Phase stability research of diethyl ether/rapeseed oil blends

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Abstract. The paper presents results of the research focused on stability of diethyl ether/rapeseed oil blends. Rapeseed oil (RO) and diethyl ether (DEE) are cheap, oxygenated fuels which are produced from renewable sources. Rapeseed oil is not the most appropriate fuel for diesel engines but addition of DEE significantly improves same physicochemical properties of the blend. On the other hand due to the low polarity and low density of DEE compared with RO, it is possible that such mixtures can be unstable. For this reason, in this research a stability of DEE/RO blends was empirically examined using a Turbiscan Lab research equipment. Necessary tests were carried out during 28 days of measurements. In particular a RO with addition of 10, 20, 30 and 40 % by vol. of DEE has been tested. Results confirm that RO/DEE blends constitute stable one phase and transparent mixtures without any symptoms of fluids stratification.

1. Introduction

Rapeseed oil has significantly higher kinematic viscosity and density but lower cetane number compared with the requirements set by EN590's standard for diesel fuel. For this reason, rapeseed oil is not the most appropriate fuel for diesel engines. However, plant oils can be transesterified to methyl esters commonly known as a Fatty Acid Methyl Esters (FAME) or Biodiesel (B100). Properties of such biodiesel are similar to regular diesel fuel (DF). Hence, according to EN590 standard, the FAME fuel can be added to DF in the volume of max. 7%. It is widely known that kinematic viscosity and density of plant oils are affected by temperature variations. In particular, higher temperature reduces values of both mentioned parameters. Taking this into consideration, selected physicochemical properties of plant raw fuels can be improved by heating. Thus, fuel heating systems adopted for the specific diesel engine are available on the market. Moreover, plant oils can be blended with diesel fuel or other chemical compounds, i.e. selected alcohols and ethers. Properties of these chemicals are notably different in comparison to plant oils. However, sometimes a conjunction of these compounds results in a mixture with favorable fuel properties for diesel engines. Literature review suggests that diethyl ether (DEE) appears to be one of such solution [1-4].

DEE is low polar, high cetane (CN) chemical with the low value of viscosity, density and surface tension. In 1997 Bailey et al. [5] presented one of the first literature review on DEE as a renewable diesel fuel. In particular they concluded that literature survey and brief laboratory analysis were insufficient for a comprehensive evaluation of DEE as a transportation fuel. However, Bailey citied

Southwest Research Institute (SRI) tests on DEE self-ignition in a Constant Volume Bomb Chamber (CVBC). These research confirmed that derivative CN of DEE is higher than 125. Such promising CN value of DEE encourages for further research of diesel fuels containing addition of DEE. In 2014 Górski et al. [6] carried out research on a direct injection diesel engine fuelled with DEE-diesel fuel blends. Results of these research showed that the addition of DEE only slightly increases the CN of the blend tested according to EN ISO 5165 requirements on the Waukesha research engine. However, it has not any impact on shortening of ignition-delay in AD3.152 diesel engine fuelled with DEE-DF blends. Also, Fikiri et al. [7] expressed that DEE commonly shared cetane number is surprisingly too high when compared with alkane with the same molecular size (e.g., 22 for butane and 30 for pentane). Clothier et al. [8] investigated DEE/DF blends. They concluded that DEE inhibits the ignition of DF. For this reason adding DEE will actually decrease the cetane number of the diesel fuel. Clothier's experiments suggested that DEE may interact with aromatics in diesel fuel, delaying the onset of ignition. All above mentioned results suggest that high derivative CN of DEE estimated in CVBC has not significant relationship with the shortening of ignition delay in diesel engine. For this reason, in the engine research ASTM D613 or EN ISO 5165 standard seems to be more appropriate. In these methods the Waukesha research engine is used for determining and certifying the ignition quality of diesel fuels. However, it should be pointed that both these methods refers to traditional fossil fuels. Tests for other fuels are not recommended.

