Storage Stability of Biodiesel and Ultralow Sulfur Diesel Fuel Blends

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A biodiesel storage stability study was conducted on ultralow sulfur diesel fuel (ULSDF) and three biodiesel basestocks (B100) and fuel blends (B2, B5, B10, and B20). The storage stability study consisted in measuring and monitoring the changes in acid number (AN, ASTM D664-04) and kinematic viscosity (ASTM D445) over 10 months with different samples stored at 5°C, 40°C, and cyclic thermal conditions. Among the three biodiesel base fuels (B100) studied, Bio1 (from tallow) and Bio2 (from yellow grease) showed the largest increase in AN throughout 6 months of storage at 40°C while Bio3 (from canola) showed the least increase in AN. Bio1, Bio2, and Bio3 samples stored at 5°C showed very little increases in acidity after 10 month, while samples stored under thermal cycling conditions were comparable to those stored at 40°C. The AN for ULSDF and all blends between B2 and B20 for Bio1, Bio2 and Bio3 remained in the range of $0.1–0.3$ mg KOH g^{-1} for all temperatures and throughout the storage period well below the ASTM 6751 limit of 0.5 mg KOH g^{-1}. All blends showed a lower increase in AN than any of the base fuels. All fuels were submitted to accelerated oxidative testing, which also revealed a greater stability of the blends than for the biodiesel base fuels. Bio1 (from tallow) blends displayed a greater stability under accelerated oxidative testing while Bio2 (from yellow grease) displayed the least. The impact of storage conditions on the viscosities of all the base fuels and blends was negligible. [DOI: 10.1115/1.4000177]

Keywords: biodiesel, ultralow sulfur diesel, methyl esters, blends, storage, stability

1 Introduction

More contemporary attention and planning have been focused on the promotion of renewable energy sources as replacements or diluents for distillate petroleum fuels in the automotive industry. Alternate fuels from indigenous sources have gained further momentum in the recent rise of the world oil prices and uncertainties shrouding the security of future conventional petroleum supplies. The bioderived liquid fuels have acquired a substantial market share and led the way in partial replacement of petroleum diesel fuels for a variety of diesel engine driven applications.

Biodiesel, a long chain fatty acid alkyl ester derived from base-catalyzed transesterification of vegetable oils and animal fats, has assumed the leading supplementary role to the conventional diesel fuel in many parts of the world. The production of oils and fats reached close to 160×10^6 tons worldwide in 2008. Almost half of the production came from palm and soya oils, while oils from Rapeseed and canola ranked third with 19×10^6 tons. The production of tallow and greases (including yellow grease) was just over 8×10^6 tons with almost half coming out of the U.S. [1]. Based on the current price of petrodiesel, biodiesel is not a cost effective replacement for petrodiesel but makes sense as a fuel additive or blend component with petrodiesel in order to reduce green house gas emissions, improve the lubricity of ultralow sulfur diesel fuel (ULSDF), and reduce fossil fuel dependency. When comparing feed, it is much more cost effective to produce a biodiesel from waste vegetable oils and fats, which is about half the cost of a biodiesel produced from an edible crop like canola [2].

The most common form of biodiesel in the European Union originates from rapeseed oil while soybean oil is the predominant feedstock in the U.S. Production of biodiesel from waste cooking oils and animal fat also came to the forefront as a way to reduce raw material costs and alleviate waste oil disposal [3,4]. A comprehensive review spanning all the aspects of biodiesel from production to combustion was compiled [5]. Biodiesel shares many common physical and chemical features with conventional diesel fuel, and as such, the two are compatible at any mixture ratio. The addition of 20% biodiesel to petroleum diesel by volume in a blend (B20) is under consideration for transportation fuels including marine applications [6]. The Washington State Ferry system tested the performance of methyl ester biodiesels from various feeds including waste animal fats, soya, and canola [7]. The advantage of canola methyl ester (CME) is its cloud point below freezing, which is better adapted to the winter temperatures of North America.

The spectrum of advantages inherent to biodiesel ranges from environmental issues to economic and strategic benefits. The chemical and physical properties such as heat of combustion, absence of sulfur, and aromatic components, somewhat offset some long-term stability issues.

