Lauric Acid-based Polyol Esters as Potential Bio-based Lubricants for Diesel Fuel

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In this paper, lubricants based on lauric acid and different polyols – neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) – were synthesized. After purification, their purity of > 97 mol% was confirmed by infrared spectroscopy and proton nuclear magnetic resonance. Synthesized lubricants 100 to 5000 ppm formulations with diesel showed similar density, kinematic viscosity, and low-temperature behavior to diesel according to standard tests, meaning that they can be used in current diesel engines. They have improved the lubricity of the formulations, as confirmed by a lower coefficient of friction, and an almost 50 % improvement in wear scar diameter (according to EN 12156-1).

Keywords
lubricants, polyols, diesel fuel, lauric acid, esters, friction

Introduction

The tightening of standards for sulfur and nitrogen containing compounds, and polycyclic aromatic hydrocarbons in diesel fuel is aimed at reducing pollutant emissions into the atmosphere. This is an important issue because these pollutants can have negative effects on human health and the environment[1,2]. According to regulations, diesel fuel sold in industrially developed countries must not contain more than 10 parts per million (ppm) of sulfur[3]. Reducing the content of sulfur and other heteroatom containing compounds in diesel fuel reduces pollutant emissions but has adverse effects on some properties of diesel fuel. One of the most important negative effects of reducing the content of these compounds is the reduced lubricity of the fuel, which can lead to increased wear of fuel system components[4]. In addition, the reduced lubricity of the fuel can also lead to increased wear, which in turn can contribute to premature failure of fuel pumping system components. However, these negative effects can be mitigated by using additives and other measures to improve the lubricity and protective properties of the fuel to maintain proper operating conditions[5,6].

The use of natural triglycerides as lubricants is becoming increasingly popular as they are environmentally friendly and have better lubricity compared to mineral-oil-based lubricants. These oils are derived from natural sources, such as vegetable and animal fats, and have a number of beneficial properties. For example, they are low in toxicity and readily biodegradable, making them less harmful to the environment[7,8]. They also have high wear protection and good friction and load-carrying properties, making them suitable for a variety of applications for which conventional lubricants may not be suitable[9–11]. A disadvantage of natural triglycerides is that they can decompose at high temperatures, leading to a decrease in viscosity and the formation of precipitate particles. They can also negatively affect low-temperature properties and consequently other application properties in fuel mixtures[12]. However, this problem can be solved by using other polyhydric alcohols, such as neopentyl glycol (NPG), trimethylolpropane (TMP), or pentaerythritol (PE). These alcohols are more stable at high temperatures and are less easily degraded[8,13].

In the research of Aguieiras *et al.*[14], the enzymatic synthesis of neopentyl glycol-based lubricants was carried out using biodiesel from soybean and castor bean as feedstock and commercial immobilized lipases. The potential application of the synthetic esters from soybean and castor as components of environmentally friendly lubricants was demonstrated by characterizing their properties. The physicochemical properties of the lubricant were dependent on the composition of the biodiesel source, which directly affected the final application of the product. Various works also showed the suitability of TMP for the synthesis of lubricants in reaction

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with biodiesel[15] and caprylic acid[16,17]. Many researchers have compared the influence of different polyols with the same feedstock, such as soybean oil[18], castor oil[19], palm oil[20] and microbial oil from *Rhodotorula toruloides* and *Cryptococcus curvatus*[21].

Ji *et al*.[22] synthesized various lubricants from levulinic acid and polyols NPG, TMP and PE in the presence of sulfuric acid. The wear prevention properties of these esters were tested and found to have a low coefficient of friction and small wear scar diameters. In the study of Arumugam *et al*.[23] the properties and tribological characteristics of neopentyl glycol, trimethylolpropane and pentaerythritol esters were also evaluated, and found that the viscosity, cloud point, pour point and flash point of PE esters showed better values compared to NPGL and TMP esters.

In this work, we synthesized lubricants from lauric acid and polyols NPG, TMP and PE in the presence of catalyst *p*-toluenesulfonic acid monohydrate (PTSA). The synthesized additives were added to diesel fuel and the effects on application properties were studied, focusing on low-temperature properties according to EN 116 for the Cold Filter Plugging Point (CFPP), ASTM D5950 for the Pour Point (PP), and lubrication properties by measuring the coefficient of friction and wear scar diameter according to the test method EN 12156-1.

