MODIFICATION OF BIOFUEL USABLE PROPERTIES IN THE ASPECT OF ISSUES INVOLVING OPERATION OF FARM

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Abstract. Authors of the publication focus on increased RME susceptibility to microbiological decomposition resulting from prolonged steam condensation process during farm vehicles stoppage. The work contains classification of reasons for damage of fuel system components in engines, mainly caused by the presence of impurities and chemical substances that have not reacted in the transesterification process. The researchers indicate factors improving RME anticorrosive properties and the need to improve rheological - low-temperature characteristics of biofuels, based on farm equipment storage conditions beyond harvest season. At the same time, they determine the selection of a depressator for farm vehicle fuels manufactured in refinery production line.

Key words: FAME biofuel, supply for combustion engines, physical and chemical properties of biofuels

Introduction

Operation of farm vehicles determined by seasonal character of field works introduces additional requirements as regards standard properties of biofuels produced in the triglyceride transesterification process, primarily with methyl or ethyl alcohol, in the presence of alkaline or acidic catalyst. As a result of this, alkyl esters of higher fatty acids (FAME) and glycerol are obtained.

Technological progress in the field of vehicle and working machinery engines is stimulated by required low nuisance index for natural environment, low emission level for toxic substances in exhaust gas, standard noise emission level and small unit fuel consumption. Prospects for running out of fossil fuel resources, fears for natural environment condition, and first of all crude oil prices growing until recently, have brought forward interest in renewable energy sources including biofuel [Jakóbiec, Ambroziak 2007; Koenig 1997]. Launching into the market new diesel oil and biofuel biocomponents characterised by physical and chemical properties that significantly differ in their chemical structure, generates fears that hydrocarbon fuel technologies, developed for years and used in self-ignition engines, will be dangerously disturbed [Kruczyński, Jakóbiec 2004]. In case of using diesel oil and RME blends, there are many areas that require further analyses, especially as regards joint work of biofuel and engine oil, compatibility of engine constructional materials and biofuel, fuel equipment durability, and stability of RME physical and chemical properties during storage [Cieślikowski 2009].

Assessment of physical and chemical properties of rape-seed oil fatty acid methyl esters (FAME)

Employing methyl esters of higher rape-seed oil fatty acids to power farm vehicles constitutes one of the most important research problems due to the need to meet quality requirements equivalent to those set for hydrocarbon fuels. The content of acids, methanol, metals, catalyst residues and free glycerol that have not reacted during FAME production process, causes increased biofuel susceptibility to degradation. Methanol, free fatty acids and/or free glycerol contribute to aluminium and zinc alloys corrosion in contact with fuel [Łukasik, Łynek 2008; Cieślikowski 2009]. Unsaturated compounds with multiple bonds occurring in the FAME are characterised by low stability, are subject to oxidation and prone to polymerisation. As a result of this, apart from storage problems, polymerised deposits are formed and accumulated during combustion of this fuel on injection system components and inside engine combustion chamber. FAME oxidation processes occurring during storage are free-radical type reactions, which cause increase in viscosity and acid number, and modify smell and colour. Moreover, presence of deposits becomes noticeable as well. Secondary oxidation reaction products are: aldehydes, aliphatic alcohols, and formic acid ester and formic acid, as well as fatty acids characterised by shorter carbon chain than in vegetable oil triglycerides [Kruczyński, Jakóbiec 2004]. Ageing processes in rape-seed oil fatty acid methyl esters proceed definitely faster compared to changes occurring in diesel oil [Prankl 2004]. They depend not only on raw product quality, but also on chosen fuel production technology and employed rape-seed oil purification method. FAME production process and determination of physical, chemical and usable/functional properties require special procedures and test methods, different than those for petroleum derivative fuels. Due to different characteristics of FAME ageing processes, the conventional methods allowing to assess fuel susceptibility to oxidation, which have been used in diesel oil tests for many years, do not illustrate these processes in ester fuels [Skręt, Duda 1996].

