Storage and Oxidation Stabilities of Biodiesel Derived from Waste Cooking Oil

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ABSTRACT

The present work investigates the storage and oxidation stabilities of 100% biodiesel (B100) derived from waste cooking oil. Physical properties and chemical composition of B100, including viscosity, density, peroxide value, heat of combustion, acid number, and phase behavior, were measured. The analysis showed that this B100 contains over 60% unsaturated esters. The long-term storage stability was studied based on ASTM D4625 which simulates up to two years storage by holding samples at 43 °C. Modified ASTM D5304 and D2274 tests were conducted to investigate oxidation processes of B100. An extended ASTM D2274 method was also employed to investigate the influence of oxidation time on stability. The influence of long-term storage and oxidation reactions on physicochemical properties and phase behavior was investigated using ASTM methods. The existence of three stages of B100 oxidation was identified based on the property changes after the modified ASTM D5304 and D2274 tests.

Keywords: biodiesel; oxidation stability; storage stability; waste cooking oil.

Introduction

Biodiesel is defined as “a fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100” by the American Society for Testing and Materials (ASTM) [1]. Generally, biodiesel is produced by a transesterification process in which triglycerides from the vegetable- and animal-derived feedstocks are alcoholized with methanol in the presence of catalyst to obtain fatty acid methyl esters (FAME) and glycerol as a byproduct. The fatty acid composition of the feedstock is not altered by the transesterification reaction. Table 1 lists the five most common compounds in biodiesel. [2] Interest in biodiesel is continuously increasing worldwide motivated by its renewable and environmental benefits. In the U.S., the most common feedstocks for biodiesel are soybean oil, canola oil, used cooking oil, waste grease and tallow. It is commonly used for ground transportation in pure form (B100) or as 5 or 20% blends with petroleum diesel, B5 and B20, respectively. In 2012, approximately 991 million gallons of biodiesel were produced in U.S., and this value increased to over 1,200 million gallon in 2014 [3]. As of January, 2015, there were 97 biodiesel plants in the U.S. with capacity of over 2.0 billion gallons per year [3].

Although biodiesel has many prominent advantages over petroleum diesel, it is more prone to oxidation than conventional petroleum diesel owing to the presence of unsaturated bonds in the molecules inherited from its parent feedstock. This susceptibility to oxidation has significant impact on the diesel quality during long-term storage and handling. The general oxidation mechanism of unsaturated FAME is reasonably well understood [4, 5], and the reaction generally involves two types: autooxidation and photo-oxidation [4]. Autooxidation is the major cause of biodiesel degradation, and it generally comprises four steps: (i) release of hydrogen radicals by radical initiators; (ii) formation of peroxide and carbon radicals when hydrogen radicals interact with oxygen, (iii) further reaction of carbon radicals with oxygen; (iv) formation of stable oxidized product [4]. Temperature also impacts the oxidation reaction of biodiesel. Highly-stable, conjugated structures are formed by the Diels-Alder reaction of polyunsaturated methyl esters [4]. In general, the oxidation process of commercial biodiesel has three stages: (i) induction stage,

in which free radicals react with antioxidant compounds preferentially rather than FAME; (ii) exponential stage, in which ~80-90% antioxidants have been consumed and FAMEs start to rapidly react with oxygen; (iii) termination stage, in which the rate of peroxide degradation exceeds the rate of peroxide formation and the fuel quality is significantly changed [5].

The storage and oxidation stabilities of biodiesel derived from various feedstocks have been investigated [4-27]. The oxidation stability concerns the tendency of fuels to react with oxygen, while the storage stability concerns the general stability of the fuel under long-term storage. Both types of biodiesel stability depend on its susceptibility to degradation by oxidation reactions, which are highly influenced by the makeup of unsaturated esters. Generally, the oxidation rate of FAME depends on the number of double bonds and their position [28, 29], and is mainly affected by the number of bis-allylic methylene groups adjacent to the double bond compared to the allylic methylene groups, e.g. methyl linoleate is more susceptible to oxidation than the methyl oleate, and methyl linolenate is more susceptible to oxidation than methyl linoleate owing to the presence of additional bis-allylic methylene configuration [4, 13].

In this article, the physicochemical properties and chemical composition of commercial biodiesel derived from waste cooking oil produced by Pacific Biodiesel are reported. Method ASTM D4625 [30] was employed to investigate the long-term storage stability of biodiesel. Modified methods ASTM D5304 [31] and ASTM D2274 [32] were used to study oxidation processes of biodiesel under various conditions. Additionally, the influence of oxidation on fuel physicochemical properties and low-temperature qualities, such as density, viscosity, peroxide value, acid number, heat of combustion, fusion and crystallization temperature and enthalpies, were also investigated using ASTM methods.

