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Density and Viscosity Measurements for Diesel-Decanol-Oxymethylene ether Blends

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Advanced fuels can be used as an alternative for conventional fossil fuels. Out of many promising candidates, alcohols and ethers are well-studied substances for application in internal combustion engines. This study investigates the possibility of decanol and oxymethylene ether usage in compression ignition engines. To use diesel-decanol-oxymethylene ether blends in diesel engines, the properties of the mixtures need to be close to diesel fuels. For this, the blending ratios need to be chosen carefully to ensure good ignitability, fuel delivery and atomization of the fuel. This study focuses on the density and viscosity blending calculations and compares the predicted results to the actual values. The used formulas are found to be the most accurate for binary blends, and the accuracy gets worse whenever there is a big difference in the properties of the components.

1. Introduction

Climate change is a big talking point nowadays, and its effects can be felt in our lives all around the world. Scientists agree that climate change is undoubtedly caused by human activities, mainly due to the ever-growing greenhouse gas (GHG) emissions (Mahboub 2017). The automotive industry is a big contributor to these emissions, because with the usage of fossil fuels many pollutants, as well as carbon-dioxide (CO_2) is released into the atmosphere. Due to this, the transport sector accounts for around one-fifth of the worldwide CO_2 emissions (Ritchie, 2020).

One of the many ways we can mitigate the effects of climate change is by reducing emissions, therefore increasingly stricter emission standards are being implemented throughout the world. To meet the requirements of the standards, manufacturers started developing alternative drivetrains such as battery electric or hydrogen fuel cell technology, which are expected to replace internal combustion engines (ICE) in the future. The market share of these new, zero-emission vehicles is growing, but currently it is a slow process. Cars with electrified drivetrains are more expensive than their ICE counterparts, and they are not well suited for all the possible applications yet (Zöldy and Zsombok 2018).

In the short and medium term, advanced fuels can be an answer to this problem. The term advanced fuel is given to any kind of fuel that can be used as a replacement of conventional fossil fuels. Advanced fuels have the potential to reduce tailpipe emissions, and significant progress can be achieved by their production methods. They can be made from sustainable resources using renewable energy, so their well-to-wheel (WTW) emissions can be reduced drastically compared to diesel fuels. These benefits are not limited to new vehicles, as these fuels can be used in older cars as well.

Advanced fuels have already made their way into our cars. The usage of ethanol is common around the world, there are even countries that offer petrol with up to 85 percent ethanol. For diesel engines, biodiesel can be produced from plant oils or animal fats. Recently, many other compounds are being tested as alternative fuels for diesel engines, for example different kind of alcohols or ethers.

Creating a new alternative for diesel fuels is challenging, as many different aspects need to be considered, like the properties, production methods, price, and economic viability of the fuel. In this paper, the focus is on the density and viscosity of diesel-decanol-oxymethylene ether blends, as these two properties have big impacts on the operation of the engine, and they can be easily measured. Making a new fuel from scratch requires preliminary investigations, in which blending equations play a big part. This study aims to investigate the differences between the calculated and measured properties, and the possible inaccuracies of the blending equations. For future projects, accurate formulas are essential to make the creation of new blends easier and faster.

2. Materials

Alcohols can be divided into two groups based on the number of carbon atoms. Short-chain alcohols have up to five carbon atoms, any more than that can be considered as a long-chain alcohol (Noweck and Grafahrend, 2006). For the usage in compression ignition engines, long-chain alcohols seem to be more advantageous, as their properties are closer to diesel fuels, which also consist of long-chain hydrocarbons (Zöldy, 2007). One of these alcohols is decanol, which recently have been a well-studied substance for potential application in diesel engines.