Materials and methods

Materials

Diesel used in this study was without additives (Table 1), and it was obtained from INA PLC, Croatia. Chemicals for lubricants production, lauric acid (LA, 99 %) and corresponding alcohols – neopentyl glycol (NPG, 2,2-dimethylpropane-1,3-diol, 99 %), trimethylolpropane (TMP, 2-ethyl-2 (hydroxymethyl)propane-1,3-diol, 98 %) and pentaerythritol (PE, 2,2-bis(hydroxymethyl)propane-1,3-diol, 98 %) with the catalyst *p*-toluenesulfonic acid monohydrate (PTSA), were all obtained from Acros Organics. Chemicals for lubricants purification, sodium chloride (NaCl), sodium carbonate (Na_2CO_3), dichloromethane (CH_2Cl_2), and ethyl acetate ($CH_3COOC_2H_5$) were all laboratory grade and obtained from Lach-Ner.

Table 1 – *Physical and chemical properties of diesel without additives*

Test	Method	Value
Density at 15 °C (kg m^{-3})	EN ISO 12185	829.5
Lubricity (μm)	EN ISO 12156-1	570
Cetane index (–)	EN ISO 4264	53.4
Cold filter plugging point (°C)	EN 116	–8.0
Pour point (°C)	ASTM D 5950	–18.0

Synthesis of lubricants

Lubricants were synthesized by the esterification reaction (Fig. 1) of lauric acid (LA) and the corresponding alcohol with the acid catalyst PTSA. The polyols used in the synthesis were neopentyl glycol with two hydroxyl groups, trimethylolpropane with three hydroxyl groups, and pentaerythritol with four hydroxyl groups. According to the alcohols used, the synthesized lubricants were named neopentyl glycol dilaureate (NPGL), trimethylolpropane trilaureate (TMPL), and pentaerythrol tetralaurate (PEL). Esterification reaction was carried out at 120 °C for 7 hours with a catalyst mass fraction of 1 % of the mass of reactants. In the reaction mixture, lauric acid was added in excess to ensure that all the alcohol was reacted. All reactions were carried out in vials with a total mass of the reaction mixture of 8 g. The apparatus for carrying out the synthesis consisted of an oil bath, a magnetic stirrer with a heater and a temperature controller.

Purification of lubricants

The purification methods used to purify lubricants were extraction and column chromatography.

