



Research article

Thin film testing of biodiesel degradation residues and their solubility

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ABSTRACT

With broader application of biodiesel, reports about residues, varnish and other solid deposits in engines emerge more frequently. A thin film degradation test, originally developed for lubricant studies, was employed to investigate fuel vaporization, acid buildup and solubility of degradation products. Films of 25, 100 and 500 μm thickness of rapeseed and palm fatty acid methyl esters (FAME) as well as hexadecane were exposed to 50 °C and 90 °C for up to 3000 h in dry or humid atmosphere on steel surface. Hexadecane produced clean steel surfaces, while FAME films would leave at least 10% residues or more in thicker films. Simple soaking in acetone or tetrahydrofuran dissolved FAME films nearly completely, if degradation was shorter than 1000 h at 90 °C. But in non-polar solvents FAME films became insoluble after much less degradation. As little as 50 h degradation at 50 °C was enough to produce a viscous bottom layer, which would not dissolve in fresh FAME or heptane. Other solvents were tested as well, further showing that FAME degradation products are poorly compatible with fuel-like solvents, such as xylene, heptane or fresh FAME. Formation of immiscible bottom phase may promote buildup of residues, deposits and varnish in fuel systems.

1. Introduction

Biodiesel is known to often lead to more frequent engine cleanliness problems, compared to conventional diesel fuel [1]. Fatty Acid Methyl Esters (FAME) are more likely to reside longer in engines, because their volatility is lower and they condense more rapidly. Depending on the engine design and usage, after shut-down some fuel can stay as a film on various parts, which gradually cool down to ambient temperatures. In hot environment these films can be exposed to significant heat for various durations, sometimes several months. This is usually not addressed in fuel bench tests or engine tests, because procedures typically involve continuous operation. Consequently, the films, which are formed on heated surfaces, are usually replenished before any significant degradation begins. In field, however, the engines are usually started up and shut down many times, exposing stagnant fuel films to heated surfaces. While the heat generated by the engine plays a major role, thermal stress can become even more severe under hot climate conditions. This stress might be sufficient to cause significant degradation, especially if fuel molecules are vulnerable to oxidation. Such degradation products usually become less soluble in fresh fuel. Therefore, reduced solubility can result in cleanliness, homogeneity, filtration and other technical issues. Although FAME contains unsaturation and oxidizes faster than typical petroleum fuels, solubility of degraded

FAME films has not been scrutinized in standard fuel stability tests. So it remains mostly unknown, if the technical performance might be jeopardized due to exposure of fuel films on heated surfaces for prolonged durations and subsequent solubility issues.

Not only fuel systems may be affected by the degradation of stagnant FAME films. Amounts of unburnt fuel, which penetrate the piston rings, can also be significant. The crankcase dilution with fuel can reach 10% or more in terms of the engine oil volume [2–4] even with conventional petroleum-based fuels, which are more volatile than FAME. First of all, unburnt FAME reduces lubricant viscosity dramatically [5] due to its exceptional thinning power. But also FAME are considerably less stable oxidatively than saturated or aromatic hydrocarbons, so the degradation of diluted lubricant proceeds much faster [6]. In more severe cases solid residues, deposits, varnish and other types of solids can form. Such residues might block oil or fuel passages and interfere with the engine operation [7]. In case of FAME residues in a lubricant crankcase, oil circulation becomes restricted with less lubricant entrained into the friction zones, which produces excessive wear, friction, overheating and eventual damage to the engine.

Oxidative polymerization is considered mainly responsible for the residue formation in FAME [8–10]. However, it is hard to predict even approximately, how much of FAME degradation can be tolerated in order to avoid the residue formation. A major attempt to understand the

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mechanisms of residue formation during degradation of B20 was recently made [11], where 200 mL sample was heated in a flask with air bubbling. A strongly emphasized conclusion was drawn that no residues could form below 140 °C despite prolonged heating. Unfortunately, it has not yet been established, whether fuels with higher contents of FAME might also be resistant to residue formation. In addition, much faster degradation of FAME in films (rather than in bulk liquid) on metal surface was not considered.

A clear distinction must be made between the solid and semisolid products of oxidative degradation and those produced during fuel combustion, as well as the contaminants, which might become solids during degradation. Solid deposits can form during combustion, primarily around the injectors. Such deposits are usually produced as a result of deviation from the optimum combustion regime or substantial contamination of diesel fuel with heavy components. Plasma reactions are mostly responsible for the formation of the carbonaceous deposits in the injector zone. Since petroleum diesel is non-polar, it might not be effective in dissolving oxidized carbonaceous deposits. Apparently, FAME is known to frequently act as a solvent capable of dispersing the deposits of petroleum diesel around the fuel injectors. Polarity of FAME is helpful in penetrating the deposits and often eliminating them from the injector surfaces. FAME has been reported as beneficial in that respect [12,13] Nevertheless, sometimes FAME themselves can also contribute to the formation of carbonaceous deposits in the injector zone, as reported in the study involving winter conditions [14], when excessive carbonization on the injectors was observed because of insufficient combustion. Increased carbonaceous deposits were reported to be caused by deteriorated or poor quality FAME as well [15]. They might also become more abundant due to higher FAME contents in diesel fuel [16], in addition, their appearance and morphology seems to depend on FAME contents significantly. As opposed to the carbonaceous deposits in the injector zone, insoluble residues can be produced without any involvement of plasma, because polymerization can take place due to peroxide decomposition during autoxidation. Compared to FAME, petroleum diesel is many times less susceptible to autoxidation, which is beneficial for the fuel storage and cleanliness of the fuel lines, but not too important for combustion kinetics. Therefore, the carbonaceous deposits around the injector zone should be viewed differently than insoluble residues elsewhere in the fuel system.