Biodiesel is more susceptible to oxidative attack than diesel fuel [8,9] and in its advanced stages, this process may render the biodiesel unsuitable for use in modern diesel engines. The rate of oxidation is largely determined by the degree of unsaturation in the fatty acid alkyl ester chain [10], water content, and environmental factors such as temperature, nature of the storage container [11], and air exposure [12] during storage. The end product of oxidation includes short chain carboxylic acids and polymeric sediments resulting in an increase in total acid number and viscosity of biodiesel under storage. These negative impacts on the chemical and physical properties of biodiesel could be accelerated if the initial oils and fats used in its production originated from cooking waste [13]. The addition of synthetic antioxidants to biodiesel proved effective in countering the oxidative degradation and in increasing the stability of the fuel [10,13,14].

As a concern for the environment, several countries have set deadlines for the use of diesel fuels with lower sulfur contents. The maximum sulfur content in North America for ULSDF is currently 15 ppm. However, a limit of 50 ppm is also in effect or being implemented in many parts of the world [15]. The hydrodesulfurization process of diesel fuels leads to lower lubricity [16], which affects fuel pumps and injectors. Biodiesel was proposed as a potential component to ULSDF to alleviate low lubricity performance [17]. The instability of biodiesel in blends with ULSDF is also a matter of concern [10], which was not fully explored due to the recent introduction of ULSDF.

Military fuel requirements are more restrictive in many aspects than the commercial sector. In this context, fuel stability and additives must meet more stringent standards in order to satisfy operational requirements. It is common for army units to be deployed overseas with initial bulk supplies to sustain operational capability beyond several months. These supplies routinely include bulk fuel storage drums containing ground transportation fuels that will be exposed to a wide variety of temperatures daily and seasonally as well as to low levels of moisture or oxygen. This investigation was aimed at studying the thermal effects on long-term storage in a limited oxidative environment. The fuels studied in this report were ULSDF and three biodiesels (B100) and some of their blends (B2, B5, B10, and B20). This storage stability investigation consisted in monitoring the changes in acid number (ASTM D664-04) and kinematic viscosity (ASTM D445), two test methods widely used to monitor changes in biodiesel, over a 10 month period. Fuel samples were stored at $5\,^\circ C$, $40\,^\circ C$, and under thermal cyclic conditions. The selected biodiesel fuels covered a spectrum of feed source, composition and initial acidity. The studied fuels were submitted to nuclear magnetic resonance (NMR) spectroscopy in order to compare their difference in chemical structure and detect potential changes throughout the storage period.

2 Materials and Methodology

2.1 Fuels and Blends. Ultralow sulfur diesel fuel was obtained from PetroCanada (Montreal, QC, Canada) and blended with biodiesels from three different sources: Bio1, a tallow-based methyl ester fuel (TME); Bio2, a yellow grease-based methyl ester fuel (YGME); and Bio3, a CME. The biodiesels were obtained from Canadian suppliers but their names were withheld due to confidentiality agreements. All fuels were studied as received without modification. Some fuel testing were contracted out to the Alberta Research Council (ASTM D86, D1160, D613, and EN 14112) and Quality Engineering Test Establishment (ASTM D5773, D6217, D874, and EN 14103) to measure the base fuel properties against the specification stipulated in ASTM D6751. The studied biodiesel blends with ULSDF consisted of 2% (B2), 5% (B5), 10% (B10), and 20% (B20) (v/v) and were stored in Brown Qorpak® Bottles (Fisher Scientific Co., Whitby, ON, Canada).

2.2 Storage Conditions. Three sets of base fuels and blends samples were prepared in a limited oxidative environment in tightly caped one liter glass bottles. The first set was stored at $40\,^\circ C$ in a temperature controlled oven. The second set was stored at $5\,^\circ C$ in a refrigerator. The third set was alternated on a daily basis between $40\,^\circ C$ and $5\,^\circ C$. The aforementioned temperature regiments were maintained for the 10 month duration of the project. Sampling was performed once per month for the first set and every second month for the other two series.

2.3 AN. ASTM D 664-04 standard test method was used in the determination of the AN of all fuels and their blends and to indicate relative changes that occur during storage. The electrode system (model 420Aplus pH meters and Triode pH electrodes) was obtained from Thermo Orion (Beverly, MA). Solvents, buffer solutions (pH 4, pH 7, and pH 10), and electrode storage solutions were all obtained from Caledon Laboratories Ltd. (Georgetown, ON, Canada). For each AN determination, approximately 20 g of base fuel or fuel blend was used. The uncertainty for AN in this study ranges from 3% to 13% for Bio1-TME and ULSDF, respectively.