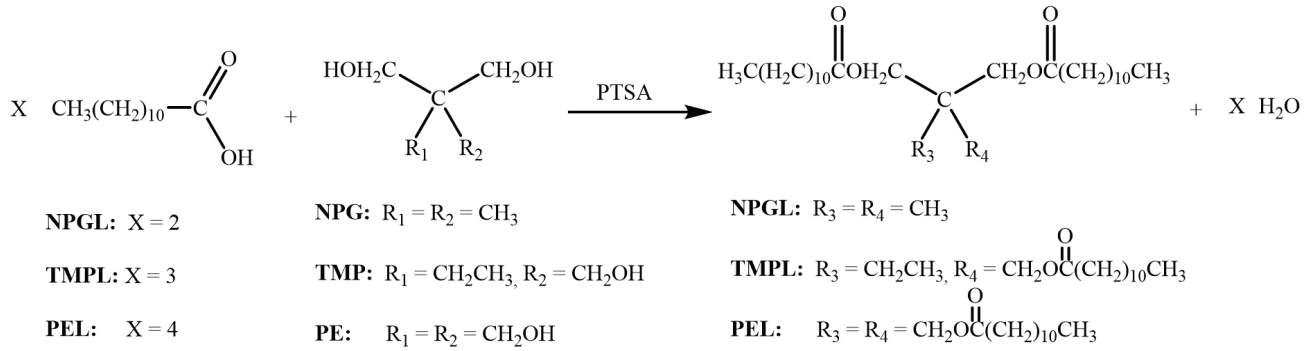

Fig. 1 – *Schematic of the lubricant synthesis*

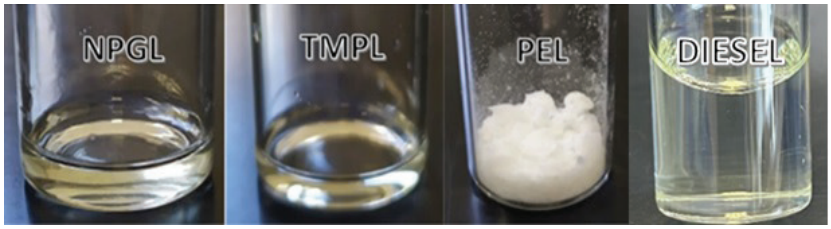

Fig. 2 – *Synthesized lubricants after purification and diesel fuel*

Excess lauric acid and catalyst were removed from the product mixture by extraction with ethyl acetate and aqueous sodium chloride and sodium carbonate. The unpurified lubricant was first dissolved in ethyl acetate, after which it was mixed with an aqueous solution of sodium salts. The aqueous phase was prepared so that the content of both salts was 4 wt.%. Then, 6 to 10 g of ethyl acetate were needed to dissolve 1 g of an unpurified sample of lubricants NPGL and TMPL, while 20 g of ethyl acetate were needed for lubricant PEL. After separating the layers, the upper organic layer was taken and evaporated on a rotavapor. With this method, excess lauric acid passed into the aqueous phase, resulting in sodium laureate salt. In this way, lauric acid was separated from the ester that remained in the organic phase. Column chromatography was used to separate esters from products formed by an incomplete esterification reaction. Column chromatography was performed with silica gel as the stationary phase and dichloromethane as the mobile phase. Fractions of 10 mL each were collected and evaporated on a rotary evaporator at a temperature of 75–90 °C under reduced pressure (5–20 kPa) and with rotation speed of 110 min^{-1}. After purification, a white solid (Fig. 2) was obtained in the case of PEL lubricants, while in the case of NPGL and TMPL lubricants, a transparent gel was obtained.

Characterization of lubricants, diesel, and lubricant/diesel formulations

The chemical structures and purity of synthesized lubricants were characterized using a Fourier – transform infrared (FTIR) spectrometer (Perkin Elmer Spectrum One FT-IR Spectrometer with Attenuated Total Reflectance (ATR) technique and a proton nuclear magnetic resonance (^{1}H NMR) spectrometer (Bruker Avance Instrument). The ^{1}H NMR spectra of the lubricants were recorded at 600 MHz using deuterated chloroform ($CDCl_3$) as solvent. The thermal properties of the lubricants and their formulations with diesel were measured using a Mettler Toledo DSC1 Differential Scanning Calorimetry (DSC) analyzer. Samples were scanned from +45 °C to –80 °C at 10 °C min^{-1} in a nitrogen atmosphere. The kinematic viscositiy of lubricant/diesel formulations was measured at 40 °C according to EN ISO 3104 and density with an Anton-Paar density meter at 15 °C. Standard tests for low-temperature properties of lubricant/diesel formulations were performed according to EN 116 for the Cold Filter Plugging Point (CFPP) and ASTM D 5950 for the Pour Point (PP). The coefficient of friction of lubricant/diesel formulation was determined by a HR30 Rheometer from TA Instruments. The lubricity of diesel without and with lubricants was determined measuring the wear scar diameter according the EN 12156-1 test method.

Results and discussion

Structure and purity determination of lubricants

FTIR spectroscopy was used to determine if the reaction was carried out successfully with the formation of the desired product, and to analyze the success of the purification method. The FTIR spectrum (Fig. 3) of lauric acid (LA) shows an absorption band in the region of 2850–2955 cm^{-1} that corresponds to the stretching of the C–H bond. At 1695 cm^{-1} is the most pronounced signal corresponding to the stretching of the C=O bond. In the case of

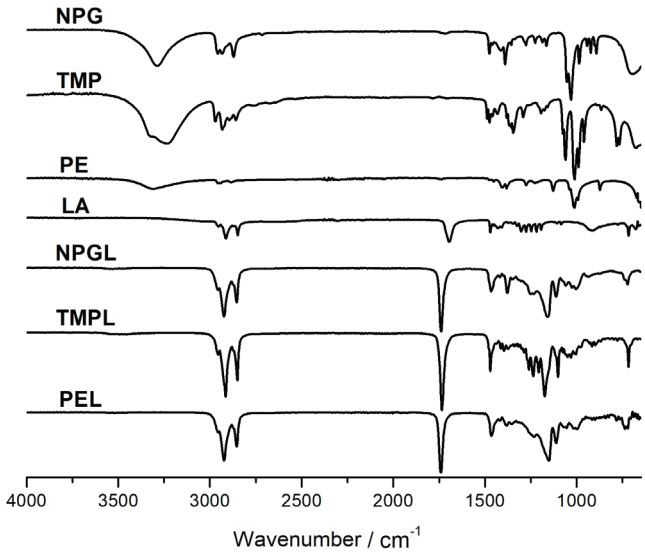

Fig. 3 – *FTIR spectra of lauric acid (LA), alcohols – neopentyl glycol (NPG), trimethylolpropane (TMP), pentaerythritol (PE) and synthesized lubricants – neopentyl glycol dilaureate (NPGL), trimethylolpropane trilaureate (TMPL) and pentaerythritol tetralaurate (PEL)*

