

Experimental Study of the Impact of Diesel/Biodiesel Blends Oxidation on the Fuel Injection System

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ABSTRACT

The stability of Diesel/Biodiesel blends can play an important role in deposits formation inside the fuel injection system (FIS). The impact of the stability of FAME/Diesel fuel blends on lacquer deposits formation and on the behavior and reliability of the FIS was investigated using blends of Rapeseed and Soybean methyl esters (RME, SME) and conventional Diesel fuel (volume fractions of RME and SME range from 0 to 20%v/v). Fuels were aged under accelerated conditions and tested on an injection test rig according to an operating cycle developed to provoke injector needle blocking. The soaking duration was found to affect injector fouling. A relationship between the injector fouling tendency and the fuel stability was established. Under current test condition, injectors fouling increased with fuel oxidation measured with Total-Acid-Number. Needle fouling occurred at a TAN level of 0.25mg KOH/g and needle blocking occurred at a TAN level of 0.5 and 1 mg KOH/g for B20-SME and B20-RME, respectively. The FAME composition and the fuel ageing procedure can have a significant impact on FIS fouling tendency.

KEYWORDS: FAME, biodiesel, stability, oxidation, Total Acid Number, TAN, fuel injection system, internal deposits, lacquer

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1. INTRODUCTION

Biodiesel is today introduced within conventional Diesel to fulfill the EU target of 10% of renewable energy for transport applications and of 6% reduction in greenhouse emissions by 2020 [1]. First-generation biodiesel, mainly present under the fatty acid methyl ester (FAME) form, is produced from vegetable oils or animals fats by transesterification [2]. First-generation biodiesel has several advantages such as good combustion, lubricity, compatibility with both Diesel fuel and Diesel technology, renewability, biodegradability and industrial availability of the process technology. Besides, its use provides a reduction of many harmful exhaust emissions such as particulate and soot, polycyclic aromatic hydrocarbons and sulfur oxide (SOx). However, first-generation biodiesel raises several questions about the interaction of alternative fuel production with food sector and land use [3], about NOx emissions and about the influence on engine operation and durability [4]. Second-generation biodiesel, which results from the conversion of biomass lingo-cellulosic material (woody

crops or forest and agricultural residues) into synthetic biofuels [3], are interesting alternatives to first-generation biodiesel. However, the process technology is expensive compared to oil-based Diesel fuel or FAME and is not yet industrially available for mass production [5]. Therefore, it is most likely that first-generation biodiesel (mainly FAME) will remain of use for the next few years.

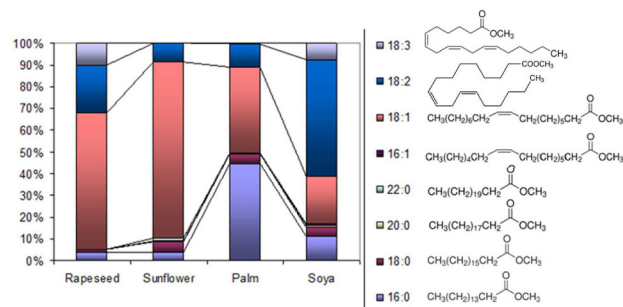


Figure 1. Composition of standard vegetable oils for FAME [3]

Most commonly used FAMES in the EU market are produced from rapeseed, sunflower, soya and palm oils [3][6]. They are characterized by a high content in mono- and poly-unsaturated compounds (Figure 1). In a recent work, Moser [7] illustrated the dependency of the oxidation rate of methyl esters on the number of unsaturations, their type (bisallylic sites) or their proximity to the ester head group. These compounds undergo more easily peroxidation process leading to the formation of hydroperoxides as primary oxidation products, which decompose into a wide range of carbonyl compounds, dimers and higher oligomers [8][9][10]. Mixed with conventional Diesel, FAMES play an oxidation promoting role [11][12].

Diesel Injection System Internal Deposits

Internal deposits have been widely studied for modern Diesel injection systems. As reported in literature [13][14][15][16] [17] [18][19][20][21][22][23], internal deposits can be classified into three main classes: Carboxylate salt deposits, carbonaceous deposits and lacquer deposits. These deposits can build and co-build inside the fuel injection system impacting its behavior and durability [13]. Carboxylate salt deposits are formed mostly from the reaction of sodium (and less frequently from calcium or potassium) with carboxylic acids. Significant progress has been made in the assessment of this type of deposits mainly yielding to several recommendations regarding the control of additives synergy and their interactions with internal parts [16] [17][18]. Carbonaceous deposits, mostly known to build on the injector nozzle on the combustion chamber side, were proven by Venkataraman and co-workers to form at temperatures as low as 160°C [19] for n-hexadecane. In recent study, Barker et al. identified carbon deposits on the injector needle by TOF-SIMS [20]. Lacquer-type deposits were correlated to either additive origins (typically PIBSI) [24] or to fuel oxidation [22]. The latter oxidative deposits are found in Diesel systems in the injectors on the armature, magnet and needle. Several works reported their impact the overall engine performance, noise and components durability [13][14][16][21][22][23][24]. Their formation pathways remain however poorly understood as several physical and chemical parameters can have an influence. Particularly, the impact of fuel composition and stability are not perfectly understood while they are known to interact with the injection system. Therefore, extensive studies are still regarded as necessary to clarify these impacts and to provide alternative solutions.

