Table 11, the effect of additional oxymethylene units on the water solubility is negligible compared to the alkyl group effect, where increasing the alkyl group by one carbon per side reduces water solubility by roughly an order of magnitude each time. The mean CoV of these data is 6.9%, with B-3-B having the highest CoV at 19%. All of the B-n-B fuels exhibited high CoV due to measurable amounts of the fuels being only one order of magnitude greater the resolution of the balance used. Of the various properties tested, this one makes one of the strongest cases for the suitability of extended-alkyl (particularly butyl) OMEs for diesel blending. One anomaly is the behavior of iB-1-iB – while iP-1-iP is slightly higher than P-1-P, but within the same order of magnitude, iB-1-iB is an order of magnitude higher in water solubility than B-1-B. This result was sufficiently surprising that the entire series of iB-1-iB was retested with fresh samples, and the same result was found.

It is currently unclear what the chemical basis for this significant difference is, and more investigation is warranted.

Boiling Temperature

Boiling temperatures were measured as a necessary result of the distillation process for purification. Distillation was generally performed under vacuum (150 torr, 100 torr, or 30 torr, depending on the lightest component) except for when M-1-M was expected to be present. The equivalent temperature at standard conditions (AET) was calculated using the procedure in ASTM D1160 Appendix A7,[43] assuming a K factor of 12 (this value is recommended in the standard unless another value can be clearly established) and using units of torr and °C. A pressure correction A is first calculated from the distillation pressure P, a temperature correction Δt from K and the pressure P, and then the AET calculated from A, T, and Δt:

$$\Delta t = -1.4(K-12)log_{10}\left(\frac{760}{P}\right) \tag{4}$$

$$A = \frac{5.994295 - 0.972546log_{10}P}{2663.129 - 95.76log_{10}P} \tag{5}$$

$$AET = \frac{748.1A}{(T+273.15)^{-1} + 0.3861A - 0.00051606} - 273.15 + \Delta t \tag{6}$$

The most likely source of error in these measurements is not from average boiling temperatures observed at reduced pressure, which were typically within +/- 1°C, but rather the uncertainty of the K factor. This is recommended in the standard as 12, but differing behavior of OMEs from typical distillate fuels may require a different K value. As an example, a +/-2 difference in K produces (at 30 and 150 torr reduced pressures, respectively) +/-3.93°C and +/-1.97°C differences (where higher K leads to lower calculated temperature).

Table 12: Boiling temperature of various OMEs [°C]

End Group	Number of CH_2O Units				
	1	2	3	4	5
Methyl	42	112	161	207	243
Ethyl	88	142	186		
Propyl	141	184	223		
Butyl	179	223	257		
Isopropyl	119				
Isobutyl	164				
Typical Diesel (T10)	200				

The 10% distillation and 50% distillation temperatures (T10 and T50) of diesel fuel vary based on the specific blend but are often around 200°C and 250°C, respectively.[47] From the data in Table 12, it is clear that most of the tested OMEs are more volatile than even the low distillation components of a diesel; the only OMEs tested with boiling temperatures above T10 are M-4-M, M-5-M, P-3-P, B-2-B, and B-3-B, and only one tested OME (B-3-B) has a boiling temperature comparable to diesel T50. Consequently, diesels with OME components may experience preferential vaporization effects; effects of this on the combustion characteristics of diesel sprays is worthy of investigation.

Material Compatibility

Due to high required volumes of fuel for the material compatibility, this testing was performed only on a subset of OMEs with n=1. The effect of various chain lengths of M-n-M has been documented in literature,[8,11,12] so this work focuses on the end group effect. Additionally, there is a wide range of possible sealant materials, and varying properties within categories of material, so it will be necessary for any engine development programs to do in-depth testing of the specifically selected materials. Thus, we present these data as being informative, but

not necessarily generalized.

The results of the material compatibility tests are provided in Figs. 10 and 11, where the results are shown as mass increase due to fuel absorption (i.e. a 50% change represents the material absorbing a mass of fuel equal to 50% of the original material), and thus the desired result is to minimize this effect. The largest change in mass (due to fuel absorption) occurred in the first 24 hours (Fig. 10), and equilibrium was reached by 72 hours (Fig. 11) for all fuels and materials. For most, the change from the first measurement to equilibrium was negligible; only FKM and NBR in M-1-M, silicone in E-1-E, and FKM in iP-1-iP had significant (>5% by mass) changes after 24 hours. These measurements are an average of 2 samples, where the average deviation from the mean is 1.6%, with iP-1-iP having the widest variation at 5.5%.