Technical determinants for powering self-ignition engines with biofuel

Despite completion of numerous research works on powering self-ignition engines with biofuel, there is still controversy regarding operation of modern engines equipped with Common Rail type fuel injection system [Jakóbiec, Ambrozik 2007]. It should be emphasised that the specificity of a given fuel market, automotive vehicles and farm machines used there, and the way they are operated, each time requires identification of biofuel-generated hazards for self-ignition engines.

There are still many areas that require further studies, especially as regards e.g. joint work of biofuel and engine oil, compatibility of engine constructional materials and biofuel, durability of fuel injection system components, as well as operating and proecological properties of the examined farm vehicles. Currently, none of self-ignition engine manufacturers or automotive vehicle importers in Polish market allow using with their products any fuel not satisfying requirements of the PN-EN 590 standard, which limits maximum FAME content in diesel oil. In case of diesel oil category 1, 2 and 3, World-Wide Fuel Charter issued in September 2006 allows FAME content up to 5% (V/V), and in case of diesel oil category 4 FAME content may not exceed detectable values. Failure to abide by these requirements may result in warranty loss, and thus incurring costs of possible engine repairs. In this place we should emphasise that so far no complex biofuel usable property tests have been carried out in Poland, especially as regards using biofuels to power modern self-ignition engines. Ceaseless striving to improve durability of combustion engines, including those powered with biofuel, requires further research work, including operating tests involving engine durability in fuel - lubricating oil configuration. These studies to a considerable degree may bring us closer to describing the mechanism of lubricating oil degradation processes.

Assessment of usable properties for rape-seed oil fatty acid methyl esters

An important element of functional assessment for rape-seed fatty acid methyl esters is its susceptibility to microbiological decomposition, which involves growth of microorganisms triggered off by presence of released water or steam condensation in fuel tank [Prankl 2004]. Unbounded water present in the FAME indirectly causes corrosive effect in contact with metals, facilitating microbiological life growth during its storage. Temperature and oxygen presence are important factors affecting growth. Methyl esters of higher rape-seed oil fatty acids (RME) are highly susceptible to microbiological decomposition compared to diesel oil, and constitute a nutrient medium. Negative outcome of microorganism presence in biofuels include logistic and operational problems, which may occur during storage, handling and use. Formation of substantial biomass volume in FAME may be the reason for filter choking in engine fuel system with sludge or deposit present at farm tractor or harvester tank bottom. Other negative results of this phenomenon include occurrence of organic acids as a product of microorganism metabolism due to improvers package destruction and microbiological corrosion [Skręt, Duda 1996]. Bacteria growth in rape-seed oil fatty acid methyl esters accelerates progress of electrochemical and pitting corrosion in injection system components. Methyl esters of higher rape-seed oil fatty acids (RME) should prove consistence with the requirements regarding anticorrosive properties in contact with metals. It is particularly important at biofuel storage and distribution stage, as well as at direct contact with engine constructional materials, especially fuel system including injection equipment [Cieślikowski 2009]. In their jointly issued declaration, fuel injection equipment (FIE) manufacturers including Delphi, Bosch, Siemens, Denso and Stanadyne point out potential problems involved in using the FAME as fuel for self-ignition engines. Table 1 presents selected characteristic features of fatty acid methyl esters as fuels, which may have negative effect on engine technical state. Consequences of engine powering with FAME include corrosive action in contact with metals and tendency to deposit precipitation on engine working elements.

According to literature data [Skręt, Duda 1996], RME anticorrosive properties depend on many determining factors, including:
- rape variety being raw product for RME production;
- production technology, including the type and number of catalysts being used, e.g. mineral acids, methanol/catalyst molar ratio;
- content of free fatty acids formed as a result of soap decomposition, present in reaction environment;
- unbounded water presence;
- potential for fungi and bacteria growth and RME susceptibility to microbiological contamination;
- the level of RME oxidation and degradation during storage period, proceeding gradually with hydrolytic breaking of ester bonds.

