SELECTED PHYSICOCHEMICAL PROPERTIES OF WATER-FUEL MICROEMULSION AS AN ALTERNATIVE FUEL FOR DIESEL ENGINE

MILENA GÓRSKA[1], PAWEŁ BUKREJEWSKI[2], JERZY STOBIECKI[3]

Abstract

The paper focuses on the assessment of selected physicochemical properties of microemulsion containing 5% by mass (m/m) of surface active compounds (SAC), i.e. Span20 and Crillet4 as well as 10% (m/m) of distilled water dispersed in diesel fuel (DF). In particular temperature dependent properties such as: flash point (FP) and cold filter plugging point (CFPP) as well as lubricity, friction coefficient, corrosiveness and kinematic viscosity of tested fuels were examined. It was found that the tested surfactants and water added to DF increase microemulsion FP by 13°C. For this reason, it can be stated that tested microemulsion is safer than typical DF. On the other hand it was found that the CFPP of the tested microemulsion is also adequately higher. It means less usefulness of such fuel during winter periods. Based on the research results it can be stated that addition of tested surfactants slightly worsens the lubricity of DF. However, the same surfactants in the presence of dispersed water reduce the friction in the tribological node and improve the lubricity of the tested microemulsion. Research showed that tested microemulsion system is not corrosive as well as its kinematic viscosity meet requirements of EN 590 standard. Based on all these findings, microemulsion is considered as safe and such fuel can be recommended for engine tests.

Keywords: microemulsion, alternative fuel, diesel engine, environmental protection

1. Introduction

The progressing ecological requirements related with the emission of harmful exhaust components from self-ignition engines make their design more and more complex. It has an impact on the growing costs of their manufacture and repair in the event of damage. Taking into account the increase in diesel oil prices in relation to gasoline, it can be concluded that the popularity of light vehicles equipped with self-ignition engines is decreasing. It has been confirmed in the statistics of the European Association of Vehicle

[1] Faculty of Materials Science and Design, Kazimierz Pulaski University of Technology and Humanities in Radom, ul. Malczewskiego 29, 26-600 Radom, Poland

[2] Analytical Laboratory, Łukasiewicz Research Network - Automotive Industry Institute, ul. Jagiellońska 55, 03-301 Warszawa, Poland, e-mail: p.bukrejewski@pimot.eu

[3] Faculty of Mechanical Engineering, Kazimierz Pulaski University of Technology and Humanities in Radom, ul. Malczewskiego 29, 26-600 Radom, Poland

Manufacturers (ACEA), according to which vehicles equipped with gasoline engines gain popularity.

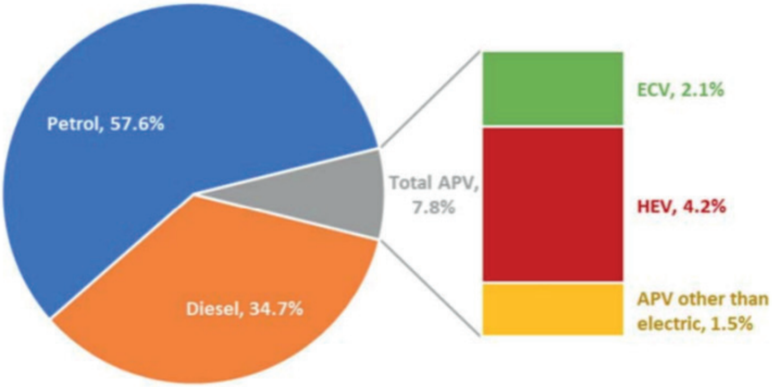

Fig. 1. New passenger car registrations by fuel type in the European Union (EU); quarter 3, 2018 [7]