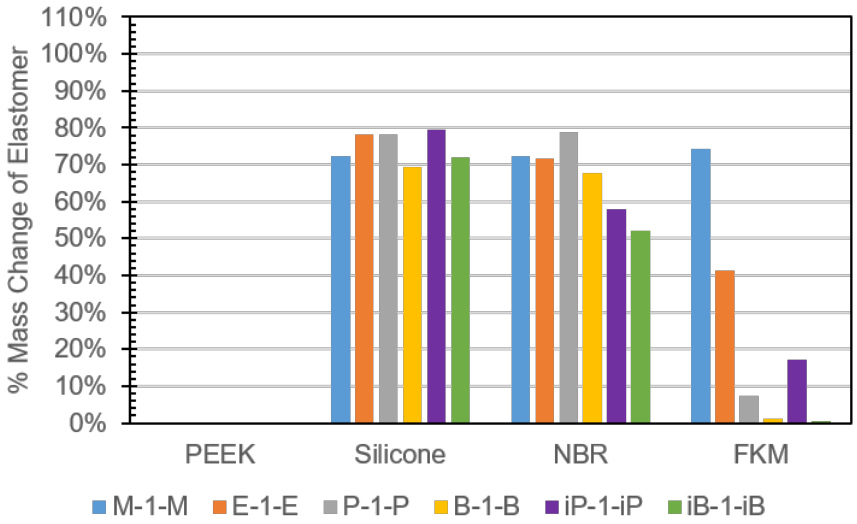

Figure 10: Percent change in mass of elastomer sample coupons after 24hr submerged exposure

One of the most important takeaways is the suitability of PEEK as a hard sealing or handling material for OMEs; no absorption was observed for any of the tested OMEs at any duration of exposure. For the elastomers, FKM was the only one which was suitable for use with OMEs, and only for the extended alkyl OMEs – it has poor performance for M-1-M, but shows significant reductions in mass of fuel absorbed as the alkyl group

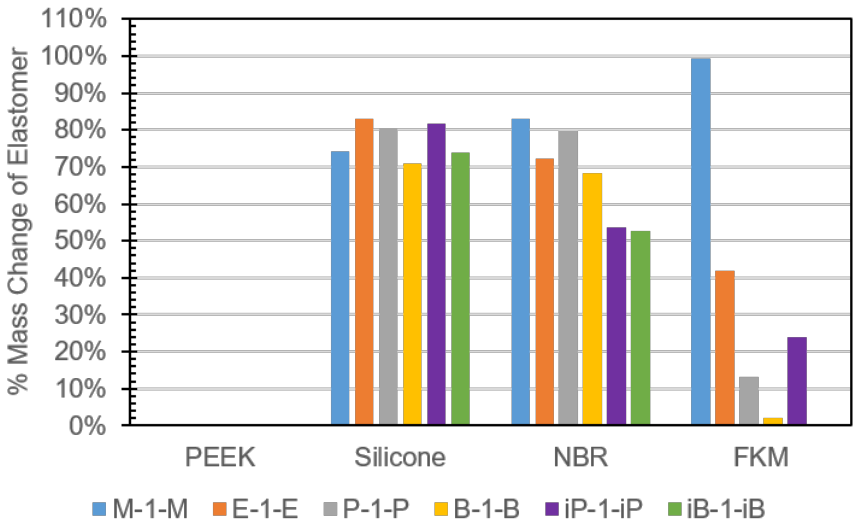

Figure 11: Percent change in mass of elastomer sample coupons after 72hr submerged exposure

is lengthened. Additionally, it is noted that the common trend observed in most other properties regarding the iso-OMEs, namely that they have somewhat inferior properties to their linear counterparts, does not hold here – iP-1-iP and iB-1-iB had less absorption than P-1-P and B-1-B for NBR samples, iB-1-iB less absorption than B-1-B in the FKM samples, and essentially comparable effects on silicone.

Conclusions

In this work, the properties of a wide array of OMEs are considered in the context of their suitability for use as diesel fuel blendstocks or substitutes. Methyl-terminated OMEs have been well studied with some attention given to ethyl-terminated OMEs, so the weaknesses of these fuels are well understood. Extending the range of possible OMEs to various propyl- and butyl-terminated OMEs allows a wider range of possible fuel properties and behaviors with which to balance the needs of any given application. Fig. 12 provides an overview of the trends in major properties with end group changes, with respect to diesel fuel.