2.4 Kinematic Viscosity. The ASTM D 445-04 standard test method was used in the determination of the kinematic viscosity. Three ubbelode viscometers with capillary constant of $K = 0.01$ (Schott Instruments, GmbH, Mainz, Germany) were used to determine the kinematic viscosities of biodiesels and their blends with ULSDF at $40.0 \pm 0.1\,^\circ C$. These viscometers were calibrated with S6 viscosity reference standard (ISO 17025; certificate number, KA0598, Koehler Instrument Co., Inc., Bohemia, NY). The viscosity measurements were carried out in a Lauda PVS1 automatic viscometer system, comprised of Lauda clear-view thermostat (D 15 KP) with Edition 2000 temperature controller (Lauda, Germany). The uncertainty for kinematic viscosity values in this study remains below 0.4%.

2.5 NMR. The ^1H NMR spectra were measured in deuterated chloroform ($CDCl_3$; 0.05% TMS, CDN Isotopes, Pointe-Claire, QC, Canada) on a Varian 300 MHz spectrometer. The uncertainty for NMR peak integration values in this study is below 1%.

3 Results and Discussion

3.1 Storage Stability. The selected biodiesel fuels varied from their feed source and composition. The characterization data for the three biodiesel fuels is provided in Table 1. The data presented in Table 1 meet the standard for biofuels stipulated under ASTM 6751 and provide a basis for comparison of the properties for the base fuels studied.

In Fig. 1, the AN was plotted as a function of the storage period at $40\,^\circ C$ for Bio1-TME, Bio2-YGME, Bio3-CME, and ULSDF. Both Bio1-TME and Bio2-YGME displayed an initial AN below the pre-2006 limit of 0.8 mg KOH g^{-1}, which was in effect at the time of the investigation under ASTM D6751 but above the new acceptable limit of 0.5 mg KOH g^{-1} in accordance with the 2006 revision of the ASTM. Bio3-CME was the only B100 that met the new limit throughout the storage period. All fuels displayed a steady increase in AN throughout the storage duration at $40\,^\circ C$. Bio1-TME degraded the most, reaching an AN of 0.9 mg KOH g^{-1} after 6 months of storage. ULSDF was evaluated with the same ASTM in order to compare the fuels and the blends. AN values recorded with ULSDF were at the lower limit of the method.

Bio3-CME was clearly the better B100 fuel with lower AN that remained stable for months. From Table 1, TME and YGME reported higher values for free water and sediment (D2709), particle contamination (D6217), and sulfated ash (D874), which could explain their higher initial values in AN and their larger increase in AN over 6 months. Sulfated ashes typically contain traces of various metals and also phosphor and sulfur, which are an indication of residual catalyst in the fuel while particle contamination can include less soluble organic molecules with some containing more polar groups such as free fatty acids. The combination of larger amounts of residual catalyst, acidic molecules, and water can promote reactions leading to a faster rise of AN values over the same storage period.

In Figs. 2–4, the AN was plotted for Bio1-TME, Bio2-YGME, and Bio3-CME B100 biodiesel base fuels, respectively. The AN was reported in each case as a function of the period of storage at $5\,^\circ C$, $40\,^\circ C$, and under thermal cycling. The AN for the fuels stored at $40\,^\circ C$ increased more rapidly than for storage at $5\,^\circ C$. The fuels stored under thermal cycling conditions displayed increases in AN comparable to those stored at $40\,^\circ C$. The AN increase was evident from the first month of storage for all fuels

