ISSN: 1231-4005
e-ISSN: 2354-0133
DOI: 10.5604/12314005.1165415

THE INFLUENCE OF OXYGENATES ON LUBRICITY OF FUELS FOR CI ENGINES

Andrzej Kulczycki

Air Force Institute of Technology
Ksiecia Boleslawa Street 6, 01-494 Warsaw, Poland
tel.: +48 22 6851416, fax: +48 22 6851416
e-mail: andrzej.kulczycki@itwl.pl

Abstract

Lubricity of fuels for CI engines becomes one of very important parameter since the sulphur content was decreased to 50 and actually 10 ppm. To provide effective lubrication of fuel pumps and unit injectors elements, in case fuel does not contain organic sulphur compounds, the oxygen containing organic compounds are added as lubrication additives. Biocomponents are usually introduced into mineral diesel fuel containing additives package, which includes lubricating additive (organic acid). The aim of this paper is investigation of the influence of polar oxygenates added to petroleum diesel fuel in concentration between 5 and 20% (V/V) on lubricating additive effectiveness in protective layer creation.

The results of HFRR tests obtained for blends of commercial diesel fuel containing lubricating additive with biobuthanol models (MB) leads to conclusion that:

- *generally the buthanol isomers addition increases wear of upper ball of HFRR apparatus,*
- *wear of upper ball of HFRR apparatus depends on the average film thickness and does not depend on tested fuels viscosity at 40°C,*
- *dilution of commercial diesel fuel by biobuthanol models and consequently decreasing of lubricating additive concentration cannot be the only reason of deterioration of tested blends lubricity.*

It was concluded, that the possible reason of lubricity deterioration by buthanol added to commercial diesel fuel in concentration between 5 and 20% (V/V) are antagonistic interactions between oxygenates (buthyl alcohol) and lubricating additive. These antagonistic interactions depend on the structure of buthanol isomers.

Keywords: *CI engine, CI engine fuel, lubrication additives, fuel lubricity*

1. Introduction

Lubricity of fuels for CI engines becomes one of very important parameter since the sulphur content was decreased to 50 and actually 10 ppm. In mineral distillates sulphides, polysulphides and thiols are the main sulphur containing compounds. Sulphur removal from distillate practically eliminates these compounds. Organic sulphur compounds are well known as very effective lubricating additives, used for many years in lubricants. The sulphur containing additives are active in protective layers creation on the surface of lubricated elements of machines. Their activity depends on their chemical structure and operation conditions of machine [8, 12]. Thiols and sulphides are effective in Anti-war layer creation since polysulphides are effective EP additives [13, 14]. Elimination of organic sulphur compounds from diesel fuel dramatically decreases the fuels ability to protective layer creation. As the result fuel pumps and unit injector's elements, cannot be protect against intensive wear and seizure. To provide effective lubrication of fuel pumps and unit injectors elements in case fuel does not contain organic sulphur compounds, the oxygen containing organic compounds are added as lubrication additives. These additives are mainly organic acids with long hydrocarbon chains [8, 9, 10, 11].

Lubricating additives effectiveness depends on their chemical structure, concentration in the fuel and on chemical structure and properties of base fuel. Use of biocomponents as substitute for petroleum fuels is from more than 10 years important part of energy policy, both all over the EU and in individual member countries. Increasing demand for fuels and energy connected with economy growth, due to decreasing sources of fossil fuels, means searching and supporting the use of biocomponents, liquid biofuels and other renewable fuels [2, 3, 7]. Biocomponents contribution in total sum of consumed fuels, computed in relation to calorific value, shall increase successively up to 10 % in 2020. The mostly used biocomponent added to diesel fuel is FAME – fatty acids methyl esters, which chemical structure is different from the structure of petroleum diesel fuel [5, 6]. Biocomponents are usually introduced into mineral diesel fuel containing additives package, which includes lubricating additive (organic acid), effective in protective film creation with petroleum diesel fuels hydrocarbons [17].