alcohol (NPG, TMP and PE), the absorption band of the O–H functional group is visible in the region of 3000–3500 cm^{-1} and there is a different signal in the "fingerprint" region, with the C–O–C stretching signal appearing at 1157 cm^{-1} in NPGL, 1150 cm^{-1} in TMPL, and 1175 cm^{-1} in PEL lubricant. Successfulness of the reaction can be confirmed by the appearance of the new band at 1740 cm^{-1} corresponding to the C=O bond of synthesized esters NPGL, TMPL, and PEL. After purification, absence of C=O bond signal of lauric acid at 1695 cm^{-1} and absence of alcohol O–H group in the range of 3000–3500 cm^{-1}, confirms that the purification was carried out successfully.

The synthesized lubricants were characterized by NMR to confirm the structure and the purity of the products. The ^{1}H NMR spectrum of pentaerythritol tetralaurate (PEL) can be seen in Fig 4. At

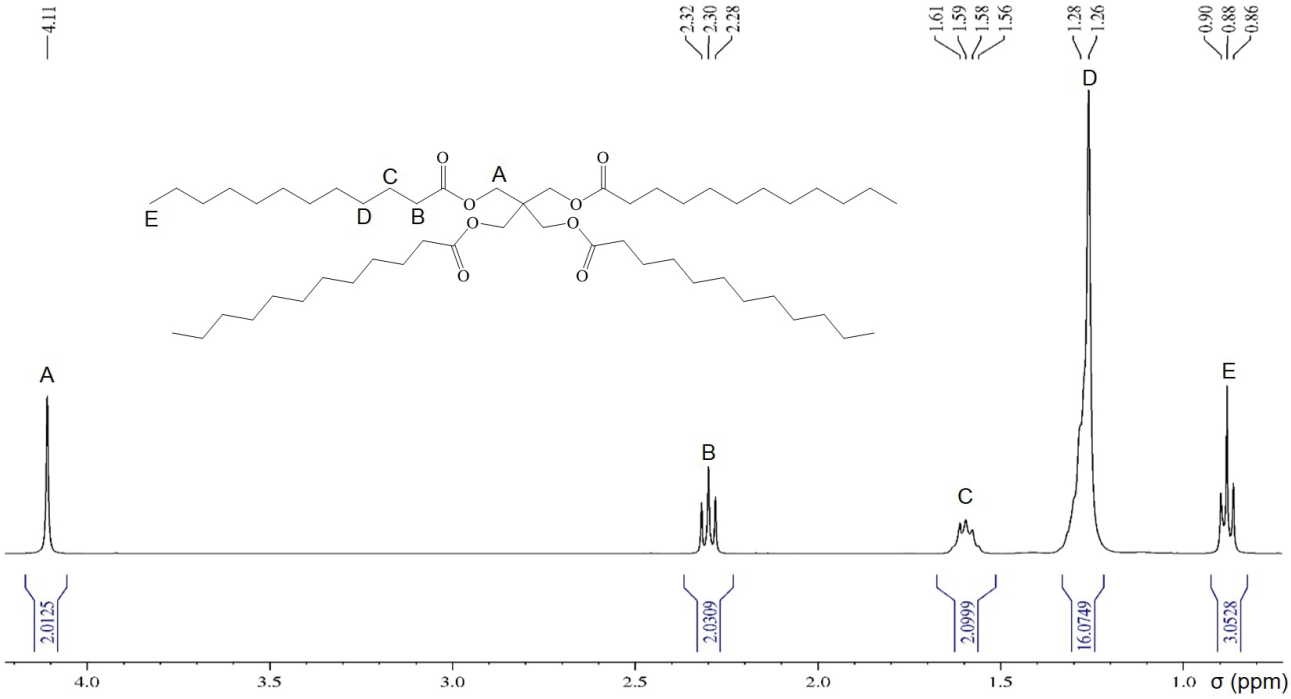

Fig. 4 – *^{1}H NMR spectrum of pentaerythritol tetralaurate (PEL)*

Fig. 5 – *^{1}H NMR spectrum of neopentyl glycol dilaureate (NPGL)*

4.11 ppm (signal A) there is a singlet corresponding to the protons of the CH_2 group of the formed ester. The triplet at 2.30 ppm (signal B) corresponds to the CH_2 protons next to the carbonyl group, and the CH_2 group immediately next to them gives a quintuplet at 1.59 ppm (signal C). The protons of the methyl group correspond to a triplet at 0.88 ppm (signal E). The integral of the multiplet at 1.27 ppm (signal D) corresponds to the number of protons of the other methylene groups of the hydrocarbon chain.