The present work aims to investigate the stability of the FAME/ Diesel fuel blends on the behavior and the reliability of the fuel injection system using fuels aged under accelerated conditions.

2. MATERIAL AND METHODS

An overview of the test sequence is presented in Figure 2. Fuels were prepared through blending of FAME and B0 Diesel fuel in step 1. Then, fuels were aged under accelerated conditions in a stirred reactor under oxygen atmosphere in step

2 before being tested on an injection test rig in step 3. The description of the experimental setup and methodology of each step are detailed in sections 2.1, 2.2 and 2.4 respectively.

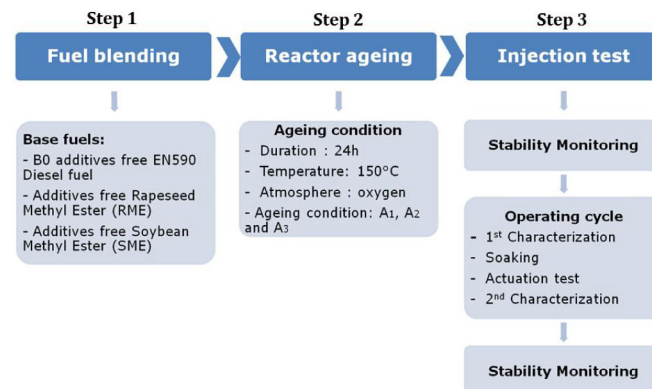


Figure 2. Overview of the test sequence

2.1. Base Fuels and Blends

B0 Diesel fuel is a commercial fuel conforming with the European automotive Diesel fuel specification EN590 from Total ADDITIVES & SPECIAL FUELS and free from FAME as well as any performance or antioxidant additives. FAME (or B100) are *Rapeseed Methyl Ester* (RME) and *Soybean Methyl Ester* (SME) containing no antioxidant additives processed at Analytic Service Gesellschaft (ASG) by transesterification of rapeseed and soybean oils. Physical and chemical properties of B100 and B0 fuels are illustrated in Appendix 1 and Appendix 2 respectively. Several stability criteria were evaluated for the base fuels: The Induction Period (IP), which evaluates the stability reserve of the fuel, was measured using two test methods Rancimat at 110°C and PetroOxy both at 120 and 140°C, and the Total acid number (TAN), which measures the amount of acid species contained in the fuel and reflects its current oxidation level. Stability criteria of B0 and B100 fulfill the European specifications EN590 and EN14214 respectively.

In the frame of the present study, two fuels were formulated; B20 RME composed of 80%v/v B0 and 20%v/v RME and B20 SME composed of 80%v/v B0 and 20%v/v SME. The main stability properties of the two blends were measured by TAN, delta TAN, Rancimat and PetroOxy IP. These fuels were further prepared by ageing and blending prior to injection experiments (sections 2.2 and 2.3).

Table 1. Stability properties of the fresh B20-RME and B20-SME blends

Fuel	Density (kg/m ³)	Delta TAN (mg KOH/g)	TAN (mg KOH/g)	Rancimat induction period (h)	PetroOxy induction period (min)	
					140°C	120°C
B20 RME	0.845	6.9	0.032	9.3	23	60.3
B20 SME	0.845	7.9	0.054	7.4	28	46