Despite this, many other studies confirmed that DEE added to different diesel fuels has positive impact on selected ecology parameters of diesels' engine. Senthil et al. [9] have studied effect of DEE - eucalyptus oil blends on the performance and emission of a diesel engine. It was found that the main ecology parameters of a diesel engine fuelled with DEE - eucalyptus oil blends are significantly better compared with neat diesel fuel. In particular at full load condition of the engine work the emission of HC, CO and smoke was respectively by 30, 10 and 35.7% lower than for an engine fuelled with diesel fuel. Also, Rakopoulos et. al [10] studied the performance and exhaust emissions of a single-cylinder, four – stroke, high speed direct injection diesel engine fuelled with diesel oil blends with 8, 16 and 24 % by vol. DEE. They observed reduction of NOx, CO and smoke emission with the higher content of DEE in a fuel blend. Imtenan et al. [11] worked with a turbocharged diesel engine fuelled with blends of palm biodiesel - diesel oil - DEE. On the base of these investigation they concluded that addition of DEE to the palm biodiesel - diesel blend has significant impact on the combustion process. In particular DEE reduces effect of advanced combustion of biodiesel increasing the ignition delay. In case of tested engine it reduces combustion peak temperature due to higher latent heat of evaporation. For this reason emission of NO, CO and smoke is reduced compared with biodiesel blends. Also Krishnamoorthi et al. [12] reported lower emission of HC by 18 % and NOx by 26% for an engine fuelled with waste fried oil - DEE blend compared with neat diesel fuel. They concluded that addition of DEE into biodiesel-diesel blend increases the combustion efficiency. Similar results were shown by Ashok et al. [13]. They research confirmed that the oxygenated additive diethyl ether added emulsified fuel shows increase in brake thermal efficiency and decrease in specific fuel consumption, smoke density, particulate matter, and nitrogen oxides compared with the diesel fuel.

Above mentioned researches confirmed that DEE blended with conventional or renewable fuels has mainly positive impact on ecology parameters of diesel engines. However, these researches do not contain any information on stability of such mixtures. It is known that DEE is slowly oxidized by atmospheric oxygen, heat and light, resulting in the formation of explosive peroxides [14]. The accumulation of these compounds during storage can lead even to unexpected explosions. Also plant oils and their derivatives tend to oxidize [15]. These oils contain polyunsaturated fatty acid chains that are also less thermal stable. For this reason fatty acid chains tend to form polymeric species with higher molecular weights. It is known that polymer formation increases the oil viscosity. Moreover, oxidation process increases the acid value of biodiesel. In this way changes in the stability of oils impact on their usefulness as a fuel for diesel engines. It should be pointed that biofuels are more hygroscopic than fossil fuels. For this reason a vegetable oils contain dispersed water that can promote bacterial growth. This may cause a fuel system fouling, oil degradation, increased steel corrosion and increased particle loads [16]. All of these changes in chemical and microbiological stability of vegetable oils can be additionally stimulated or inhibited by DEE. The knowledge on this subject is still insufficient. The low density of DEE molecules and high density of RO can promote phase stratification of the blends. Furthermore, some differences in polarity of RO and DEE molecules can impact on the blend stability too. On the other hand, DEE is commonly regarded as a solvent. However, the phase stability of DEE/RO blends has never been confirmed in long term empirical research. Results of these research are particularly important for power generators.

2. Materials and methods

2.1. Tested fuels

In this study low erucid rapeseed oil (RO) with the addition of 10, 20, 30 and 40 % by vol. of DEE has been tested. These fuel samples were coded as DEE10, DEE20, DEE30 and DEE40, respectively. Figure 1a shows sample of DEE40 before components of the blend were mixed together. Figure 1b presents transparent and one-phase DEE40 sample directly after mixing.