Table 1 Characterization of the base fuels used in this study

|	Bio1-TME	Bio2-YGME	Bio3-CME	ULSDF
Feed source (from supplier)	Tallow	Yellow grease	Canola	Petrodiesel
Kinematic viscosity (mm² s⁻¹) ASTM D445	4.70	4.92	4.93	1.41
Cloud point (°C) ASTM D5773	12	4	−3	−26
Free water and sediment (vol %) ASTM D2709	0.05	0.03	0.01	0.05
Particle contamination (mg L⁻¹) ASTM D6217	9.3	25.5	4.7	0.2
Sulfated ash (wt %) ASTM D874	0.0005	0.0006	0.0002	0.0001
Ester content (wt %) EN 14103	97.9	97.9	99.5	—
Cetane number ASTM D613	63.7	54.2	54.7	46.4
Initial boiling point (°C) ASTM D86 (D1160 for B100)	325.6	321.5	339.6	150.9
10% distillate recovered (°C)	339.5	343.8	347.0	171.2
50% distillate recovered (°C)	346.3	349.0	349.5	203.4
90% distillate recovered (°C)	353.1	355.5	352.5	259.2
Final boiling point (°C)	408.0	425.0	408.0	291.6
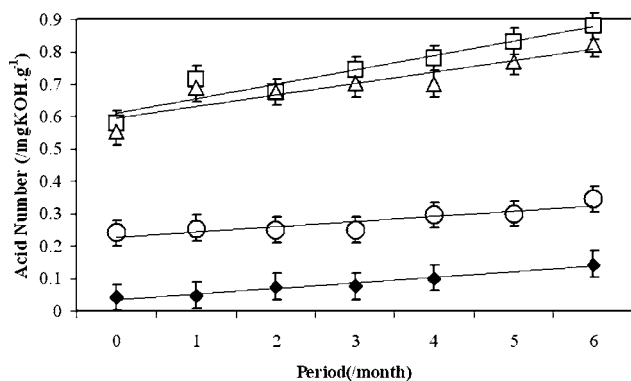
Fig. 1 Acid number of the three biodiesel base fuels B100 of TME (□), YGME (△), and CME (○), respectively, and ULSDF (◆) as a function of the storage duration at 40°C; lines indicate trends only
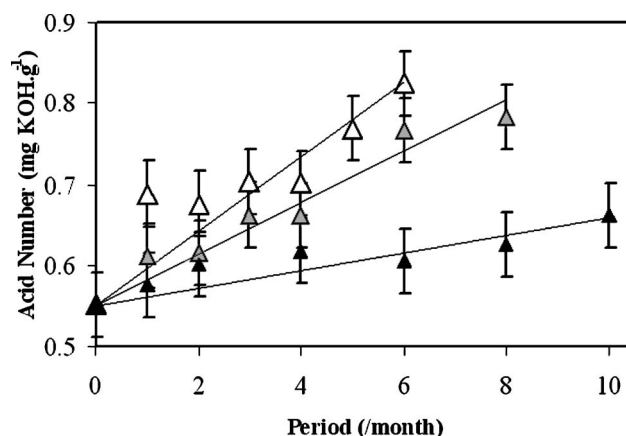

Fig. 3 Acid number of the Bio2-YGME B100 biodiesel base fuel as a function of the period of storage at 5°C (black) and 40°C (white) and under thermal cycling (gray); lines indicate trends only
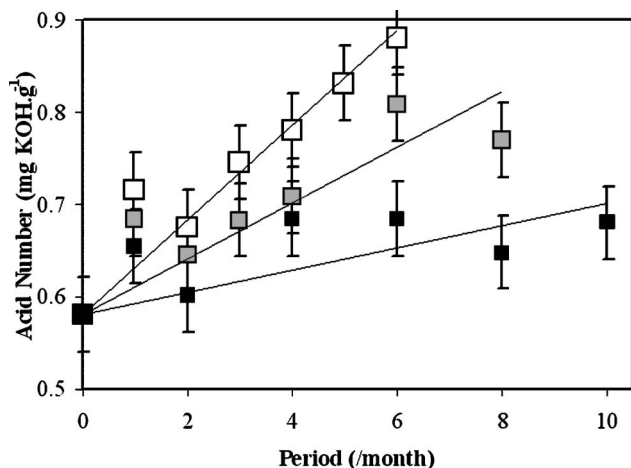