Table 1. Characteristic features of FAME fuel, their impact on engine constructional materials, and resulting consequences [Łukasik, Łynek 2008]

Fuel characteristic	Fuel quality impact on constructional materials	Unfavourable symptoms in engine technical state
Presence of higher fatty acid methyl esters (FAME)	Softening, swelling, or hardening and cracking of some elastomers (effect depends on elastomers constitution) Displacement of deposits/buildup formed during self-ignition engine operation	Lack of tightness and leaks in engine Fuel filter blocking
Occurrence of methanol	Corrosion of aluminium and zinc alloys Low ignition temperature	FIE corrosion
Presence of impurities and chemical substances that have not reacted in FAME production process	Sodium and potassium and alkaline earth metals form salts with organic acids (soaps) Free fatty acids trigger off corrosion in parts made of non-ferrous materials (zinc) Sedimentation	Fuel filter blocking FIE corrosion Jamming of moving engine parts
Occurrence of unbounded water	FAME hydrolysis into fatty acids and methanol Corrosion Constant growth of microbiological life Increase in fuel electrical conductance	FIE corrosion Fuel filter blocking
Presence of free glycerol and mono-, di- and triglycerides	Corrosion in parts made of non-ferrous alloys Cellulose filters soaking Deposits/buildup on moving parts and covering with lake layer	Coking of fuel atomisers

Fuel characteristic	Fuel quality impact on constructional materials	Unfavourable symptoms in engine technical state
High viscosity at low temperatures	Higher resistance values, drop in operation efficiency of components	Fuel feeding problems. Pump seizures, higher failure frequency, insufficient fuel stream atomisation
Solid impurities	Possible occurrence of lubricity problems	Reduced time of use Atomiser seat wear Blocking of fuel atomisers
FAME ageing products		
Acids triggering off corrosion (formic and/or acetic acid)	Corrosion of metal parts, or single corrosion centres may form	FIE corrosion
High-molecule organic acids	Same as for fatty acid methyl esters	
Unsaturated compound polymerisation products	Buildup and sludge, especially in case of fuel blends	Fuel filter blocking Soluble polymers form lakes on hot parts

One of the main problems concerning operation of engines powered with methyl ester of higher rape-seed oil fatty acids (RME) is to ensure proper start-up even at the temperature of -5^{o}C. Low-temperature characteristics of this product differ from analogical properties of diesel oils. This is due to uniformity of chemical compounds constituting RME components, which results in higher tendency to form specific suspension (sludge) type structures. Their occurrence restricts fuel flow into the engine and causes gradual fuel filter blocking, which usually ends with its stopping [Kruczyński, Jakóbiec 2004]. Results of the research on matching functioning efficiency for depressators in RME are shown in tab. 2.

Symbols A, B, C indicating depressators correspond to reserved chemical substances, which were supplied by chemical laboratory of the refinery only for the purposes of carrying out conformity certification tests for biofuels without possibility to perform own chemical analyses aimed to identify their chemical constitution.

The following factors have direct effect on low-temperature characteristics of this product: raw product quality, its chemical constitution, and thus distillation curve (no low-boiling fractions) and content of individual esters. Narrow RME distillation range dependent on raw product origin diversifies low-temperature characteristics, and for esters obtained from rape-seed oil it is ca. 30^{o}C, whereas for esters derived from used vegetable oils (ready-made food processing) - ca. 10-15^{o}C. Low-temperature characteristics deteriorate with increasing concentration of esters characterised by higher number of carbon atoms in a molecule. Higher concentration of unsaturated bonds in ester molecule improves discussed properties. In operation practice of RME-powered cars it has been observed that rheological – low-temperature characteristics of plant derivative fuel are definitely worse than those of diesel oil [Jakóbiec, Ambrozik 2007]. It is possible to improve the discussed properties by selecting depressator characterised by proper quality.