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Decanol has a cetane number of 50 (Yanowitz et al., 2017), and its lower heating value (LHV) is also comparable to diesel fuels. In studies, decanol is usually mixed with biodiesel. The high viscosity of decanol needs to be addressed, therefore other substances are usually mixed to it, such as diesel or other alcohols. The addition of decanol has great effects on the emissions and combustion. Multiple studies conclude that the higher blends of decanol reduces the carbon-monoxide (CO), hydrocarbon (HC) and particulate matter (PM) emissions, while the nitrogen oxides (NO_x) emission increase (Nanthagopal et al., 2019). The addition of decanol also increase the heat release rate and the brake thermal efficiency. Up to 40 % blend of decanol can be used in unmodified diesel engines without any negative impact on the performance (El-Seesy et al., 2020)

A different oxygenated compound, oxymethylene ether (OME) is also a promising candidate as a fuel additive in diesel engines. Multiple OMEs exist, and they differ by their chain length, represented by *n* in their molecular structure of CH3-O-(CH2-O)$_n$-CH3. OMEs with various chain lengths have different properties, the ones with longer chain lengths have higher cetane numbers, greater viscosity, and higher flashpoint. Oxygen content also rises with the chain length, resulting in a decreasing lower heating value. For diesel engines, the blends of OME_3 to OME_6 are investigated the most, usually in diesel-OME mixtures. Different studies reported great reduction in PM-emissions thanks to the OME content, along with the improvements achieved in the NO_x-PM trade-off (Saupe and Atzler, 2022). The brake specific fuel consumption rises with the greater OME-content, but it is an expected result due to the reduction in LHV. This effect is slightly compensated by the increased brake thermal efficiency (Virt and Arnold, 2022).

Regarding their production methods, both decanol and OME can be made in a carbon neutral way. Decanol, along with other long-chain alcohols are commonly used components in lubricants, waxes, creams, and cosmetics, and they are produced either by natural processes, or synthetically (Cipriano et al 2022). Large-scale natural production often has high environmental impacts, as it requires big plantations of oil palms, which can lead to deforestation and therefore biodiversity loss. Synthetic production can be achieved by the Ziegler-Epal or the Ziegler-Alfol processes, both of which require aluminium, hydrogen, and ethylene and other hydrocarbons for the making of long-chain alcohols (Noweck and Grafahrend, 2006). Some recent studies are dealing with novel ways of sustainable decanol production, for example from the oleaginous yeast *Yarrowia lipolytica* (Rutter and Rao, 2016) or bacterial strains of *Escherichia coli* (Hamilton-Kemp et al., 2005).

OME can be produced from methanol or dimethyl ether (DME). These two hydrocarbons can be obtained from fossil fuels, but there are other, more sustainable production methods. With carbon capture, the CO_2 content of the atmosphere can be collected and stored, and green hydrogen can be acquired by water electrolysis using renewable energy sources. Combining various amounts of CO_2 and hydrogen result in methanol or DME, which then can be used to make OME in an environmentally friendly way (Dieterich et al., 2020).

3. Methodology

The main goal of this study is to create advanced fuels that are compatible with the latest standard for diesel fuels in the European Union, EN590. As mentioned earlier, the viscosity of decanol is too high, and it needs to be compensated. For this purpose, OME_{3-5} was used, which has lower viscosity than decanol and diesel. Table 1 shows the properties of each investigated substance, along with the EN590 standard as a comparison. Apart from the density and viscosity, which were measured, all the values are from previously cited literature.

Table 1. Properties of the investigated B7 diesel, decanol and OME_{3-5}, and the EN590 standard

	Decanol	OME_{3-5}	B7 diesel	EN590
Cetane number [-]	50,3	80,35	57,5	>55
Density at 15°C [kg/m^3]	832.6	1063.2	844.2	820-845
Viscosity at 40 °C [mm^2/s]	6.91	1.163	2.78	2-4.5
Lower heating value [MJ/kg]	41.8	19.16	42.8	-
Flashpoint [°C]	108	-	77	55
Oxygen content [wt%]	10.11	47.73	0.8	-