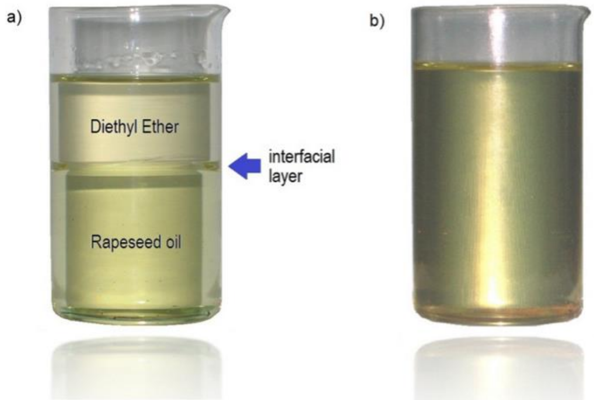

Figure 1. Example of DEE40 sample: a) before mixing, b) after mixing

The main physicochemical properties of DEE and RO are listed in Table 1. As it can be seen, the kinematic viscosity of RO is approx. 15 times higher than DEE. According to EN 590 standard, the kinematic viscosity of diesel fuel measured at a temperature of 40 °C should remain in the range of 2.0 – 4.5 mm^2/s. Also the density of RO is significantly higher compared with DEE. In both cases the density value is out of the range specified in EN 590 standard.

Table 1. Selected physicochemical properties of DEE and RO

Property	Value	
	DEE	RO
Cetane number, [-]	125	36
Kinematic viscosity at 40 °C, [mm^2/s]	0.22	33.5
Density at 15 °C, [g/cm^3]	0.71	0.92
Lubricity at 60 °C, [μm]	-	120
Surface tension, [N/m]	17	33
Flash point, [°C]	-40	>300
Lower heating value, [MJ/kg]	33.9	34.0
Cooper corrosion, [-]	Class 1	Class 1

Plant oils and their derivatives such as Fatty Acid Methyl Esters (FAME) are known from their excellent lubricity properties. For this reason the lubricity value of tested RO was significantly below the upper limit of 460 μm set by EN 12156 standard. Table 1 contains value of surface tension of DEE and RO. As it can be seen the RO surface tension is twice higher than DEE. It should be pointed that the value of surface tension is not described in EN 590 standard. However, lower value of surface tension promotes better atomization of the fuel injected to the combustion chamber. Also, the value of flash point of DEE and RO varies considerably. DEE is an extremely flammable and ignites at -40 °C whereas the flash point of rapeseed oil exceeds 300 °C.

2.2. Methods

The stability of DEE-RO blends was determined on the base of measurements carried out with an optical Turbiscan Lab apparatus (Fig. 2) made by Formulcation Inc. Turbiscan is designed to detect different forms of destabilization phenomenon including phase separation that can occurs in mixtures of liquids with different densities.

Figure 2. View of the Turbiscan Lab research equipment

Turbiscan measurement head is equipped with a near-infrared LED light source at a wavelength of 880 nm and two photo detectors. The first one detects the light passing through the fuel sample whereas the second detects the light backscattered at an angle of 45° (Fig. 3). The Turbiscan light parameters allow detect phase separation phenomenon as well as particles growth with a diameter higher than 10 nm. It means that the Turbiscan should detect not only particles migration in order to quantify destabilization phenomena but also bacteria growth in fuel samples if any.

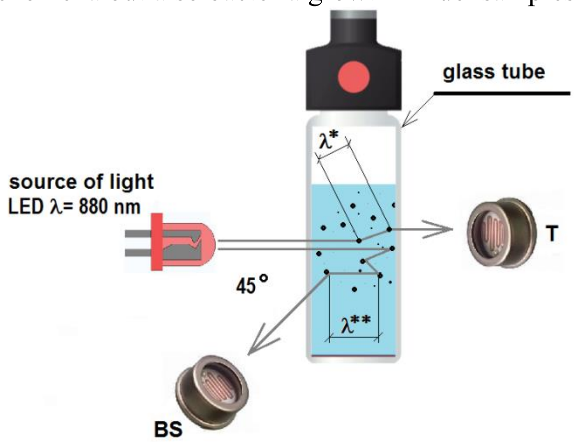

Figure 3. The main components of the Turbiscan measurement head: BS - backscattering light detector, T - transmission light detector, λ^* - the photon mean wavelength detected by T photodiode, λ^{**} - the photon mean wavelength detected by BS photodiode

Details of the Turbiscan measurement methodology were described by Mengual et. al. [17]. In our research all tested fuel samples were loaded into glass tubes and scanned along entire height of 40 mm. Necessary measurements were carried out for a samples stored at temp. of 25 °C. Scan data were collected every few days until the last 28th day of observation.