In 2018, the share of new vehicles equipped with gasoline engines increased by 7% compared to the same period in 2017. It can also be stated that electric vehicles (EV) are more and more popular. This is particularly evident among the group of Western European EU countries [7]. Despite the trend indicated, it is expected that vehicles powered by self-ignition engines will be produced and improved. This is due to the fact that the development of electric powertrains and batteries does not allow their use, among others for driving heavy duty vehicles and buses. Therefore, there is a motivation to look for new fuels that help protect the environment against hazards resulting from the combustion of traditional fuels in internal combustion engines. Research in this area suggests that so called oxygenated fuels such as alcohols and fatty acid methyl esters can have important influence on reduction of harmful engine gases. Also selected ethers such as ethyl tert-butyl (ETBE) as well diethyl ether (DEE) are considered as favourable component of the diesel fuel combustion system [6, 22]. In case of self-ignition engines, the main environmental problem is emission of soot particles and nitrogen oxides. Based on the analysis of literature data, it can be concluded that the soot particles arise most intensively in those areas of the combustion chamber, where the temperature reaches 1700 ^{o}C and there is an excess of fuel in relation to air (high value of equivalence ratio, Figure 2). In such conditions hydrocarbons molecules are pyrolyzed and then the Polycyclic Aromatic Hydrocarbons (PAH) growth forming the first soot nuclei [25]. Some of them are burnt but the remaining part is emitted to the environment through the exhaust pipe.

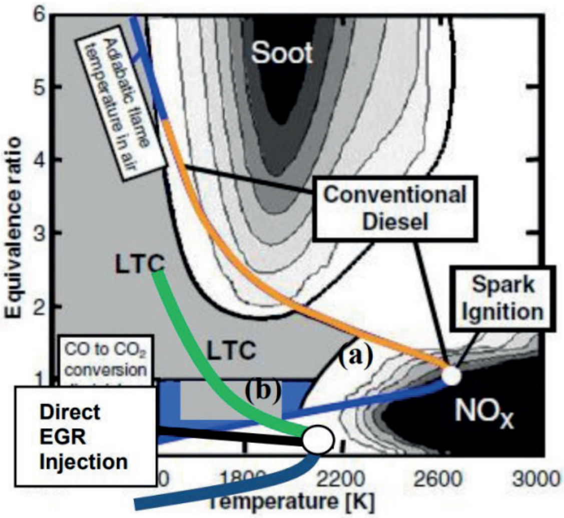

Fig. 2. Regimes of NO_x and soot formation in relationship to the flame equivalence ratio (Fuel/Air ratio) and flame temperature [4]