To use a diesel-decanol-OME_{3-5} ternary mixture as a fuel, its blending ratios needs to be chosen carefully, using the limits of the EN590 standard as a guideline. Knowing the properties of the individual blending components, the properties of the mixture can be calculated based on the blending ratios. Preliminary calculations are useful, as the blending ratios can be determined without actually mixing the substances, and it can save time and money. The main limitation of these calculations is the accuracy of the used formulas. This study focuses on the calculation methods for density and viscosity of blends and comparing them to the measurements. Density and viscosity of a liquid mixture can be calculated by the following equations (Nour et al., 2022) (Zhmud, 2014):

$$\rho_b = \sum x_i \cdot \rho_i \tag{1}$$

$$\ln \eta_b = \sum x_i \cdot \ln \eta_i \tag{2}$$

where x_i is the volumetric ratio, ρ_i is the density, and η_i is the viscosity of each component. Equation (1) is based on the linear combination of the densities, while the viscosities can be calculated in a similar way, but the natural logarithm of the viscosities needs to be used. This equation is called the Arrhenius mixing rule, and it is based on the dynamic viscosity of the liquids. This is different from the kinematic viscosity, which is defined by the ratio of the dynamic viscosity and the density, as seen in the following equation:

$$\nu = \frac{\eta}{\rho} \qquad (3)$$

The EN590 standard defines its limits with kinematic viscosity. The viscosities were measured with Cannon-Fenske viscometer (Csemány et al., 2022) (Hidegh et al., 2023), which also gives the results in mm^2/s, which is a unit of measurement for kinematic viscosity. To get the kinematic viscosity of a mixture, not only equation (2) is used, but the result of equation (1) is also needed to convert the value from dynamic viscosity.

The next step in creating advanced fuels after choosing its components is to decide what blending ratios produce mixtures that can be used in an engine. As infinitely many ratios can be considered, it is best to visually illustrate the achievable properties, as seen in Figure 1. and Figure 2. In these diagrams, the properties are shown as a function of diesel content. The array of lines represents the ratios between decanol and OME_{3-5}. Lower amounts of diesel allow for more decanol and OME_{3-5} content, so the properties of the components have higher impact on the final properties of the mixtures.

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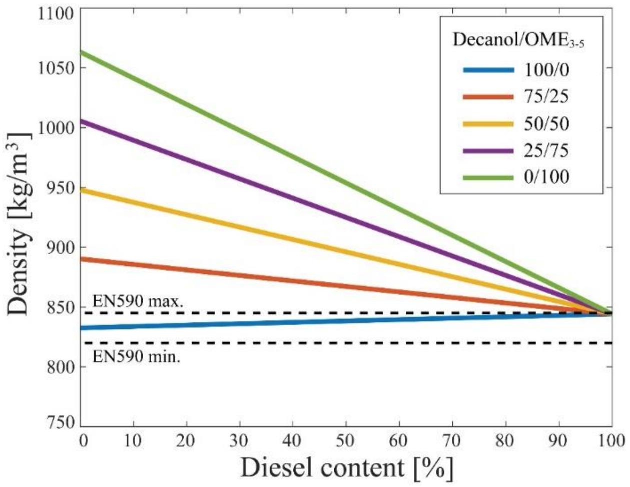

Figure 1: The effect of diesel content on density at different decanol/OME_{3-5} rates

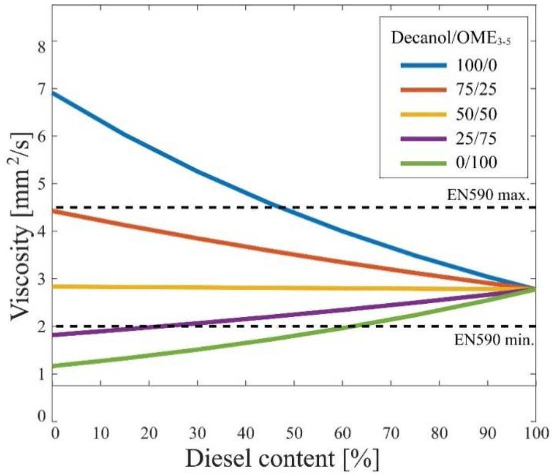

Figure 2: The effect of diesel content on viscosity at different decanol/OME_{3-5} rates