The ^{1}H NMR spectrum of neopentyl glycol dilaureate (NPGL) is shown in Fig. 5. Compared to PEL, the signal given by the protons of the CH_2 group (signal A) of the formed ester is shifted towards high field area. One higher signal is also visible at 0.96 ppm (signal F) corresponding to the proton signal of the methyl group of the alcohol part of the ester.

In Fig. 6 the ^{1}H NMR spectrum of trimethylolpropane trilaureate (TMPL) is presented. The new signal that appears is a quadruplet at 1.48 ppm (signal G) which corresponds to the signal of the proton of the CH_2 group next to the CH_3 group of the alcohol part of the ester. Purity according to NMR for all esters was above 97 %.

Physical properties of lubricant/diesel formulations

To test whether the addition of lubricants affects the physical properties of the formulations prepared in this way, the viscosity at 40 °C and the density at 15 °C were measured, since these values are specified for diesel fuel according to the HR EN 590 standard. The addition of lubricants at a concentration of 2000 ppm did not significantly affect the values of kinematic viscosity or density. The addition of lubricants to diesel fuel insignificantly increased the density in all formulations from 0.8295 g cm^{-3} to 0.8300 g cm^{-3}, while the kinematic viscosity of diesel fuel did not change.

Thermal characterization of lubricants and formulations in diesel

The crystallization behavior of the lubricants and their formulations with diesel was measured by DSC. It can be seen that the TMPL additive has the lowest crystallization temperature (Fig. 7) of all the additives measured, while the PEL additive crystallizes at much higher temperatures, which is already evident from the fact that it is a solid at room temperature.