In case of NO_X formation, the thermal and prompt mechanism is dominant [17]. It is known that higher NO_X emission is closely related with higher temperature in combustion chamber especially in areas rich in oxygen, i.e. forehead of the flame. In these areas the local temperature of the combustion process can reach a value higher than 2000°C. Therefore, reduction of soot and nitrogen oxide emissions can be achieved by reducing the temperature of the combustion process and improving the mixing of fuel with air, so as to obtain a mixture as close as possible to the so-called homogeneous. This combustion strategy is implemented under the Homogeneous Charge Compression Ignition (HCCI) technology. It is difficult to implement and therefore it is not widely used in self-ignition engines. Selected aspects of this issue are presented in literature data [13, 15, 20]. For many years, it has been believed that improving the environmental performance of self-ignition engines can also be achieved by using water as a fuel additive. It is known that water injected into the combustion chamber evaporates and for this reason the temperature in combustion chamber is reduced. Ballestar et al. [2] in their research confirmed that the heat absorbed by the water injected in the emulsion reduces the flame temperature by 65 K. For this reason the rate of NO formation was decreased. Simultaneously solid particles emissions were significantly reduced too. Also, Serrano et al. [21] tested an impact of adding water into the intake manifold with a flow-blurring injector. They achieved even 70% reduction of NO_X. Ithnin et al. [8] tested water - diesel emulsion and found that NO_X and PM emissions were reduced by 41% and 45% respectively as compared to diesel fuel. It should be pointed that disintegration of the water molecule provides oxygen, which can have a beneficial effect on the oxidation of the soot nuclei inside of fuel jet. For this reason particles emission from diesel engines fuelled with water-fuel emulsion is reduced too. As stated above, review studies of fuel emulsions confirm that their combustion allow reduce the emission of harmful exhaust components. It is emphasized that droplets of microemulsion fuel undergo micro-explosion phenomenon. A lot of papers suggest that mentioned phenomenon improves the quality of fuel atomization. Some other studies suggest that micro-explosion phenomenon undergoes only in specific conditions. This was confirmed by tests carried out for water-diesel emulsions [12, 19, 24] as well as for water-biodiesel emulsion [10]. Despite these benefits, the technology of using water as part of the combustion system has not been developed due to the fact that until recently, engine exhaust emission standards did not justify the introduction of this technology to engines. Now the situation has changed and vehicle manufacturers are looking for ways to meet restrictive environmental standards for particulate matter and nitrogen oxide emissions. Therefore, it is worth developing research on the use of water as a component of the combustion system. As mentioned, water can be delivered to the combustion chamber in the form of an emulsion formed together with surface active compounds (SAC). Figure 3 shows an example of a water-fuel emulsion which was obtained by mixing water with diesel fuel and tween20 surfactant. The light colored emulsions were stable for several minutes after completing the mixing of all ingredients. Phase separation was visible after an hour. For this reason, water-fuel emulsions are not so popular as a fuel for internal combustion engines. Nevertheless, it is possible to obtain more stable emulsions, but this requires the use of suitable emulsion stabilizing surfactants. The progress in the field of water-oil emulsions has led to the development of commercial products, which took place, among others in France and Italy.

a. 0 min left. b. 20 min left. c. 60 min left. d.1 day left.

Fig. 3. Water – diesel emulsion samples [18]

Taking into account the indicated problems related with the stability of water-oil emulsions, more and more attention is focused on microemulsions, which are significantly more stable and favourable for internal combustion engines. A characteristic feature of the microemulsion is that they are transparent and look like a typical diesel fuel. Microemulsion can be achieved by mixing distilled water with diesel fuel and the appropriate surfactants/co-surfactants. The kind of these chemicals and their ratio impact on the physicochemical properties of the water – fuel microemulsion obtained. It should be noted that presence of water in the fuel increases the wear of the fuel supply system components which is due to worse lubrication [14]. Moreover, water promotes corrosion of the fuel injection system. However, water in microemulsion is dispersed in micelles surrounded by a layer of surfactans/co-surfactants. For this reason water content in typical diesel fuel and microemulsion has different impact on the physicochemical properties of these fuels. Based on the literature review it can be stated that knowledge on tribological properties of microemulsions is limited. However, Uchoa et al. [23] evaluated lubricity properties of microemulsion containing glycerin in aqueous solution. The surfactants used in their tests were alkyl-phenyl glycolic polyether and ethylene oxide. They found that increased concentration of glycerin improves lubricity of tested microemulsion. Also, the knowledge on temperature dependent properties and corrosiveness of microemulsions is limited. Acharya et al. [1] tested microemulsion with surfactant Tween80 and co-surfactant n-butanol at ratio 1:1. Results of these research showed that the cloud point decreased with decrease in diesel content and increase in total surface active agent content. Neto et al. [3] investigated emulsion with 15% ethoxylated nonylphenol surfactant. They concluded that cloud point and corrosiveness were not significantly affected by the water and surfactant. Górska et al. [5] reported that microemulsions with Crillet-6/Span-20 containing 4% and 8% of water had acceptable corrosiveness properties after 3 hours of test carried out at temperature of 50°C. However, results of 24 hours tests were significantly worse. Similar results were reported by Kaźmierczyk et al. [9]. They stated that emulsions are characterized by a number of disadvantages i.e. limited stability, unacceptable low temperature properties and strong tendency to cause corrosion of metals. Ochoterena et al. [16] tested emulsion and microemulsion prepared using sorbitan monooleate, penta(ethylene glycol)monoundecyl ether and 10% by weight of water. They confirmed that the viscosity of the water-containing fuels is higher compared with diesel fuel. However the surface tension of the emulsion and diesel fuel was similar. Summarized literature review on the microemulsion features such as presented by Khan et al. [11] it is clear that the most papers are focused on engine emission problems such PM or NO_x. On this background it can stated that physicochemical properties of water-diesel fuel microemulsion are not so well defined, especially in the aspect of engine operation.