Based on the calculations, the density limits of the standard can only be met with mixtures that barely have OME_{3-5} in it. This is because the investigated diesel was already near the upper limit, and OME_{3-5} has significantly higher density. On the other hand, optimal viscosity can be achieved with higher ratios of OME_{3-5}, as it compensates the high viscosity of decanol. One of the goals of this study is to make fuels with little to no diesel content, therefore a compromise is needed. Too high viscosities can cause problems in the fuel delivery, and during the atomization process. Higher densities are less problematic, so the main objective was to choose mixtures that have viscosities between the limits of the standard.

4. Results and Discussion

Overall, seven mixtures were chosen for measurement, with increasingly smaller amounts of diesel content. The differences between the calculated and measured values can be seen in Table 2. The mixtures were named based on their components, Dx-Oy designates a mixture with x % decanol and y % OME_{3-5} content, and the rest is diesel fuel. Out of these seven mixtures, two (D10 and D70-O30) are binary blends, the other five are diesel-decanol-OME_{3-5} ternary blends.

Table 2. Differences between the calculated and measured values for density and viscosity

	Density at 15°C [kg/m³]		Viscosity at 40 °C [mm²/s]	
	Calculated	Measured	Calculated	Measured
D10	841,24	842,3	3,04	3,23
D20-O5	851,33	836	3,19	2,99
D30-O10	861,42	851,4	3,34	2,9
D40-O15	871,51	850,6	3,5	2,94
D50-O20	881,6	863,2	3,66	2,93
D60-O25	891,69	887,8	3,84	2,89
D70-O30	901,78	898	4,02	2,99

The calculated values for density increase in steps of 10 kg/m^3, but the measured results do not show such linearity. The results show less than 0.5 % of relative error for three mixtures, D10, D60-O25, and D70-O30. Out of these three, D10 and D70-O30 are binary blends, for which the predictions are usually more accurate. The density of decanol and diesel is close to each other, but both are much smaller than the density of $OME_{3\text{-}5}$. This means that mixtures with higher decanol content are close to being a binary blend, and therefore being more accurately predicted, as the low diesel content only skews the calculations by a little.

Due to the even bigger differences between the viscosities of each component, the viscosity prediction proved to be more inaccurate. The calculated values increase almost evenly, but apart from the D10 blend, all the mixtures have a viscosity of around 2.9-3 mm^2/s. This results in an increase in the absolute value of the relative errors of the calculation, as seen in Figure 3.