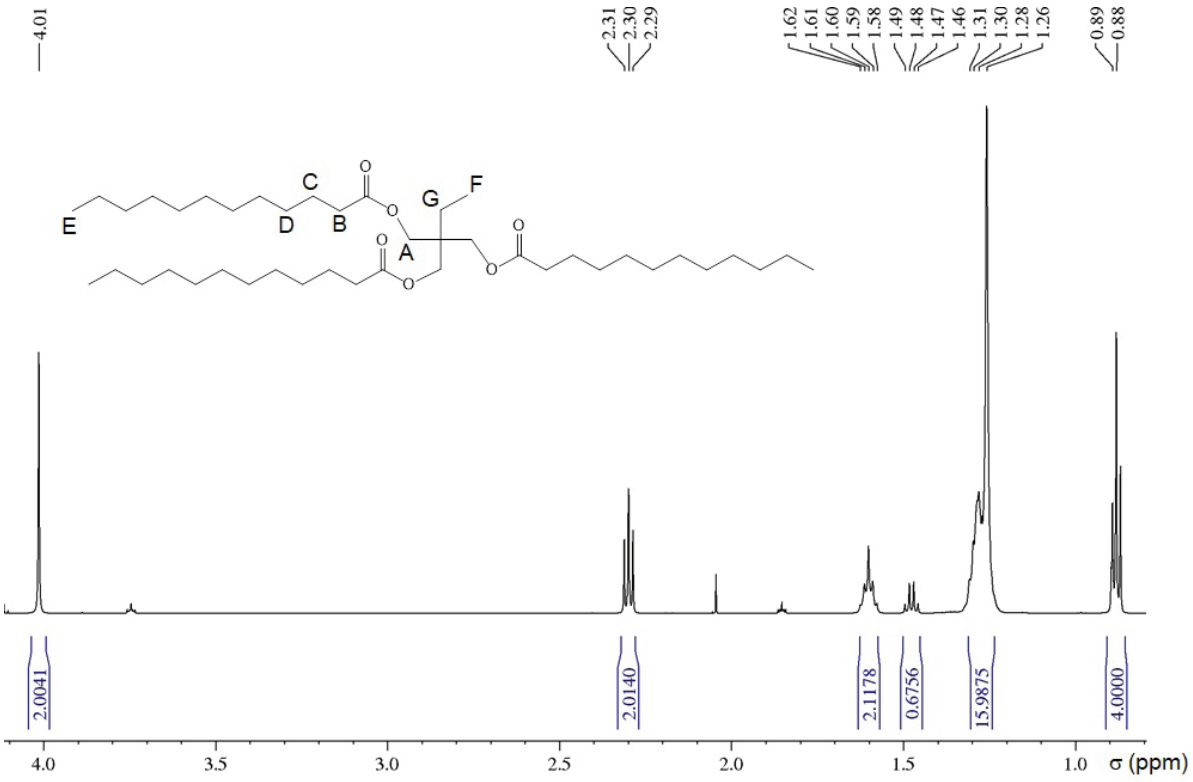

Fig. 6 – *^{1}H NMR spectrum of trimethylolpropane trilaureate (TMPL)*

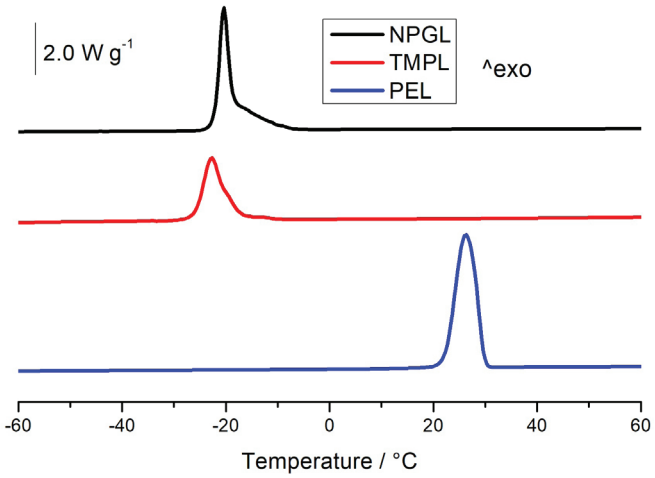

Fig. 7 – *DSC spectrum of lubricants after purification*

Table 2 – *CFPP and PP values of lubricant/diesel formulations*

Lubricant concentration in diesel	2000 ppm		5000 ppm	
Lubricant	T_{CFPP} (°C)	T_{PP} (°C)	T_{CFPP} (°C)	T_{PP} (°C)
NPGL	–7	–18	–7	–18
TMPL	–7	–18	–7	–18
PEL	–8	–21	–7	–18

*CFPP– cold filter plugging point; PP– pour point

Pure lubricants were added to diesel fuel at a concentration of 2000 ppm and their influence on the crystallization temperature of diesel fuel was compared. From Fig. 8, it can be seen that the addition of lubricants to diesel fuel resulted in a decrease in the crystallization temperature. NPGL decreased the temperature of crystallization of diesel fuel from –16.1 °C to –19.4 °C, TMPL to –18.7 °C while the highest decrease, for more than 3 °C, can be seen with the addition of PEL additives, *i. e.* to –19.7 °C.

The influence of lubricants addition in diesel on the low-temperature properties was determined according to standardized methods (Table 2). The pour point (PP) was determined according to ASTM D5950 and the cold filter plugging point (CFPP) according to EN 116. First, mixtures of lubricants with diesel were prepared in a concentration of 2000 ppm. The CFPP of diesel without additives was –7 °C, while the PP was –18 °C. From the obtained results, it can be concluded that only the PEL lubricant insignificantly changed the CFPP of diesel by 1 °C and the PP by 3 °C, while with the other two lubricants there was neither improvement nor deterioration of properties. New mixtures were prepared with a lubricant concentration of 5000 ppm. With increased concentration, no lubricant affected either the CFPP or PP.

As it can be seen, the influence of the addition of additives to diesel fuel on the temperature properties of the formulation is different in DSC measurements than in CFPP and PP measurements, which can be explained by different cooling rates. However, it is clear from both analyses that the PEL lubricant reduces the crystallization temperature and CFPP and PP values more than NPGL and TMPL lubricants.

Influence of lubricant addition on lubrication of corresponding diesel formulation

Fig. 9 shows the coefficient of friction plotted against the sliding speed for pristine diesel and diesel with 2000 ppm NPGL, TMPL and PEL. Coefficient of friction of diesel ranged from 0.19 to 0.15, and decreased with increasing sliding speed. The