The aim of this paper is investigation of the influence of polar oxygenates added to petroleum diesel fuel in concentration between 5 and 20% (V/V) on lubricating additive effectiveness in protective layer creation.

2. Testing lubricity of petroleum diesel fuels blends with buthanol

2.1. Method of the measurement of lubricity

Lubricity of diesel fuel is detected using HFRR (High Frequency Reciprocating Test Rig) apparatus and method according to PN-EN ISO 12 156 standard. The HFRR apparatus is shown in Fig. 1.

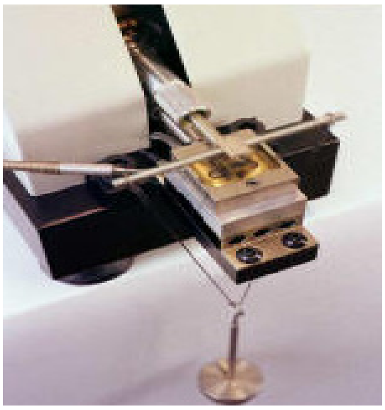

Fig. 1. HFRR apparatus-friction node

The test conditions are as follows:
- test duration – 75 min,
- frequency of upper ball vibration – 50 Hz,
- load – 200 g,
- temperature of tested fuel on the beginning of the test –60°C.

The standard criterion of fuels lubricity is wear scar diameter of upper ball. The apparatus equipment additionally allows measurement of friction force, thickness of protective film and fuels temperature. All these parameters are measured continuously during test and shown on diagram; apparatus software allows calculation of the mean value of these parameters for the test.

2.2. Blends of commercial diesel fuel and buthanol

Investigation of the influence of polar oxygenates added to petroleum diesel fuel on lubricating additive effectiveness in protective layer creation was conducted using commercial diesel fuel, containing lubricating additive (fuel meets requirements of PN EN 590) and blends containing:
- hydrocracate in concentration 10, 15 and 20 % (V/V)
- mixtures of buthanol isomers (Tab. 2) added to diesel fuel in concentration of 5 to 20% (V/V).