3. Results

Results of all measurements are showed in Figures 4 - 8. All dark blue lines, showed in these figures, relate to the measurement carried out at the beginning of the test. Green and red lines relate to the measurement carried out in the middle and in the end of research, respectively.

As can be seen in Figure 4 the transmission and backscattering profiles of RO remain unchanged during 28 days of measurements.

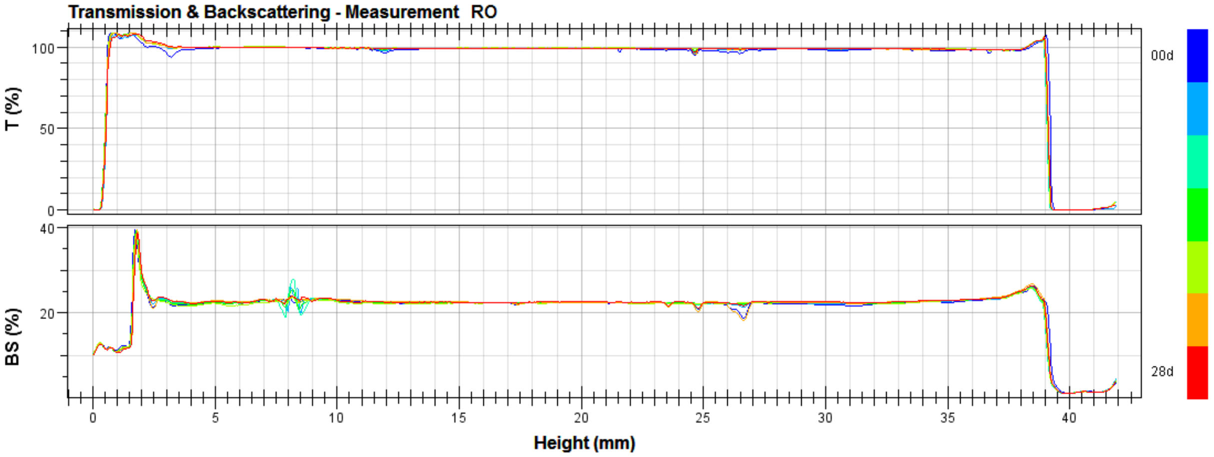

Figure 4. Transmission and backscattering profiles of RO tested during 28 days.

However, it should be pointed that all Figures 4 - 8 contain two abrupt variations located at the bottom (approx. 2 mm) and at the top (approx. 39 mm) of the fuel sample height. All these abrupt variations are caused by glass/liquid and liquid/air interface respectively.