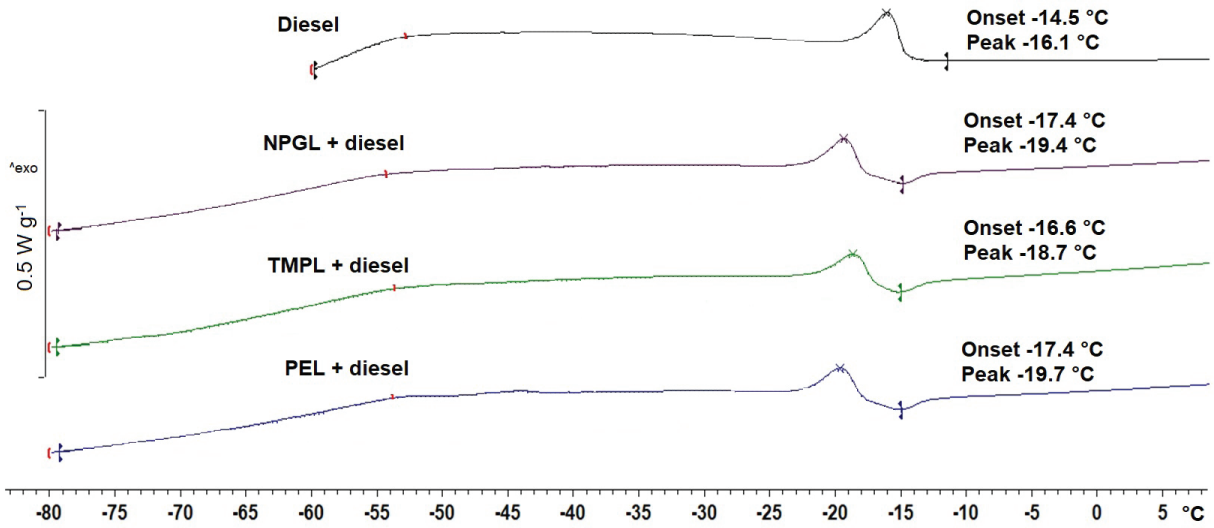

Fig. 8 – *DSC spectrum of diesel and its formulations with 2000 ppm of lubricants*

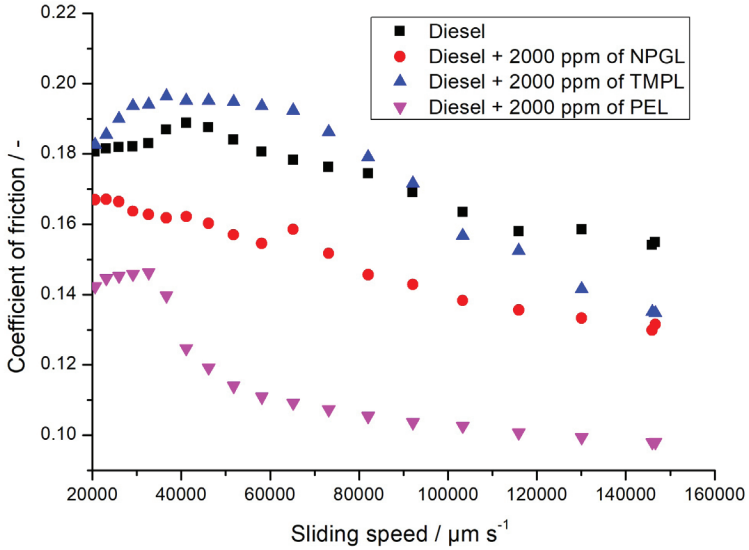

Fig. 9 – *Coefficient of friction values of diesel and formulations with 2000 ppm lubricants*

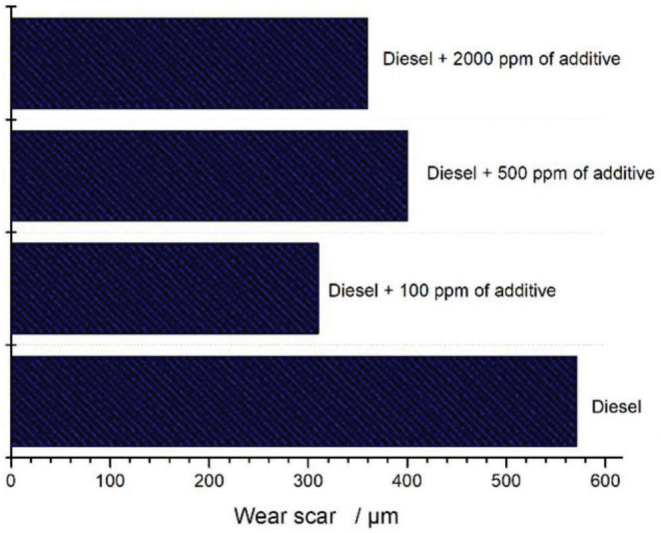

Fig. 10 – *Wear scar diameter values of diesel and formulations with 100, 500 and 2000 ppm of PEL lubricant in diesel*

addition of all synthesized additives reduced the coefficient of friction. At lower sliding speeds, the addition of TMPL additive increased the coefficient of friction up to 0.20, but when the speed was further increased, it still lowered the value to slightly above 0.14. The addition of NPGL and PEL lubricants reduced the coefficient of friction at all speeds, NPGL lowered it to slightly below 0.14, while PEL lubricants even fell below 0.10.