2. Methods and materials

In this study three fuels were tested: diesel fuel (DF100), diesel fuel mixed with 5% (m/m) of surface active compounds (DF95) and diesel fuel mixed with 5% (m/m) of surface active compounds and 10% (m/m) of distilled water (M10). Fundamental details of tested fuels are listed in Tab. 1. It should be noted that Span20 and Crillet4 used as surface active compounds (SAC) were produced by Croda Company. Physicochemical properties of both these chemicals are well known. Necessary data are available through the Chemical Abstracts Service (CAS). Span20 has a CAS Number of 1338-39-2. A unique numerical identifier assigned by the CAS to Crillet4 is 9005-65-6.

Tab. 1. Composition of tested fuels

Fuel symbol	Composition, %, m/m			
	Diesel fuel	Water	Span20	Crillet4
DF100	100	0	0	0
DF95	95	0	3.75	1.25
M10	85	10	3.75	1.25

Microemulsion M10 was obtained by mechanical mixing of DF with SAC. Then small portions of distilled water were added and still mixed at a temperature of 25°C. Process was completed when mixture became transparent. A view of all tested fuels shows Figure 4. The Figure confirms that tested microemulsion M10 was transparent without tendency to phase separation within a month of storage.

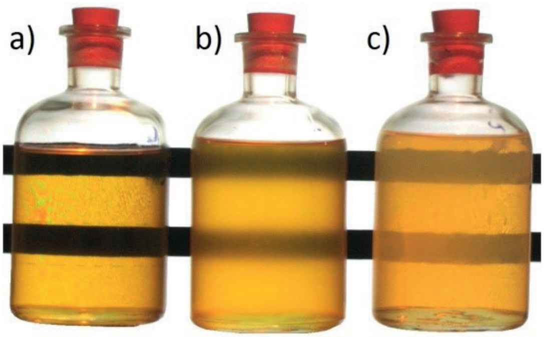

Fig. 4. View of fuel samples stored a month at temperature of 20°C: a) DF100, b) DF95, c) M10

The temperature and tribological properties of tested fuels were examined i.e.: flash point, cold filter plugging point, lubricity, friction coefficient, corrosive effect on copper and kinematic viscosity. Mentioned properties were tested according to methods listed in Table 2.

Tab. 2. Fuel test methods

Parameter	Method
Flash point	EN ISO 2719
CFPP	EN 116:2015
HFRR	EN ISO 12156-1:2006
Friction coefficient	4-ball tester T-02
Copper corrosion	ASTM D130
Kinematic viscosity	EN 3104

3. Results

According to EN 590 standard, the flash point of DF should be higher than 55°C. Based on Figure 5, it can be stated that all tested fuels meet the above mentioned requirement. In case of DF100, a flash point of 63°C was reached. Addition of surfactants to DF increased this temperature by 2°C. On the other hand, the dispersion of water in the tested fuel had significant influence on the further increase of the flash point up to 77°C, i.e. by 22°C more compared with the minimum requirements specified in the EN 590 standard. The surface active compounds used in this research are characterized by high viscosity and density as well as low volatility. Therefore, their addition to DF reduces the intensity of the formation of fuel vapors that may ignite. For this reason tested microemulsion is significantly safer compared with regular diesel fuel.