2.2. Ageing Procedure

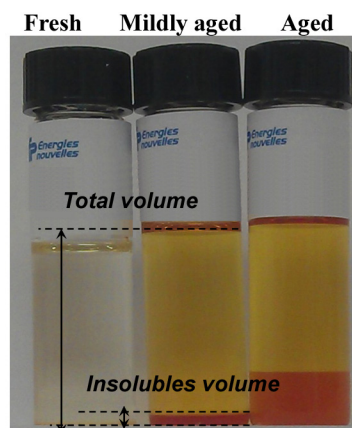
Fuels were aged in a stirred reactor illustrated in Figure 3. The test vessel allows containing up to 20L of fuel. The volume of the surrounding gas is approximately 10L and was renewed with a continuous oxygen flow rate of 12 L/s at 1atm. Gas is introduced into the vessel via a PolyTetraFluoroEthylene (PTFE) tubing and the end of the tube is placed approximately at 5cm above the surface of the sample. Besides, the test facility allows fuel stirring via an anchor-type impeller and gas bubbling in the middle of the fuel through glass frit. Temperature is regulated by a wall heat exchanger at 150°C in agreement with the standard test ASTM D6468-08. This relatively high temperature, can affect the degradation pathways of the FAME. In fact, in the case of squalane oxidation, Dugmore et al. [39] suggested a temperature-dependent effect of methyl linoleate addition, switching from promotion to inhibition at a cross-over temperature of 160°C. The involved pathways depend also on the chemical structure and of the other FAME components (glycerols, natural antioxidants, etc). These effects require a dedicated study and will not be treated in the present work. Maximum test duration was 24 hours. Regular sampling was performed in the center of the tested product each 6 hours. Stability was monitored using three stability measurements: PetroOxy induction at 140°C period, TAN and amount of precipitates evaluated by visual rating (Figure 4).



Figure 3. Fuel ageing reactor (ASG Analytic Service Gesellschaft)

For hydrocarbons, oxidation is known to undergo an autocatalytic phase leading to higher importance of mass transfer, which may become limiting during the course of the reaction even for initially oxygen-saturated fuels. Suresh and coworkers have shown that mass transfer becomes controlling starting from 5-7% of conversion [25] [26] even for intensely agitated laboratory reactors.

During this study, three conditions of mass transfer were tested to achieve different ageing progress of the fuels (Figure 5): In the first condition (A1), fuel was aged under an oxygen flow applied close to liquid surface. In the second condition (A2), fuel was, in addition, mechanically stirred at 110 rpm. In the third condition (A3), mechanical agitation was maintained while oxygen was directly bubbled within the fuel.



$$\text{Insolubles}(\%v/v) = \frac{\text{Insolubles volume (mm}^3\text{)} \cdot 100}{\text{Total volume (mm}^3\text{)}}$$

Figure 4. Indicative evaluation of precipitates (insolubles) by visual rating measured on a fuel sample after ageing.

	A1	A2	A3
Scheme of the reactor			
Liquid initial volume (L)	20	20	20
Wall Temperature (°C)	150	150	150
air flow rate (L/s)	12	12	12 (bubbling)
impeller speed (rpm)	0	110	110

Impact of the ageing condition on stability of B20-SME after 24h

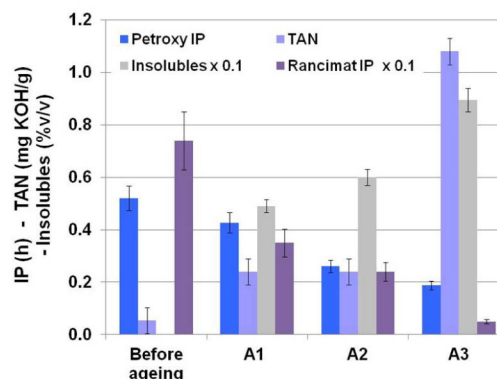


Figure 5. Impact of reactor gas-liquid contacting condition on fuel oxidation rate. Left: descriptive layout of the ageing conditions, right: stability evolution after 24h ageing on B20-SME

Results of the three conditions on a B20-SME are shown in (Figure 5). After 24h, fuel degradation was relatively low under A1 condition; Petroxy IP decreased by 20%, Rancimat Ip by 50% while TAN had a 4-fold increase. A2 stirred condition lead to a more significant oxidation by increasing the interfacial area [27]; Petroxy IP decreased by 50%, Rancimat Ip decreased by 70% while TAN remained roughly unchanged compared to A1.

Using A3 condition, the most significant oxidation level was achieved due to further increase in interfacial area and to enhanced oxygen mixing; Petroxy IP and Rancimat IP were both below the detection precision of the apparatus (0.25 and 0.5h, respectively) while TAN had a 20-fold increase after ageing.

We should note that the fuel stability of the aged fuels is far below the specification for Diesel fuels. The current work did not aim to be representative of market fuels but to carry on a comparative study to elucidate the main parameters impacting the internal deposits formation in extreme oxidation condition which can occur after improper fuel handling such as long storage or contamination. Moreover, the comparison of the different fuel stability measurements illustrates that TAN measurement appears more suitable than Rancimat or Petroxy IP for the stability monitoring of highly oxidized Diesel/Biodiesel blends used in the framework of this study.