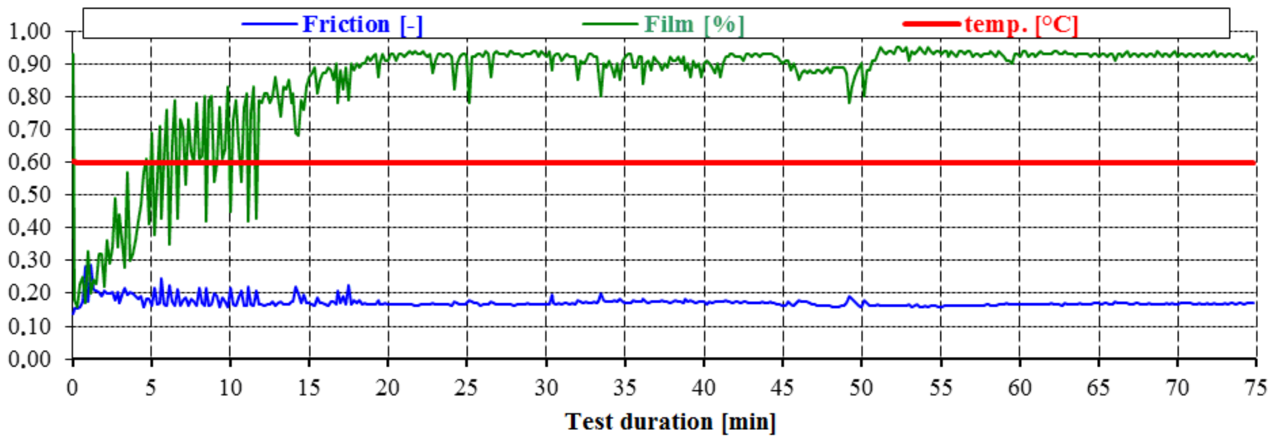

Fig. 2. The sample diagram for HFRR test

Blends of commercial diesel fuel and hydrocracate contain lubricating additive in concentration 10, 15 and 20% less than in commercial diesel fuel. Hydrocracate is one of component of diesel fuel, so its addition does not change the chemical structure of tested fuels. Addition of the mixtures of buthanol isomers [1, 15, 16] dilute lubricating additive and change the chemical structure of fuel. Comparison of the results of lubricating additive dilution by hydrocracate and buthanol eliminates difference in additive concentration and makes possible investigation of buthanol influence on this additive effectiveness.

Biobuthanol contains only buthan-1-ol (n-buthanol) or mixtures of buthan-1-ol, buthan-2-ol (sec-buthanol) and 2-methylpropane-1-ol (iso-buthanol). Physical properties of each of these isomers are different, so their influence on fuels lubricity can be different as well. In Table 2 there is shown composition of four biobuthanol models (MB).

Tab. 2. Chemical composition of biobuthanol models (MB) to be tested in blends with diesel fuel

Biobuthanol model	Buthanol isomer concentration in biobuthanol model % (V/V)		
	buthan-1-ol	buthan-2-ol	2-methylpropane-1-ol
MB1	50	0	50
MB2	0	0	100
MB3	40	20	40
MB4	60	20	20

3. HFRR tests results

HFRR tests results are shown in Tab. 3.

4. Discussion

The results of HFRR tests, shown in Tab. 3, were analysed.

It was found, that there is linear dependence between average film thickness and wear scar diameter (see Fig. 3) and there is no dependence between friction coefficient and wear scar diameter (see Fig. 4.)

Average friction coefficient and average film thickness they do not inform about protective layer creation and its durability during HFRR test.

As it is shown on Fig. 5, the addition of buthanol isomers into petroleum diesel fuel causes increasing the time until film will be durable. This is not the effect of tested blends viscosity decrease by buthanol isomers, because there is relation between film thickness and wear scar diameter and there is no relation between wear scar diameter and fuel’s viscosity (see Fig. 6.)

Tab. 3. HFRR tests results: ON – commercial diesel fuel containing lubricating additive, MB – biobuthanol model, H – hydrocracate

Blend	Film thickness (average for test) [%]	Friction coefficient (average for test)	Wear scar diameter [μm]
ON	84.6	0.172	363
ON + 5% MB1	65.7	0.239	409
ON + 10% MB1	71.6	0.183	423
ON + 15% MB1	71.8	0.208	357
ON + 20% MB1	63.7	0.212	442
ON + 5% MB2	57.6	0.188	431
ON + 10% MB2	71.1	0.187	359
ON + 20% MB2	69.4	0.184	391
ON + 5% MB3	69.4	0.184	387
ON + 10% MB3	86.1	0.210	318
ON + 15% MB3	73.7	0.177	382
ON + 20% MB3	57.7	0.177	417
ON + 5% MB4	76.5	0.176	373
ON + 10% MB4	73.6	0.176	395
ON + 15% MB4	70.5	0.177	400
ON + 20% MB4	76.4	0.175	374

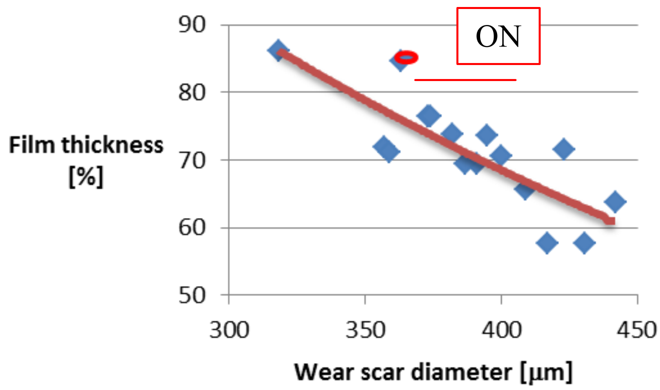

Fig. 3. Dependence between film thickness and wear scar diameter; tested fuels: commercial diesel fuel (ON) and its blends containing biobuthanol models