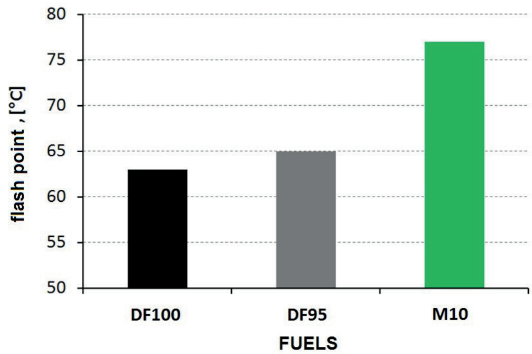

Fig. 5. Flash point of tested fuels

In case of diesel engines a low temperature properties of the fuel are crucial. For this reason summer and winter diesel fuel must meet different low temperature requirements. These requirements are set by the value of the lowest temperature of fuel pumping i.e. Cold Filter Plugging Point (CFPP). Figure 6 shows the influence of the tested fuels on variation of CFPP. As can be seen addition of SAC as well as addition of water increases the value of CFPP. For this reason it can be stated that tested microemulsion has limited suitability for the winter period.

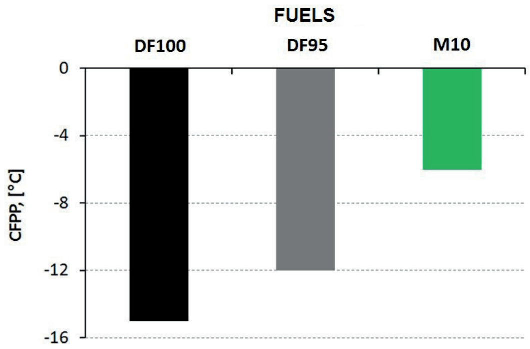

Fig. 6. Cold Filter Plugging Point of tested fuels

The fuel systems rely on the lubricating properties of diesel fuel to prevent excessive wear and seizures. For this reason necessary lubricity tests of the diesel fuel are performed. The most important research mentioned in the EN 590 standard uses bench test known as the High Frequency Reciprocating Rig (HFRR). The test can be carried out at temperature of 60°C or 25°C . The measured value is the diameter of the flattening of the steel ball dipped in tested fuel and rubbed a steel plate in period of 75 minutes. For the test carried out at temperature of 25°C the upper limit value is 380 μm.

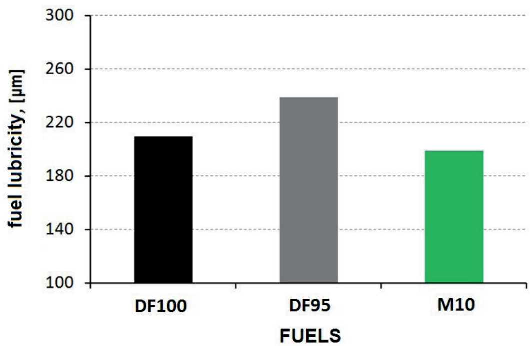

Fig. 7. The fuel lubricity tested at 25°C

Figure 7 clearly shows that all tested fuels have excellent lubricity significantly below the limit of 380 μm. It means that tested microemulsion is safe for the fuel injection equipment of the diesel engines. However, it can be stated that DF95 has worse lubricity compared with regular diesel fuel. It is known that lubricity additives are polar. These improvers adsorb to metal surfaces and soluble hydrocarbon tails that provide a boundary layer. This boundary layer protects metal surfaces from wear and scuffing. SAC are also polar and inhibit lubricity improvers. For this reason HFRR result performed for DF95 fuel was the least favourable. In case of M10 fuel sample the HFRR result is comparable with DF. It can suggest that SAC were utilized for creation of water micelles without of any impact on concentration of additives improving fuel lubricity. Usually better fuel lubricity corresponds with the lower value of the friction coefficient. It was also confirmed in the research carried out on the 4-ball apparatus. The tests were carried out at temperature of 30°C under the load of 2 kN. In such conditions a coefficient of friction was continuously recorded. Results of these researches are showed in Figure 8. Basing on this Figure it can be stated that results very well corresponds with HFRR test. The highest value of the friction coefficient has been acquired for DF95 sample and the lowest for tested microemulsion. These results were expected due the higher friction coefficient usually means higher wear of tribological node. On this ground it can be stated that M10 reached the best lubricity result and for this reason such microemulsion seems to be safe for the injection equipment of the diesel engine.