One more mechanism, which could lead to formation of solids in biodiesel, is degradation of fuel additives, contaminants and minor constituents. Broad variety of chemical compounds can be introduced during biodiesel manufacture, such as free glycerol, mono-, di- and triglycerides, methanol, catalyst carryover, scale, dust, etc. With the exception of free fatty acids, usually such constituents represent < 1% of biodiesel. Many possible chemical mechanisms might be engaged during oxidation of these constituents. Although the total amount of solids formed via this pathway is usually below 1%, their presence is important to biodiesel filterability. This aspect is thoroughly investigated by ASTM standard method D2274 and typical amounts of oxidized contaminants in commercial biodiesel average around 50 ppm [17].

An alternative approach would be helpful in assessing the risks of residue formation, so a thin film degradation concept was used for our study, capitalizing on the experience in lubricant technology, where thin film testing is frequently employed. Several oil oxidation test methods utilize thin films, such as micro-oxidation [7,18–20], Pressurised Differential Scanning Calorimetry (PDSC) [21], Panel Coker [22], TEOST-MHT [23] and others. These tests show that mineral oil films can form deposits and residues within several hours at 200 °C, while vegetable oil films degrade in a matter of minutes [20,21]. However, no reports could be uncovered, which would describe late stage degradation of FAME films on metal surfaces. But similarities in oxidation of vegetable oils and FAME suggest that thin film testing can be extended to biodiesel fuels as well. In such case the testing temperatures must be decreased in order to reduce evaporation, and the

testing duration might need to be longer. Therefore, 50 °C and 90 °C were selected in this study to investigate severe stages of FAME film degradation. Also, below 100 °C it is easier to retain significant amounts of moisture in humid environment, which resembles the conditions after engine shutdown. This helps to account for the influence of moisture during FAME degradation. Therefore, the thin film test was modified to include control of humidity. Film degradation was assessed gravimetrically, titrimetrically and by exposing to solvents. As a reference compound, hexadecane was selected. Conventional diesel fuel contains a broad variety of hydrocarbons, some sulfurized organics and many other compounds. Nevertheless, hexadecane is among the best candidates to represent diesel fuel in one molecule. Such simplification makes it easier to relate test results to thermodynamic data or physical and chemical properties, established by other researchers.

2. Material and methods

2.1. Materials

Laboratory grade solvents heptane (99% pure *n*-C₇H₁₆), isopropyl alcohol (IPA), chloroform and xylene (all technical grade) as well as acetone and tetrahydrofuran (THF, both technical grade, inhibited) were supplied by Avsista (Lithuania) and used for solvent extraction of liquid phase without additional pretreatment. With an assurance that rapeseed oil had been used as raw material, a free sample of rapeseed FAME (rFAME) was provided per courtesy of Mestilla biodiesel plant (Klaipeda, Lithuania). The sample of FAME with some palm oil constituents (pFAME) was purchased as “Bioester 100” in StanChem retail fuel station (Poland). Both rFAME and pFAME were expected to meet the biodiesel standards, but in addition they were analyzed rheologically, titrimetrically and on GC, see Table 1. Their viscosities were measured, approaching those reported elsewhere [24]. Cloud points appeared typical for a formulated biodiesel, although pFAME showed somewhat lower cloud point and higher viscosity than expected for unknown reasons, most likely related to the manufacture process. It could be inferred from Table 1 that pFAME contained < 10% of esters, originating from palm oil and such low contents helped to keep pFAME fluidity similar to that of typical biodiesel. The acquired samples were not additionally processed (no drying, no filtration, no sedimentation, etc.). Hexadecane (*n*-C₁₆H₃₄) was obtained of 99% purity (Sigma-Aldrich).

2.2. Thin film degradation and vaporization

The test procedure is often used to evaluate lubricants, as described

Table 1
Chemical and physical properties of FAME samples used in this study.

Property	Method	Molecular weight, g/mol	rFAME	pFAME
Liquid appearance (clarity and color)	visual		Clear, light yellow	Clear, medium yellow
Viscosity at 40 °C, cSt	ASTM D445		4.56	5.52
Cloud point, °C	ASTM D97		−4	−6
Acid number, mg KOH/g	ASTM D664		0.497	0.517
Composition, wt%:	GC/MS	296.49		
Oleate 18:1		294.49	51.11	58.44
Linoleate 18:2		292.49	26.27	19.68
Linolenate 18:3		270.45	11.41	2.23
Palmitate 16:0		298.50	4.82	8.58
Stearate 18:0		214.35	3.52	5.24
Laurate 12:0		242.40	< 0.1	2.15
Myristate 14:0		320+	< 0.1	0.76
C20+			2.64	1.72
other			0.22	1.2

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