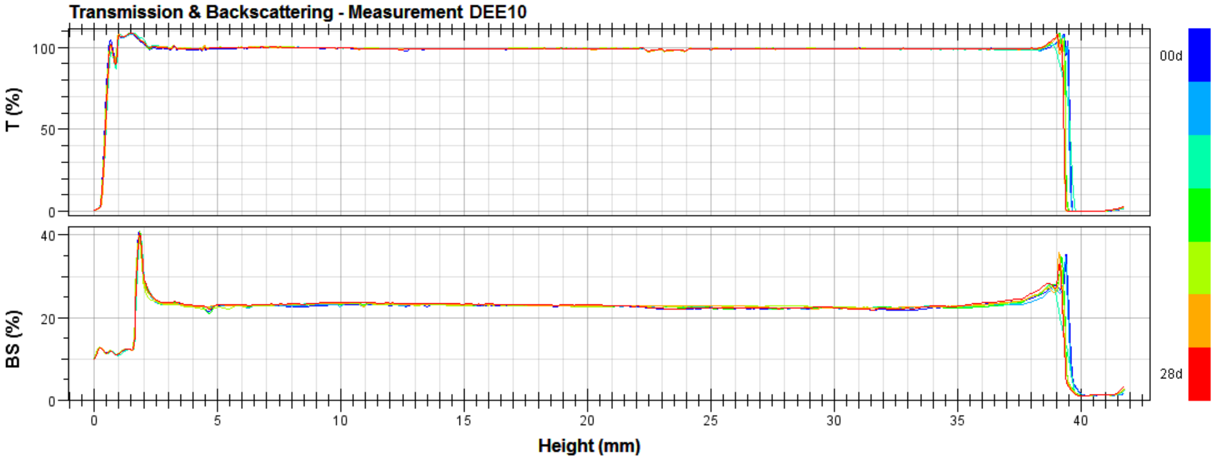

Figure 5. Transmission and backscattering profiles of DEE10 tested during 28 days.

Figures 5 - 8 represent typical data for one phase and transparent mixtures without fluids stratification symptoms. As can be seen in Figures 5 - 8, the transmission profiles are horizontal at the level of 100%. Such value confirms that all tested mixtures were transparent at the whole height of the glass tube.

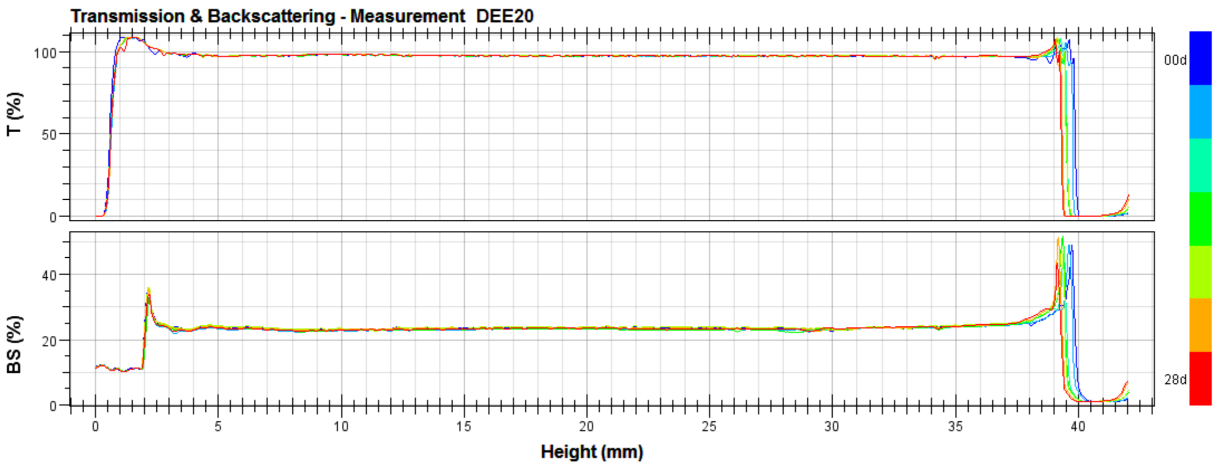

Figure 6. Transmission and backscattering profiles of DEE20 tested during 28 days.

Similar, BS profiles acquired for all tested fuels and represented in Figures 4 - 8 were horizontal at the level 20 – 25 %. Turbiscan laser light interacted with small particles of impurities present in fuel samples. It should be pointed that these particles were evenly dispersed in the sample during whole period of measurements.