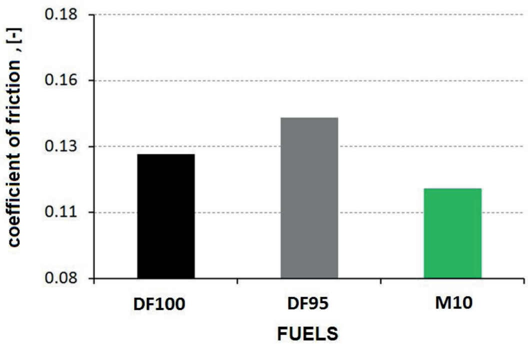

Fig. 8. Coefficient of friction in tribological node obtained for tested fuels

Another important research issue related to the durability and reliability of the diesel engine is copper corrosion testing. The test is sensitive for different chemicals harmful for the engine fuel injection system. Usually it allows to detect too low concentration of corrosion inhibitors in the fuel. The copper strip corrosion test is performed according to procedure described in ASTM D130 standard. Results are classified in four classes i.e. 1–4. According to EN 590 requirements a class 1a or 1b is allowed for the EU market. In practice it means that surface of copper strip before and after test is the same or almost the same. As can be seen from Figure 9, none of the fuels tested caused corrosion. The copper strip surface dipped in M10 sample is classified in class 1b of ASTM D130 standard.

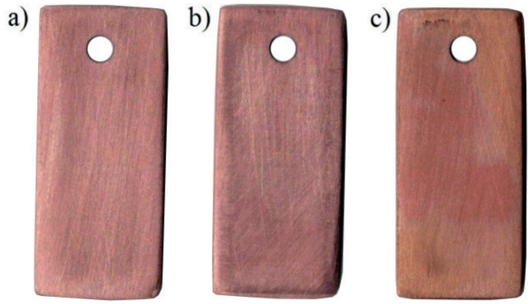

Fig. 9. View of copper strips after 3 hours of corrosion test: a) DF100, b) DF95, c) M10

The diesel fuel must meet necessary viscosity requirements, i.e. correct value must be within range of (2.0–4.5) mm^2/s. As can be seen in Figure 10, Span20 and Crillet4 increases kinematic viscosity of DF95 at around 15% compared with DF100. Addition of water in microemulsion M10 increased viscosity even by 64%. Nevertheless, it can be stated that the fuels meet viscosity requirements set up in EN 590 standard.