Lubricity determination of PEL/diesel formulation

As the PEL lubricant showed the greatest changes when added to formulations with diesel in friction and low-temperature tests, its influence on the lubricity of diesel was investigated in more detail. Lubricity measurements (Fig. 10) were made by measuring the wear scar diameter according to the EN 12156-1 test method.

The measurements showed that the value for the wear scar of untreated diesel fuel is 570 μm, which is not within the limits prescribed by the standard for diesel fuel EN 590. It states that the value for the wear scar must be below 460 μm for diesel fuel to be used.

For the formulation measurements, diesel formulations were prepared with PEL lubricant at concentrations of 100, 500, and 2000 ppm. The wear scar value of the formulation with 2000 ppm additive was 360 μm, with 500 ppm additive 400 μm, while with the addition of PEL additive at a concentration of 100 ppm, the wear scar diameter decreases to 310 μm, reducing the wear scar by almost 50 %. From the measurement results, it can be seen that the PEL additive at all concentrations improved lubricity by reducing the wear scar diameter, and lubricity values within the limit values of the EN 590 standard were obtained.

Comparison of PEL additives with commercial and recent research additives

In order to evaluate the results of the analysis of the effects of PEL additives on diesel fuel, they need to be compared with additives of similar purpose, focusing on comparisons regarding the effects on lubricity, but also on low- temperature properties.

A comparison of commercial additives based on acids of tall oils[24] produced by BASF, Clariant, Total, and Afton Chemical Corporation shows that they reduce the diameter of wear scars in diesel fuel formulations by up to 300 to 400 μm, suggesting that the PEL additive synthesized in our research can compete with them, reaching a value of 310 μm when added to diesel at a concentration of only 100 ppm.

In a recent study, Sruthi *et al.*[25] synthesized a series of methyl oleate-based diesters to improve the lubricity of diesel and improved the wear scar of diesel from 502 to 388 μm at a concentration of 300 ppm and 348 μm at a concentration of 600 ppm. Liu *et al.*[26] synthesized anhydride additives based on tung oil methyl esters and methanol or butanol. They studied the effect of the additives on the lubricity of diesel fuel in formulations containing 100 to 1000 ppm. They reduced the diameter of diesel fuel wear scars from 550 to 325 μm with methanol-based additives, and by up to 266 μm with butanol-based additives at a concentration of 1000 ppm. However, at a concentration of 100 ppm, the wear was around 480 μm in both cases, which does not meet the limits of the diesel standard EN 590.

Kondrasheva *et al.*[24] synthesized diesel fuel anti-wear bioadditives based on different raw materials and evaluated their effects on lubricity and low-temperature properties. The initial wear scar of diesel fuel was 443 μm, and with the addition of additives in an amount of 10,000 ppm, there was an improvement to 332 μm, but this had a negative effect on low-temperature properties, and the freezing point of diesel fuel deteriorated from –17 °C to –13 °C. In comparison, the addition of PEL additives in an amount of 5,000 ppm did not lead to a deterioration of the low-temperature properties of diesel, and lower wear scars were obtained with an addition of only 100 ppm than in the aforementioned studies.

Conclusions

Synthesized lubricant additives based on lauric acid and neopentyl glycol dilaureate (NPGL)/ trimethylolpropane trilaureate (TMPL)/pentaerythritol tetralaureate (PEL) were successfully synthesized, purified, and blended in diesel. The prepared formulations did not deteriorate the low-temperature properties of diesel and had negligible effects on density and viscosity, which means that they do not affect fuel atomization and can be used in current engines. Diesel formulations based on NPGL and PEL additives reduced the coefficient of friction at all measured sliding speeds compared to pristine diesel. The PEL additive exhibited the best lubricity, which was also confirmed by a standardized test (EN 12156-1) that showed an approximately 50 % reduction in wear scar compared to pristine diesels. Compared to other studies and commercial additives, PEL additives are competitive with all of them, and in most cases, they outperform them at lower concentrations without negatively affecting other diesel fuel properties.

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