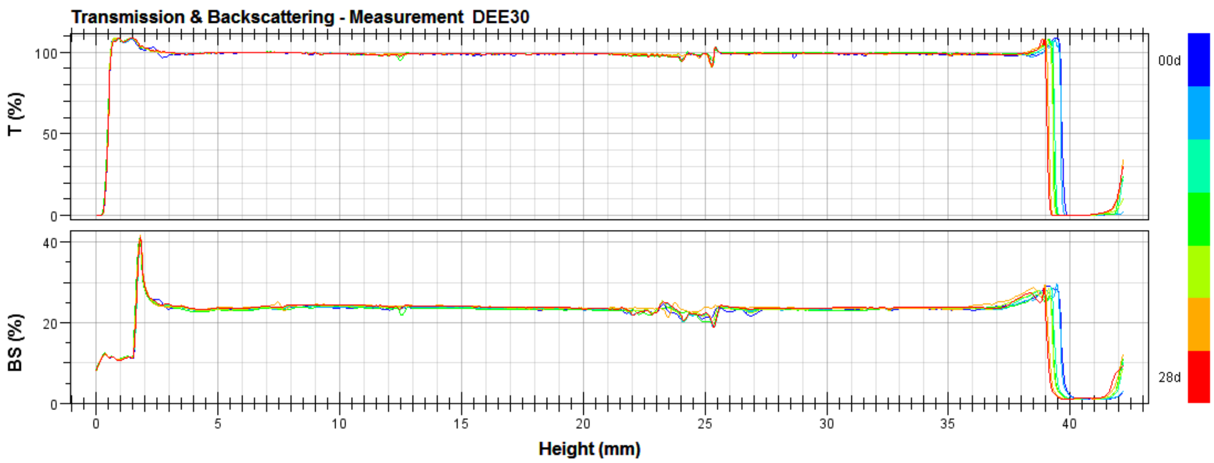

Figure 7. Transmission and backscattering profiles of DEE30 tested during 28 days.

As can be seen in Figure 8 the BS values obtained for DEE40 blend are a bit lower compared with neat RO. It should be pointed that commercial RO contains some kinds of impurities that have not been removed in the filtration process. Lower values of the BS acquired for DEE40 sample may confirm that unfiltered particles of impurities normally existing in RO were diluted by DEE.

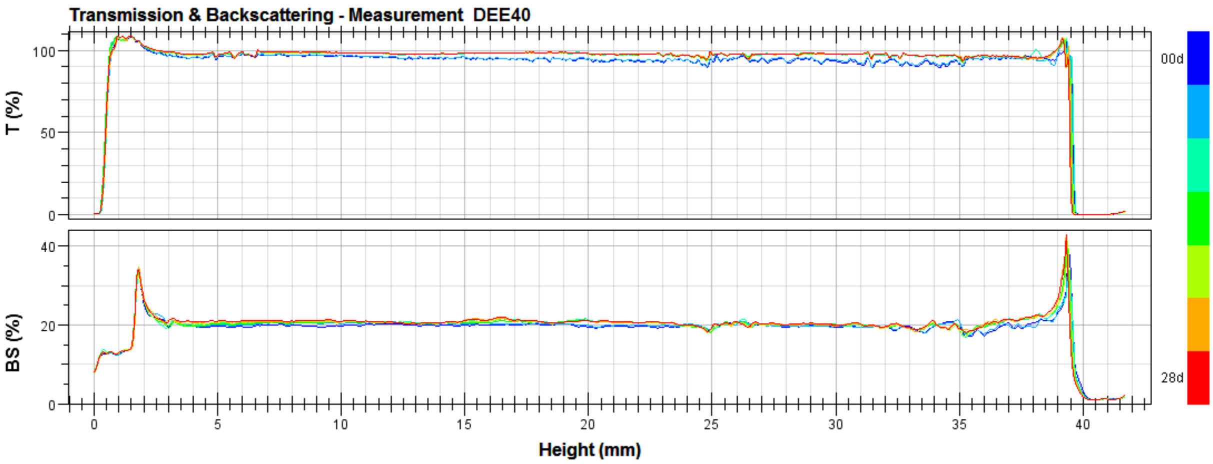

Figure 8. Transmission and backscattering profiles of DEE40 tested during 28 days.

4. Conclusions

In this research phase stability of DEE/RO fuel mixtures was empirically examined. In particular blends of RO with addition of 10, 20, 30 and 40 % by vol. DEE were examined using a Turbiscan Lab research equipment. Results confirm that all tested DEE/RO blends do not separate during 28 days of storage period. Nonetheless, oxidation stability of such blends is still unknown. Plant oils contain unsaturated fatty acids. These acids tend to oxidize and this process has negative impact on the physicochemical properties of plant fuels. An impact of DEE on this process should be empirically verified in further research.

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