Table 2. Efficiency assessment for functioning of depressators in methyl esters of higher rape-seed oil fatty acids [Jakóbiec, Ambrozik 2007]

FAME	Depressator proportioning level [mg/kg]	Depressator											
		A				B				C			
		CP [°C]	CFPP [°C]	SFPP [°C]	PP [°C]	CP [°C]	CFPP [°C]	SFPP [°C]	PP [°C]	CP [°C]	CFPP [°C]	SFPP [°C]	PP [°C]
CP= −2.8°C CFPP= −10.0°C SFPP= −9.0°C PP= −8.0°C	1500	-4.2	-15.0	-10.0	-41.0	-4.2	-17.0	-13.0	-41.0	-4.3	-18.0	-13.0	-41.0
	1600	−	−	−	−	−	−	−	−	-4.3	-20.0	-13.0	-41.0
	1800	−	−	−	−	−	−	−	−	-4.6	-51.0	-13.0	-41.0
	2000	-4.9	-17.0	-13.0	-41.0	-4.3	-18.0	-13.0	-41.0	-4.7	-23.0	-13.0	-41.0
	2200	−	−	−	−	-4.5	-19.0	-13.0	-41.0	−	−	−	−
	2300	−	−	−	−	-4.5	-20.0	-14.0	-41.0	−	−	−	−
	2500	-4.9	-19.0	-13.0	-41.0	-4.5	-21.0	-14.0	-41.0	-4.7	-24.0	-13.0	-41.0
	2600	-4.9	-19.0	-13.0	-41.0	−	−	−	−	−	−	−	−
	2700	-4.9	-20.0	-13.0	-41.0	−	−	−	−	−	−	−	−

CP − turbidity temperature
CFPP − cold filter blocking temperature
SFPP − simulated filter blocking temperature
PP − flow temperature

Summary

Production and logistic operations involved in the popularisation of methyl esters of higher rape-seed oil fatty acids (RME) as a fuel or diesel oil biocomponent, meeting requirements of specifications contained in subject standards do not guarantee stability of physical and chemical parameters and functional properties of this product during extended storage period.

The most important issues concerning operation of biofuel-powered farm vehicles include: fuel life during storage (ageing processes), required low-temperature characteristics and susceptibility to microbiological decomposition. In order to ensure desired usable properties of FAME or their mixtures with diesel oil requires multifunctional improvers package to be used. Production of rape-seed oil fatty acid methyl esters requires special procedures to be developed, and testing methods for functional assessment to be amended.

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MODYFIKACJA WŁAŚCIWOŚCI UŻYTKOWYCH BIOPALIW W ASPEKCIE ZAGADNIEŃ EKSPLOATACYJNYCH POJAZDÓW ROLNICZYCH

Streszczenie. W publikacji zwrócono uwagę na zwiększoną podatność RME na rozkład mikrobiologiczny w wyniku długotrwałego procesu kondensacji pary wodnej w okresie przestoju pojazdów rolniczych. Dokonano klasyfikacji przyczyn uszkodzeń elementów aparatury paliwowej silników wywołanych głównie obecnością zanieczyszczeń i nieprzereagowanych substancji chemicznych w procesie transestryfikacji. Wskazano na czynniki poprawiające właściwości przeciwkorozyjne RME oraz potrzebę poprawy właściwości reologicznych - niskotemperaturowych biopaliw biorąc za podstawę warunki przechowywania sprzętu rolniczego poza okresem kampanijnym. Równocześnie określono wybór depresatora dla paliw pojazdów rolniczych wytwarzanych na linii produkcyjnej w rafinerii.

Słowa kluczowe: biopaliwo FAME, zasilanie silników spalinowych, cechy fizyko-chemiczne biopaliw

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