2.3. Tested Fuels

After the ageing phase, seven fuels were selected for the injection experiment to cover a TAN range of 0.17 to 1.08 mg KOH/g as shown in Table 1. TAN levels were selected to cover a range representative of medium to high level oxidation Diesel fuels. A market survey conducted on 50 US fleets has shown a distribution of TAN on B20 of around 0.17-0.37 mg KOH/g with extreme values above than 0.7mg KOH/g [37]. Fuels 1-3 were obtained by the ageing of a fresh B20-RME; TAN levels were, respectively, 0.25, 0.5 and 1 mg KOH/g. Fuel 7 having a TAN value was 1.08 mg KOH/g was obtained by the ageing of a fresh B20-SME. Fuels 4-6 were obtained by the dilution of an aged B20-SME having a TAN level of 2.8 mg KOH/g with fresh B0. The dilution with fresh B0 aimed to simulate fuel renewal with fresh B0 which would mix with degraded fuel remaining in the fuel lines. The volume fraction of B20-SME was 3% v/v, 6.6%v/v and 15 %v/v in Fuel 4, Fuel 5 and Fuel 6, respectively. Thus, their FAME content was 0.6%v/v, 1.3%v/v and 3%v/v respectively which correspond to low levels of residual fuel in the FIS (Table 1).

Table 2. Formulation and selected stability criteria of fuels tested on the FIS

Fuel reference	Fuel formulation	TAN (mg KOH/g)	Insolubles (%vol)	PetroOxy (min)	
				140°C	120°C
Fuel 1	B20-RME	0.25	6.9	15	36
Fuel 2	B20-RME	0.51	6.2	13	33
Fuel 3	B20-RME	1		13	30
Fuel 4	B0.6-SME	0.17	6.1	46	150
Fuel 5	B1.3-SME	0.23	6.3	45	144
Fuel 6	B3-SME	0.57	7.1	38	138
Fuel 7	B20-SME	1.08	8.9	12	15

The difference in the preparation procedure of the fuels induced different fuel stability properties. TAN and induction period (IP) stability measurements illustrated in Figure 6 show on the overall coherent trends; for a higher oxidation progress, IP decreased while TAN increased (e.g. Fuels 1-3 for RME blends and Fuels 4-7 for SME blends). It shall be noted that for

a high oxidation level (Fuels 1-3 and Fuel 7), PetroOxy IP reaches the test precision limit (15min at 140°C), and is not accurate enough to characterize the oxidation level of these fuels. On the contrary TAN measurement appears more suitable for stability monitoring in this case. We note that blends obtained by dilution of a highly oxidized fuel with B0 (Fuels 4, 5 and 6) have higher IP compared to fuels having equivalent TAN (Fuels 1, 2 and 3 respectively). This may be explained by both a lower FAME content (0.6 to 3% v/v) and the low concentration of oxidizable species. Indeed, for a fuel having undergone extensive oxidation degradation, the concentration of stable products is high (Figure 7). Thus, its blending with a fresh fuel will lower the concentration in the final blend of oxidizable species which contribute to fuel reactivity during IP.

Interestingly, a good correlation between TAN and content in precipitates was obtained with a coefficient of determination R^2 equals to 0.79 (Figure 8). A poorer correlation was obtained with PetroOxy IP with $R^2=0.27$. These precipitates are representative of the total insoluble compounds present in the oxidized fuel. These compounds are thought to be precursors of deposits within FIS. Therefore, it was chosen to use TAN for fuel characterization during the injection test as being 1) representative of stability in stringent oxidation conditions and 2) indicative of the concentration of insoluble compounds which is in line with previous findings [21].

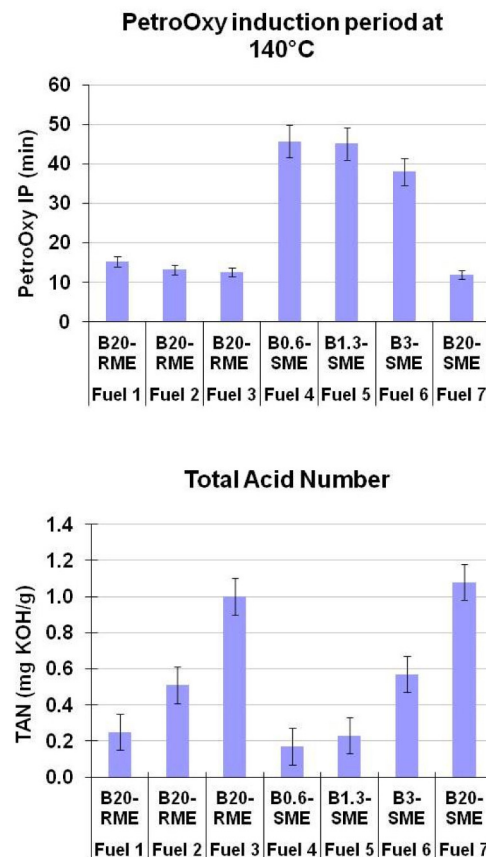


Figure 6. Induction period and TAN of the aged fuels tested on the injection experiment