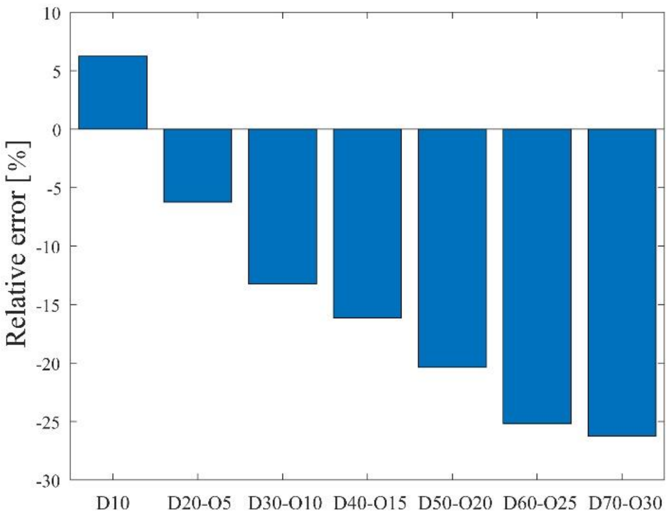

Figure 3. The relative errors of the calculated viscosities

The D10 blend is the only mixture where the calculated value is smaller than the actual, and the relative error is more than 5 %. This is a binary blend, and it shows that even a slight decanol addition can noticeably increase the viscosity. On the other hand, as little as 5 % $OME_{3\text{-}5}$ content causes the viscosity to drop in the D20-O5 blend, even though more decanol was also added. For further blends, 5 % $OME_{3\text{-}5}$ is added, compensating the 10 % rise in decanol content, so the actual viscosity remains at an almost constant level. This cannot be said for the calculated values, which rise from 3 to 4 mm^2/s, meaning that the formula predicts that the added $OME_{3\text{-}5}$ is not enough to compensate the high viscosity of the growing decanol content. The viscosity of decanol is more than six times as much as the viscosity of $OME_{3\text{-}5}$, so the viscosity of the blends is influenced by their ratios, seen in Figure 4. Although the increase $OME_{3\text{-}5}$/decanol ratio would suggest that the prediction would be more accurate, the exact opposite happens. As the ratio rises, the relative error of the calculation gets bigger in absolute terms.

To make more accurate predictions for viscosity, other formulas can be used (Csemány et al., 2022). For example, according to the Refutes rule (Nour et al., 2022), the viscosity blending number (VBN) of each component is first calculated, which then can be used to determine the VBN of the mixture using linear combination. After this, the VBN of the mixture can be converted to kinematic viscosity.

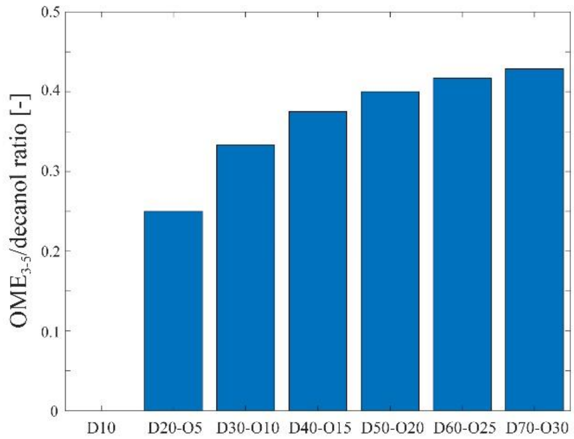

Figure 4. The ratio of $OME_{3\text{-}5}$ and decanol.

These steps require more time and computation power than the Arrhenius mixing rule, but it can provide more accurate values in some cases.

5. Conclusion

In this study, seven advanced fuel mixtures were created by mixing decanol and oxymethylene ether to diesel fuel. The density and viscosity of the blends were predicted by preliminary calculations, which were later compared to the actual values through measurements. Calculating the densities using linear combination provides accurate results for binary blends, but large differences in density can cause some bigger errors in ternary blends. The used formula was accurate enough for choosing the blending ratios. Accurate density prediction is not as important for viscosities because measuring density requires significantly less time and equipment compared to viscosity measurement.

Overall, there is no formula that can predict the exact viscosity of liquid mixtures. These formulas can be used for preliminary calculations, but their limitations need to be known beforehand. One of the major flaws of the current mixing rules that they cannot account for any changes of volume that may happen during mixing, they only work well for ideal mixtures. Most accurate predictions happen with binary blends, and the formulas works best with small differences in viscosities between the components.

Nomenclature

CO	Carbon-monoxide
CO_2	Carbon-dioxide
DME	Dimethyl ether
GHG	Greenhouse gas
HC	Hydrocarbon
ICE	Internal combustion engine
LHV	Lower heating value
NO_x	Nitrogen-oxides
OME	Oxymethylene ether
PM	Particulate matter
VBN	Viscosity blending number
WTW	Well-to-wheel

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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