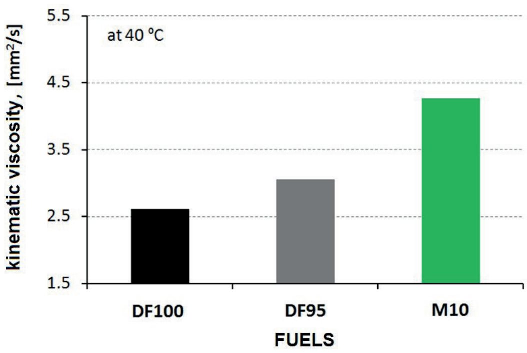

Fig. 10. Kinematic viscosity of tested fuel measured at 40°C

4. Recapitulation and conclusions

Literature reports indicate that emulsions as well as water-fuel microemulsions can be effective in the area of simultaneous reduction of soot particle and nitrogen oxide emissions from self-ignition engines. However, the dispersion of water in diesel oil requires the use of appropriate surface-active compounds, the nature of which is one of the factors affecting the physicochemical properties of the obtained microemulsions. In this work, two chemical compounds: Span20 and Crillet4 have been tested. Based on results, it can be concluded that the presence of water in the microemulsion increases FP. This is a beneficial feature, that can be particularly useful in military vehicles. It was noticed that the applied SAC after adding to DF slightly, i.e. by about 3°C, increase the temperature of CFPP. However, the dispersion of water in this mixture causes the value of this temperature to increase by another 6°C. This means less usefulness of the tested microemulsion during winter periods. As regards the lubricity assessment of the tested fuels, it was found that the addition of surfactants worsened the lubricity of DF by about 13%. This was accompanied by a corresponding increase in the coefficient of friction determined in the tribological node of the four-ball apparatus. However, in the case of tested microemulsion, a slight improvement in lubricity compared to DF was obtained. It should be noted that the lubricity of all tested fuels was significantly below the limit of 380 μm. It means that moving parts of the fuel injection system will not be exposed to excessive wear.

5. Nomenclature

CFPP	cold filter plugging point
CO	carbon monoxide
DEE	diethyl ether
DF	diesel fuel
EN	European Norm International
EV	electric vehicles
FP	flash point
HCCI	homogeneous charge compression ignition
HFRR	high frequency reciprocating rig
NO_x	nitrogen oxides
PM	particulate matter
SAC	surface active compounds

6. References

[1] Acharya B., Sarathi Guru P., Dash S.: Tween-80–n-Butanol–Diesel–Water microemulsion system - a class of alternative diesel fuel. Journal of Dispersion Sciences and Technology. 2014, 35, 1492-1501, DOI: 10.1080/01932691.2013.858348.

[2] Ballester J.M., Fueyo N., Dopazo C.: Combustion characteristics of heavy oil-water emulsions. Fuel. 1996, 75, 695-705. DOI: 10.1016/0016-2361(95)00309-6.

[3] Dants Neto A.A., Fernandes M.R., Barroso Neto E.L., Castro Dantas T.N., Moura M.C.P.A.: Alternative fuels composed by blends of nonionic surfactant with diesel and water: engine performance and emissions. Brazilian Journal of Chemical Engineering. 2011, 28, 521-531. DOI: 10.1590/S0104-66322011000300017.

[4] Dec J.E.: Advanced compression-ignition engines - understanding the in-cylinder process. Proceedings of the Combustion Institute. 2009, 32, 2727-2742. DOI: 10.1016/j.proci.2008.08.008

[5] Górska M., Chmielewski Z., Stobiecki J.: The corrosion properties of selected fuel microemulsions for diesel engines. Autobusy. 2018, 12, 407-410. DOI: 10.24136/atest.2018.423.

[6] Górski K., Asok K.S., Lotko W., Swat M.: Effects of ethyl-tert-butyl ether (ETBE) addition on the physicochemical properties of diesel oil and particulate patter and smoke emissions from diesel engines. Fuel. 2013, 103, 1138-1143, DOI: 10.1016/j.fuel.2012.09.004.

[7] https://www.acea.be/uploads/press_releases_files/20181108_PRPC_fuel_Q3_2018_FINAL.pdf (accessed on 22 March 2019).

[8] Ithnin A.M., Ahmad M.A., Abu Bakar M.A., Rajoo S., Yahya W.J.: Combustion performance and emission analysis of diesel engine fuelled with water-in-diesel emulsion fuel made from low-grade diesel fuel. Energy Conversion and Management. 2015, 90, 375-382, DOI: 10.1016/j.enconman.2014.11.025.

[9] Kaźmierczak U., Kulczycki A., Dzięgielewski W., Jankowski A.: Microemulsion fuels for piston engines. Journal of KONBIN. 2012, 1, 131-140, DOI: 10.2478/jok-2013-0012.

[10] Khan M. Y., Ambri Z., Karin A., Aziz A.A.R.: An experimental investigation of microexplosion in bio fuel emulsion. ARPN Journal of Engineering and Applied Sciences. 2016, 11, 14303-14307.