Fig. 2 Acid number of the Bio1-TME B100 biodiesel base fuel as a function of the period of storage at 5°C (black) and 40°C (white) and under thermal cycling (gray); lines indicate trends only
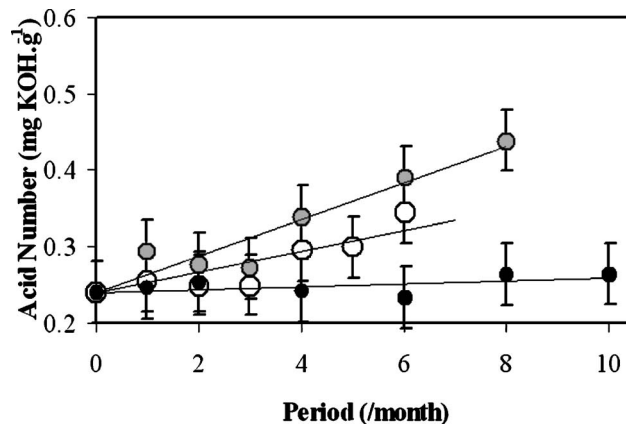

Fig. 4 Acid number of the Bio3-CME B100 biodiesel base fuel as a function of the period of storage at 5°C (black) and 40°C (white) and under thermal cycling (gray); lines indicate trends only
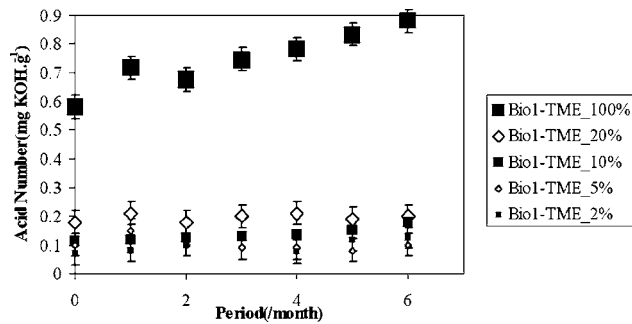
Fig. 5 Acid number of the Bio1-TME B100 biodiesel base fuel (black) and B20 (white), B10 (black), B5 (white), and B2 ((black) blends with ULSDF as a function of the period of storage at 40°C

with a less significant increase for Bio3-CME than for the other two.

In Fig. 4, the AN for Bio3-CME fuel stored under thermal cycling and at 40°C followed similar profiles. AN values started to increase steadily after 3 months of storage. Other studies attributed a greater stability to biodiesel from plant sources to the presence of natural inhibitors like sterols and tocopherols [18]. This hypothesis will be the subject of future work.

Figures 5–7 show the AN values as a function of time for storage at 40°C for all B2, B5, B10, B20 blends, and B100, respectively, for Bio1-TME, Bio2-YGME, and Bio3-CME. It is clear from those figures that the acidity of any blends was dictated by the acidity of the B100 base fuel mixed with ULSDF. The Bio1-TME and Bio2-YGME produced AN values for B20 blends below
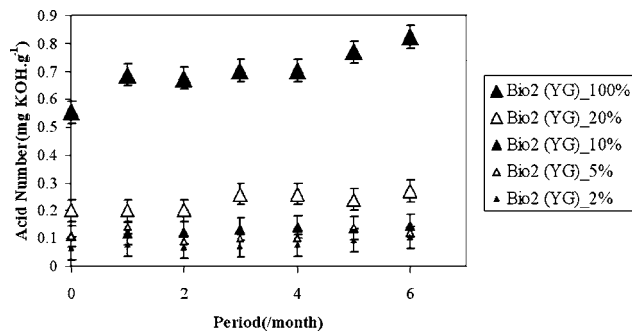

Fig. 6 Acid number of the Bio2-YGME B100 biodiesel base fuel (black) and B20 (white), B10 (black), B5 (white), and B2 ((black) blends with ULSDF as a function of the period of storage at 40°C
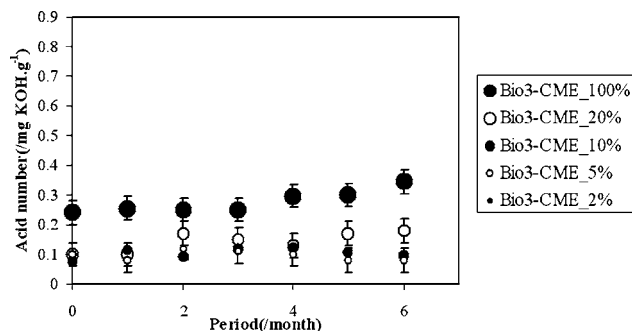