In more detail, we observe the following trends in OME behaviors:

	Methyl	Ethyl	Propyl	Butyl	Isopropyl	Isobutyl
ICN	o	o	+	++	--	o
LHV	--	--	-	-	-	-
YSI	++	++	+	+	+	+
Water Solubility	--	--	-	o	-	-

++ = Significant improvement over diesel + = Improvement over diesel
o = Comparable to diesel - = Inferior to diesel -- = Significantly inferior to diesel

Figure 12: Summary of trends in major properties with end groups, in comparison with diesel

- Most OMEs other than the lightest (M-1-M, E-1-E) and one branched version (iP-1-iP) have suitable reactivity, as measured by ICN, and B-n-B OMEs show the most consistent ICN with variance in central chain length.

- All OMEs have significant LHV reductions in comparison to diesel or even traditional biodiesels. Shorter chains with longer alkyl groups provide the highest LHV.

- All OMEs show significant reductions in soot production compared to diesel. M-n-M OMEs, the most commonly studied, retain the advantage here, but even the worst OME has a 3.1x reduction of soot per unit energy compared to diesel fuels.

- Lighter OMEs have flash points too low to be suitable diesel blendstocks, however, heavier OMEs in either chain length or alkyl group (MW>$\sim$160) have acceptable flash points.

- Shorter oligomers of OMEs have comparable densities to diesel, with longer oxymethylene chains increasing density above typical diesel fuels. All OMEs have viscosities lower than diesel standards, although heavier OMEs such as B-3-B and M-5-M approach diesel requirements.

- Many OMEs such as n=1 and methyl-terminated OMEs have high vapor pressure compared to lighter diesel components such as dodecane.

- No clear trends are apparent in oxidative stability, however, at moderate blending ratios in diesel, most OMEs appear to have acceptable stability.

- Water solubility is dominated by alkyl groups, where larger alkyl groups have order-of-magnitude reductions in solubility. B-n-B shows the lowest solubility, on the order of that observed for diesel fuel.

- Most OMEs have boiling temperatures below the typical T10 distillation temperature of traditional diesel fuel.

- Common elastomers such as nitrile and silicone appear to be insensitive to alkyl groups and will absorb n=1 OMEs equally, with significant absorption. FKM ("Viton") flouroelastomers show improved resistance to OMEs with larger alkyl groups, particularly branched alkyl groups. PEEK is entirely unaffected by OMEs.

The choice of an ideal OME for future use as a CI fuel will be dependent on balancing the various goals of the application. For example, an engine design focusing on maximizing soot removal at all costs would be best served continuing to focus on methyl-terminated OMEs, while a focus on maximum compatibility with current diesel fuels and their distribution networks and fueling systems may be best served by considering heavier OMEs with longer alkyl groups. Spark-ignited applications may consider use of iP-1-iP as a blendstock for soot reduction, as it shows high autoignition resistance compared to many OMEs while maintaining good soot reduction properties and higher LHV than ethanol, a common gasoline oxygenate. In addition to their use as soot reduction fuels, OMEs have potential to be bio-sourced, produced via e-fuel processes, or a combination thereof. Upcoming work is focusing on the techno-economic analysis and life-cycle effects of the production of butyl-terminated OMEs, which have multiple production pathways possible via bio-sources, and show promise

for reducing emissions while maintaining minimal gallon-equivalent costs. Further possible areas of research include engine optimization studies of NO_x and soot emissions, wherein, as a result of their naturally low propensity to soot, OMEs may be applied in low NO_x engine operating strategies (e.g., high EGR) while maintaining manageable levels of soot, or usage of OMEs as low-sooting option for the high-reactivity or prechamber fuel in dual-fuel applications with low-soot fuels such as methanol. It is the hope of the authors that this work will help jump-start additional research into a number of these unstudied and under-studied OMEs and their possible future engine applications, where their unique properties may aid in the reduction of emissions and life cycle environmental effects.

Acknowledgement

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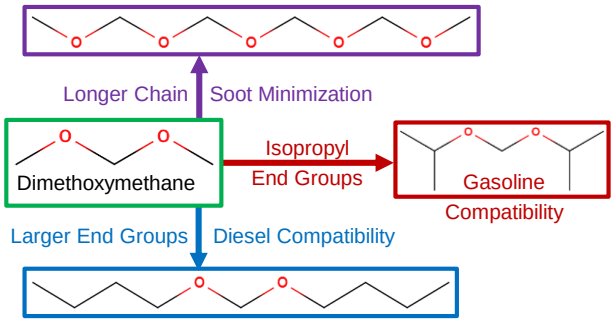

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