[11] Khan M.Y., Karim Z.A., Hagos F.Y. Aziz A.R.A., Tan I.M.: Current trends in water-in-diesel emulsion fuel. The Scientific World Journal. 2014, 1-15, DOI: 10.1155/2014/527472.

[12] Kimoto K., Owashi Y., Omae Y.: The vaporizing behaviour of water-in-oil emulsions on the hot surface. Bulletin of JSME. 1986, 29, 4247–55, DOI: 10.1299/jsme1958.29.4247.

[13] Kowalewicz A.: Spalanie jednorodnego ładunku wywołane samozapłonem wskutek sprężania – wyzwanie dla silników spalinowych. Combustion Engines. 2009, 1, 3-9.

[14] Lapuerta M., Sanchez-Valdepenas J., Sukjit E.: Effect of ambient humidity and hygroscopy on the lubricity of diesel fuel. Wear. 2014, 309, 2014, 200-207, DOI: 10.1016/j.wear.2013.11.017.

[15] Mahrafi H.: Experimental validation of a kinetic multi-component mechanism in a wide HCCI engine operating range for mixtures of n-heptane, iso-octane and toluene: Influence of EGR parameters. Energy Conversion and Management. 2008, 49, 2956-2965. DOI: 10.1016/j.enconman.2008.06.016.

[16] Ochoterena R., Lif A., Nyden M., Anderson S., Denbratt I.: Optical studies of spray development and combustion of water -in-diesel emulsion and microemulsion fuels. Fuel. 2010, 89, 122-132, DOI: 10.1016/j.fuel.2009.06.039.

[17] Palash S.M., Kalam M.A., Masjuki H.H. Masum B.M., Rizwanul Fattah I.M., Mofijur M.: Impacts of biodiesel combustion on NOx emissions and their reduction approaches. Renewable and Sustainable Energy Reviews. 2013, 23, 473-490. DOI: 10.1016/j.rser.2013.03.003.

[18] Saif Y.S.: Water-Diesel Emulsion: a Review. International Journal of Advances in Engineering & Technology. 2017, 10, 429-436. DOI: 10.7323/ijaet/v10_iss3.

[19] Segawa D., Yamasaki H., Kadota T., Tanaka H., Enomoto H., Tsue M.: Watercoalescence in an oil-in-water emulsion droplet burning under microgravity. Proceedings of the Combustion Institute. 2000, 28, 985-90. DOI: 10.1016/S0082-0784(00)80305-7.

[20] Soylu S.: Examination of combustion characteristics and phasing strategies of a natural gas HCCI engine. Energy Conversion and Management. 2005, 46, 101-119, DOI: 10.1016/j.enconman.2004.02.013.

[21] Serrano J., Jimenez-Espadafor F.J., Lora A., Modesto-Lopez L., Ganan-Calvo A., Lopez-Serrano J.: Experimental analysis of NOx reduction through water addition and comparison with exhaust gas recycling. Energy. 2019, 168, 737-752, DOI: 10.1016/j.energy.2018.11.136.

[22] Sezer I.: A Review Study on the Using of Diethyl Ether in Diesel Engines: Effect on Fuel Properties and Engine Performance. Energy Technology. 2018, 6, 2084-2114. DOI: 10.1002/ente.201800158.

[23] Uchoa I.M.A., Dantas Neto A. A., Silva Santos E., Lima L.F., Barros Neto E.L.: Evaluation of Lubriciting Properties of Diesel Fuels Micro Emulsified with Glycerin. Materials Research. 2017, 20, 701-708, DOI: 10.1590/1980-5373-mr-2016-0943.

[24] Wang C., Chen J.: An experimental investigation of the burning characteristics of water-oil emulsions. International Communications in Heat and Mass Transfer. 1996, 23, 823-34, DOI: 10.1016/0735-1933(96)00065-6.

[25] Xi J., Zhong B.J.: Soot in Diesel Combustion Systems. Chemical Engineering & Technology. 2006, 29, 665-673, DOI: 10.1002/ceat.200600016.