Fig. 7 Acid number of the Bio3-CME B100 biodiesel base fuel (black) and B20 (white), B10 (black), B5 (white), and B2 ((black) blends with ULSDF as a function of the period of storage at 40°C
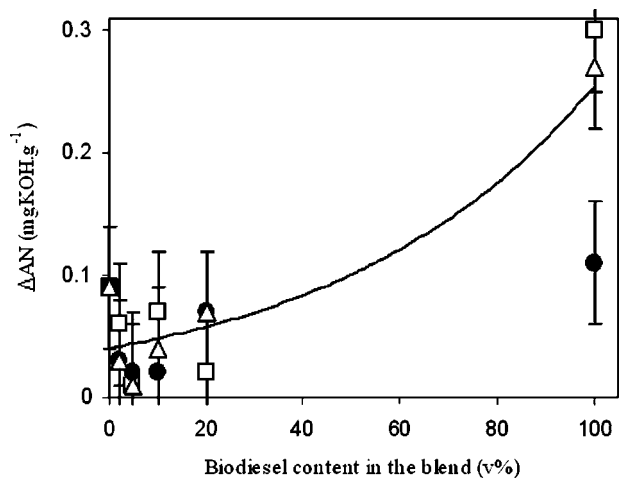

Fig. 8 Increase in acid number (ΔAN) after six months storage at 40°C for all three biodiesel fuels from TME (□), YGME (△), and CME (●), respectively, as a function of the biodiesel composition in vol %. Line indicates trend only.

0.3 mg KOH g^{-1} and approaching 0.3 mg KOH g^{-1} throughout the storage period. The Bio3-CME produced a B20 blend below 0.2 mg KOH g^{-1} and approaching 0.2 mg KOH g^{-1} after several months of storage. All other blend (B10, B5, and B2) AN values for the three biodiesel base fuels remained close to 0.1 mg KOH g^{-1} and always below 0.2 mg KOH g^{-1}. Those last results demonstrate that even B100s with AN close to 0.6 mg KOH g^{-1} can produce stable blends meeting standards for extended periods of storage under the studied conditions.

In Fig. 8, the increase in acid number (ΔAN) after 6 months storage at 40°C was reported for all fuels as a function of the biodiesel content of the blend in vol %. Interestingly, the AN of all fuel blends increased at a rate comparable to ULSDF while the AN of the three base biodiesels increased at a faster rate than for the blends. These results contain significant scatter, which may hide a slight ΔAN as a function of biodiesel content in the blend. The biodiesels that displayed the largest increase in AN were those with the highest AN values at the start of the study, namely, the TME and YGME. As mentioned before, the combination of larger amounts of residual catalyst, acidic molecules, and water for those two fuels would promote reactions increasing a faster rise of AN values over the same storage period. As observed in Figs. 1 and 7, the most stable fuel was CME, which increased the least in AN. This observation is consistent with other studies that attributed a greater stability of biodiesel from plant sources to the presence of sterols and tocopherols [18].

All biodiesel base fuels displayed viscosities between 4.5 mm^2 s^{-1} and 5 mm^2 s^{-1} as reported in Table 1, Bio2-YGME being the highest and Bio3-CME being the lowest. The kinematic viscosity of the base fuel measured at 40.0 ± 0.1°C did not change significantly under all storage conditions throughout the study period. The small changes in AN reported in Figs. 1–6 indicated some chemical changes but evidently not in sufficient amount to impact a macroscopic property like kinematic viscosity.