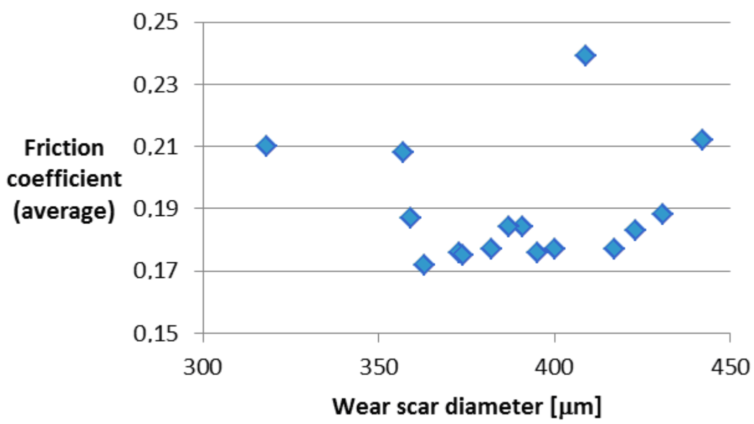

Fig. 4. Dependence between friction coefficient and wear scar diameter, tested fuels: commercial diesel fuel (ON) and its blends containing biobuthanol models

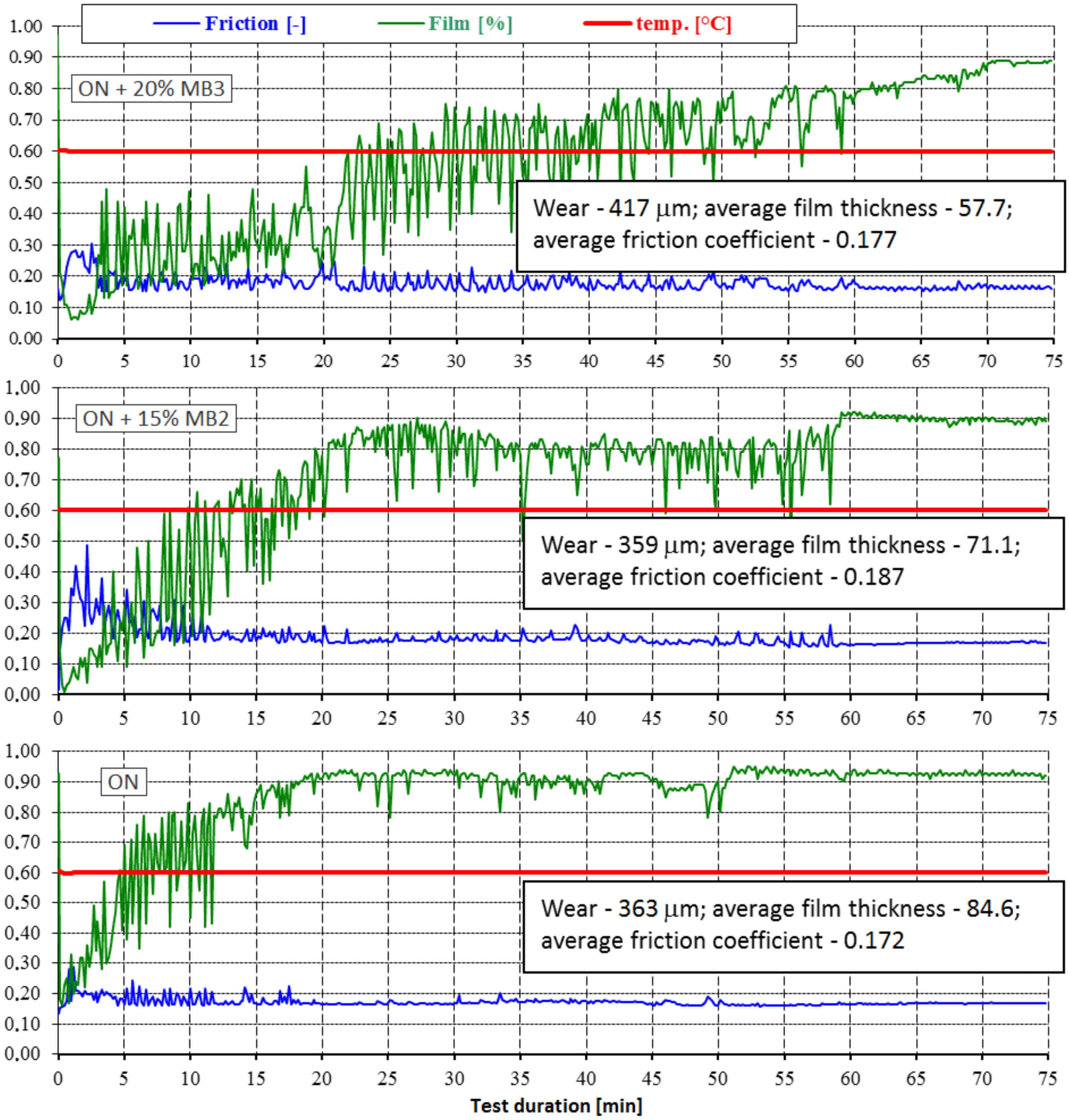

Fig. 5. Film thickness and friction coefficients change during HFRR test

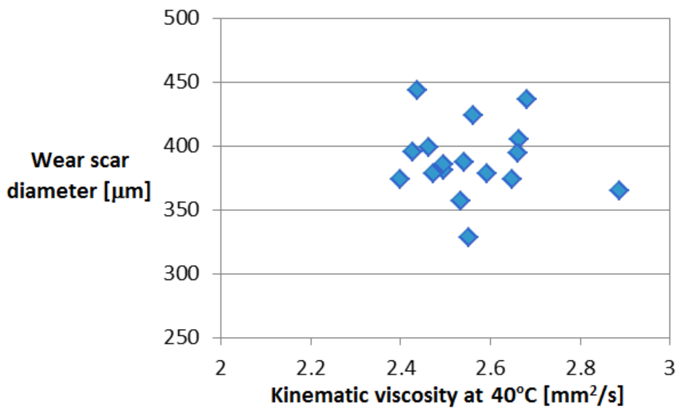

Fig. 6. Dependence between wear scar diameter and kinematic viscosity at 40°C

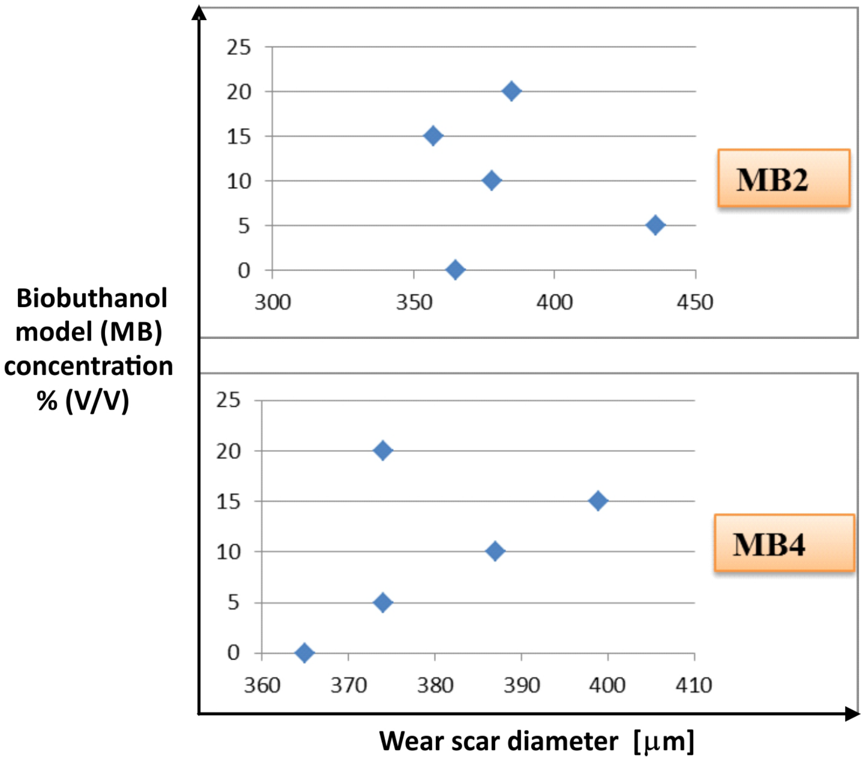

Fig. 7. Dependence between biobuthanol model's (MB2 and MB4) concentration in blends with commercial diesel fuel

The wear scar diameter increases after biobuthanol models addition to petroleum diesel fuel, but it cannot be the result of