The viscosities of the biodiesel base fuels were comparable with each other and were generally three times the viscosity of the ULSDF. No significant change in kinematic viscosity was reported throughout the storage period for all fuels and blends. The viscosity of each fuel is reported in Table 1. The blends generally displayed viscosities in accordance with the rule of mixture of the two blended fuels. Even at 20% biodiesel in ULSDF, the viscosities of all B20 blends stayed close to that of ULSDF. The viscous behavior of the blends implies minimal additional stresses for the existing fuel systems.
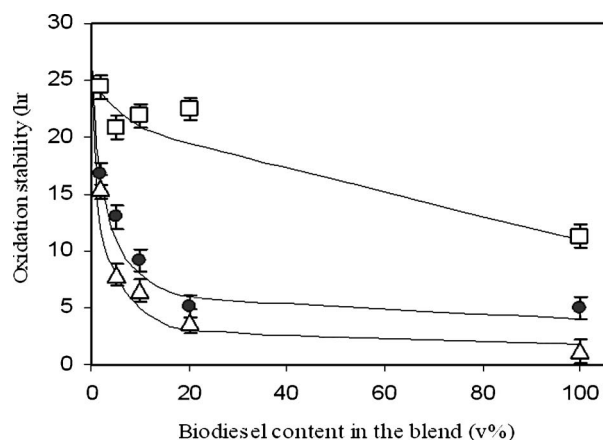
Fig. 9 Oxidation stability (hours) under EN 14112 (Rancimat) for all biodiesel fuels from TME (□), YGME (△) and CME (●), respectively, as a function of the biodiesel content in the blend in vol %; line indicates trend only
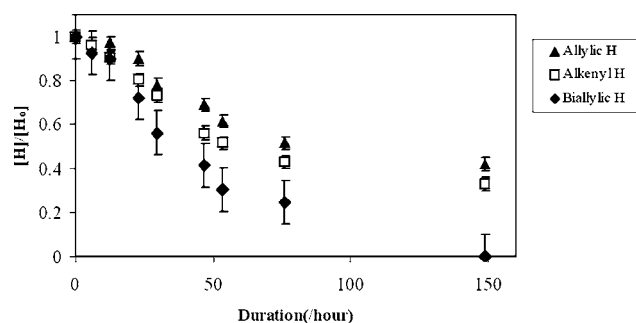

Fig. 10 Normalized proton concentration decay in Bio3-CME as a function of accelerated oxidation at 95°C for 150 h: The normalized proton concentration presented was calculated from the peak integration from the allylic hydrogens at δ =2.05 ppm, the bisallylic hydrogens at δ=2.75 ppm, and the alkenyl hydrogens at δ=5.35 ppm

3.2 Accelerated Oxidation Stability. The increased stability of the fuel blends is also supported by accelerated oxidation stability testing. In Fig. 9, the oxidation stability, under EN 14112 (Rancimat), was reported in hours as a function of biodiesel content in the blend. This test method measures the oxidation inductive period for the fuel by bubbling air through the sample at 110°C. A longer induction period indicates a greater stability of the fuel. EN 14112 was reported to be unreliable for petrodiesel due to the faster evaporation rate of the latter [19]. The distillation temperatures of ULSDF and the base biofuels are provided in Table 1. A new EN 15751 method was recently developed in Europe to address the deficiencies of EN 14112 and will be considered in future studies. The new method proposes to use 7g samples as opposed to 3g in order to compensate for the fast evaporation of petrodiesel. Extrapolation of the results in Fig. 9 to B0 actually suggests the stability for ULSDF to be greater than 25 h.

The conditions of EN 14112 are much more oxidative than the fuel storage conditions used for this research. The results show that Bio1-TME was more stable than Bio3-CME and Bio2-YGME. Under an aggressive oxidizing environment, unsaturated bonds, and the neighboring allylic and bisallylic groups are particularly reactive to oxygen [20]. Unsaturated bonds are usually found in larger concentrations in plant oils explaining why Bio1-TME, processed from tallow, displayed greater oxidation stability. Also, under this test method, all blends displayed a higher stability than the respective base biofuels. Although the oxidative conditions were different, the results in Fig. 9 are consistent with the observations made from Fig. 8 that show the blends are more

stable than the base biofuels.

In Table 2, NMR peak integrations have been normalized based on the three protons in the terminal methyl group of the fatty chain of the methyl esters base fuels. This representation shows the average number of proton in each chemical group per chain. The relative chemical group compositions per average molecule for the three base fuels are shown. The degree of unsaturation of the fuels is obtained from the last row. The number of double bonds per chain is half the number of hydrogen atoms involved in those bonds. Therefore Bio3-CME has on average 1.4 double bonds per fuel molecule as opposed to 1.0 for Bio2-YGME and 0.7 for Bio1-TME. This implies that Bio3-CME should be more sensitive to oxidation. However, no significant changes in chemical composition were reported for either of the fuels throughout any of the storage conditions. This result supports the observation on the stability of the fuels' kinematic viscosities but does not contradict the observed changes in AN.

The precision of the integration under the NMR peaks permits quantification of the concentration of chemical changes in the order of 10^{-2} to 10^{-3}. The concentration of the chemical changes observed with the AN was in the range of 10^{-3} to 10^{-4} and therefore falls just under what can be detected with NMR.