lubricating additive dilution only; as it is shown in Fig. 7 there is no clear dependence between wear scar diameter and MB concentration.

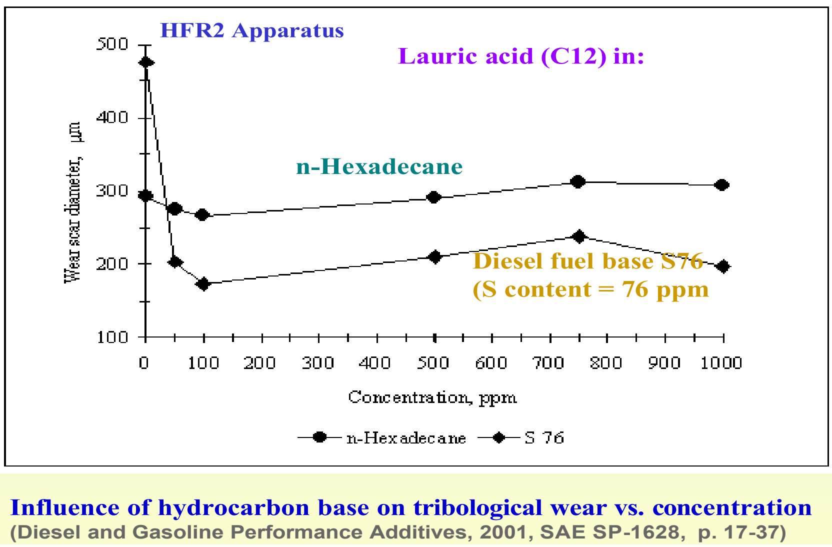

Fig. 8. Dependence between wear scar diameter after HFRR test and lubricating additive [4]

The effectiveness of lubricating additives depends on its concentration. It was found (see Fig. 8.) that:

- effectiveness depends on fuels chemistry,
- there are preferable concentrations of lubricating additive, which give the lowest wear.

This leads to conclusion, that dilution of lubricating additive cannot be the only reason of deterioration of tested blends lubricity, what is observed in case the dilutant is buthanol.

5. Conclusions

The results of HFRR tests obtained for the number of commercial diesel fuel containing lubricating additive blends with biobuthanol models (MB) leads to conclusion that:

- all tested blends meet standard (PN EN 590) requirement in relation to fuel`s lubricity (wear scar diameter less than 460 μm),
- generally the buthanol isomers addition increases wear of upper ball of HFRR apparatus,
- wear of upper ball of HFRR apparatus depends on the average film thickness and does not depend on tested fuels viscosity at 40°C,
- dilution of commercial diesel fuel by biobuthanol models and consequently decreasing of lubricating additive concentration cannot be the only reason of deterioration of tested blends lubricity.