In order to confirm the reactivity of the chemical groups in the biodiesel, an accelerated oxidation of the Bio3-CME was performed by stirring in air at 95°C. Figure 10 shows the decay of the concentration of three groups normalized over their initial concentration. The most reactive group proved to be the bisallylic followed by the alkenyl and the allylic group [21]. Those groups are defined in Table 2, which are in lower concentration in Bio1-TME, therefore supporting the better stability of the base fuels and blends under accelerated oxidation testing. However, the ac-

Table 2 Relative number of protons per chemical environment (in relation to the presence of functional groups in the molecular structure) for Bio1-TME, Bio2-YGME, and Bio3-CME: Those values were calculated from the integration under the peaks at respective NMR chemical shifts δ (ppm) relative to internal protons in TMS

Names	Methyl ester functionality	δ (ppm)	TME (B100)	YGME (B100)	CME (B100)
Primary methyl	$-CH_2-CH_3$	0.85	3.0	3.0	3.0
Secondary methyl	$-(CH_2)n-$	1.30	22.5	20.0	18.5
β-methyl	$-CH_2-CH_2-CO_2-CH_3$	1.60	2.1	2.1	2.1
Allylic	$-CH_2-CH=CH-CH_2-CH=CH-CH_2-$	2.05	2.4	3.2	3.9
α-methyl	$-CH_2-CO_2-CH_3$	2.25	2.0	2.0	2.0
Bisallylic	$-CH=CH-CH_2-CH=CH-$	2.75	0.2	0.4	0.8
Methoxy	$-O-CH_3$	3.65	3.0	3.0	3.0
Alkenyl	$-CH=CH-$	5.35	1.5	2.1	2.8

celerated oxidation at high temperature does not explain or correlate to changes in the fuel stability observed for the longer periods under limited oxygen exposure at 5°C and 40°C used in this work.

Caution should be used when extending the storage stability results of this study to other biodiesels. The results for the studied TME, YGME, and CME could be extended, only to a limited degree, to methyl ester biodiesels from feedstocks with comparable compositions in saturated, monounsaturated, and polyunsaturated fatty acids. For example, TME could be compared with some degree with a lard methyl ester or a chicken fat methyl ester although the levels of unsaturated fatty acids are slightly higher in the last two. Further examples can also be provided for extending the stability results obtained for CME to other biodiesels from plant sources. The composition of canola is comparable to that of Jatropha, especially in terms of polyunsaturated fatty acids [22], while the content of the latter in soya is almost double that of canola. A similar caution should be applied when comparing canola with palm, which is much richer in saturated fatty acids.

4 Conclusions

Among the three biodiesel base fuels (B100) studied, Bio1 (from tallow) and Bio2 (from yellow grease) showed the largest increase in ANs throughout 6 months of storage at 40°C, while Bio3 (from canola) showed the least increase in AN. Bio1, Bio2, and Bio3 samples stored at 5°C showed very little increases in acidity after 10 months while samples stored under thermal cycling conditions were comparable to those stored at 40°C. The AN for ULSDF and all blends between B2 and B20 for Bio1, Bio2, and Bio3 remained in the range of 0.1 mg KOH g^{-1} to 0.3 mg KOH g^{-1} for all temperatures and throughout the storage period, well below the ASTM 6751 limit of 0.5 mg KOH g^{-1}. All blends showed a lower increase in AN than for any of the biodiesel base fuels. All fuels were submitted to accelerated oxidative testing, which also revealed a greater stability of the blends than for the biodiesel base fuels. Bio1 (from tallow) blends displayed a greater stability under accelerated oxidative testing while Bio2 (from yellow grease) displayed the worse stability.

The impact of storage conditions on the viscosities of all the base fuels and blends was negligible. The B20 blends of Bio1, Bio2, and Bio3 showed an approximate 25% increase in viscosity from ULSDF to about 1.72 mm^2 s^{-1}. The viscosity of B20 fuels would have minimal impact on existing fuel systems.

Nuclear magnetic resonance spectra could distinguish between different levels of saturation among the three biodiesels. Bio3-CME was the least saturated and Bio1-TME was the most saturated. However, the aging process did not generate chemical changes above the detection limit of NMR at all temperatures. The accelerated oxidation of Bio-CME at 95°C showed appreciable decay in the NMR spectra in bisallylic, allylic, and alkenyl hydrogen sites.

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