It was concluded, that the possible reason of lubricity deterioration by buthanol added to commercial diesel fuel in concentration between 5 and 20% (V/V) are antagonistic interactions between oxygenates (buthyl alcohol) and lubricating additive. These antagonistic interactions depend on the structure of buthanol isomers.

References

[1] BP Fakt DuPont Biobutanol Sheet (Pdf).

[2] Christi, Y., *Biodiesel from microalgae beats bioethanol*, Trends Biotechnol., Vol. 26 (3), pp. 126-131, 2008.

[3] Christi, Y., *Biodiesel from microalgae*, Biotechnol. Advan., Vol. 25, pp. 294-306, 2007.

[4] *Diesel and Gasoline Performance Additives*, SAE SP-16-28, pp. 17-37, 2001.

[5] Dzięgielewski, W., Gawron, B., *Initial researche of the effect of FAME containing petroleum fuel blends storage on lubricity*, Journal of Polish CIMAC, Vol. 9 No. 2, pp. 35-43, Gdansk 2014.

[6] Dzięgielewski, W., *The limitation of use of biocomponents in the form of fatty acid methyl esters based on analysis of selected turbine fuel properties*, Journal of Polish CIMAC, Vol. 4, No. 2, pp. 41-47, Gdansk 2009.

[7] Fortman, J. L., Chhabra, S., Mukhopadhyay, A., Chou, H., Lee, T. S., Steen, E., Keasling, J. D., *Biofuel alternatives to ethanol: pumping the microbial well*. Trends in Biotechnol., Vol. 26 (7), pp. 375-381, 2008, Biobutanol – production and purification methods 411.

[8] Jankowski, A., *Chosen Problems of Combustion Processes of Advanced Combustion Engine,* Journal of KONES, Vol. 20, No. 3 pp. 203-208, 2013.

[9] Jankowski, A., *Reduction Emission Level of Harmful Components Exhaust Gases by Means of Control of Parameters Influencing on Spraying Process of Biofuel Components for Aircraft Engines*, Journal of KONES 2011, Vol. 18 No 3, pp. 129-135, Warszawa 2011.

[10] Jankowski, A., Baczewski, K., *Aging Processes of Biodiesel and Biodiesel/Diesel Fuel Blends*, Journal of KONES 2010, Vol. 17 No 2, pp. 167-180, Warszawa 2010.

[11] Jankowski, A., Sandel, A., *Exhaust Emission Reduction Problems of Internal Combustion Engines Fuelled with Biofuels*, Journal of KONES. Vol. 10, No 3-4, pp. 93-108, Warszawa 2003.

[12] Kaźmierczak, U., Kulczycki, A., Dzięgielewski, W., Jankowski, A., *Microemulsion Fuels for Piston Engines,* Journal of KONBiN. Volume 21, Issue 1, Pages 131-140, 2012.

[13] Kajdas, C., Karpinska, A., Kulczycki, A., *Industrial Lubricants. Chapter 8: Chemistry and Technology of Lubricants*, Third Edition, Springer Dordrecht Heidelberg, London, New York 2010.

[14] *Przemysłowe środki smarne*, Poradnik, TOTAL 2003.

[15] Qureshi, N., Saha, B. C., Hector, R. E., Hughes, S. R. Cotta, M. A., B*utanol production from wheat straw by simultaneous saccharification and fermentation using Clostridium beijerinckii: Part I – Batch fermentation*, Biomass and Bioener., Vol. 32, pp. 168-175, 2008.
[16] Wright, M., *Biomass to alcohol to jet/diesel*, Research Department, Chemistry Division Naval Air Warfare Center.
[17] Żurek, J., Jankowski, A., *Experimental and Numerical Modelling of Combustion Process of Liquid Fuels under Laminar Conditions,* Journal of KONES, Vol. 21, No. 3, pp. 309-316, 2014.