MATERIALS AND METHODS

Materials

Biodiesel produced by Pacific Biodiesel was purchased from Carl's Jr. Station in Honolulu, HI. The biodiesel purchased is defined as B99.99 with < 0.01 % impurity and approximately 0.04% v/v Eastman BioExtend™ 30 antioxidant solution, and was produced mainly from waste cooking oil collected in Hawaii. Ultra-low sulfur diesel (ULSD) was provided by United States Navy Supply Center at Patuxent River, MD. The fuels were used as received, unless otherwise noted.

Chemical and Physical Properties

The composition of biodiesel was determined by gas chromatography/mass spectrometry (GC-MS). 1.5 µL fuel samples were dissolved in 1.5 mL hexane and analyzed using a Bruker 436-GC gas chromatograph and SCION-MS select, single quadrupole mass spectrometer. The GC was equipped with an Agilent DB1701 column (low/mid polarity, 60m, (14%-cyanopropyl-phenyl)-methylpolysiloxane), with a 15 m guard-column before the back flush valve, and operated at a helium flow rate of 1.5 mL/min. The guard column protects the analytical column by trapping nonvolatile residues and preventing them from entering the analytical column. The temperature program was conducted with the following three steps: (1) equilibrate at 50 °C and hold for 4 min; (2) ramp at 10 °C/min to 200 °C and hold for 4 min; (3) ramp at 0.5 °C/min to 225 °C and hold for 10 min. The back flush of the GC starts at 78 min with 3 psi pressure. A FAME reference standard (Catalog # FAMQ-005, AccuStandard, New Haven, CT) with saturated and unsaturated esters from butyric acid methyl ester to cis-4,7,10,13,16,19-docosaheptaenoic acid methyl ester was used for identification of biodiesel components.

An Anton Paar SVM3000 Stabinger Viscometer was used to measure the viscosity and density of neat and stressed biodiesel samples at temperatures according to the ASTM D7042 method [33]. The accuracy of the viscometer was tested with a certified viscosity reference standard (Standard S3, Cannon

Instrument Company) and the measurement repeatability was ± 0.1 % of reading for viscosity, ± 0.0002 g/cm³ for density, and ± 0.005 °C for temperature.

A Parr 6200 Isoperibol Calorimeter was used to measure the heat of combustion, i.e. heating value, based on the ASTM D4809 method [34]. Approximately 0.3 g fuel sample was used for the test, and the O₂ pressure of the bomb was ~ 3 MPa. The measurements were made with 0.0001° C resolution over a 20 to 40 °C working range with an uncertainty of 0.05 – 0.1 %. The heat of combustion reported in this study is the higher heating value (HHV).

ASTM D3703 [35] was employed to determine the peroxide value (PV) before and after stressing the biodiesel. The sample was dissolved in isooctane and reacted with potassium iodide to reduce the hydroperoxides in the fuel. An equivalent amount of iodine was liberated by titrating with a sodium thiosulfate solution. The PV is expressed as milligrams of hydroperoxide per kilogram of sample. PV is an indication of the quantity of oxidizing constituents present in the fuel samples that influence various parameters, such as the cetane number (CN), density, viscosity, etc. In addition, the variation of PV value was determined as a function of time that the sample was subjected to ASTM D2274 test conditions, i.e. beginning at 16 h of test duration and every two hours thereafter up to 34 h of test duration. At each time interval, 30 ml fuel samples were removed from the oxidation cell, cooled to room temperature in the dark, and subjected to PV analysis.

ASTM D974 method [36] was also employed to measure the acid number (AN) of the biodiesel samples. In general, this method is applied to assess the relative change of carboxylic acid groups in chemical compounds resulting from fuel oxidation and to quantify the amount of acid present. The AN is expressed in milligrams of potassium hydroxide (KOH) required to neutralize the acid in one gram of the fuel sample. The sample is dissolved in a titration solvent consisting of toluene, isopropyl alcohol, and a small amount of water. The result is a homogenous single phase solution that is titrated at room temperature

with a KOH solution. The end point is identified by the color change of the p-naphtholbenzein solution added as an indicator.

Differential scanning calorimetry (DSC) analyses were conducted using a TA Q2000 system (TA Instruments, New Castle, DE) with a RCS90 temperature control which permits the DSC operation over the temperature range of -90 °C to 550 °C. A Tzero low mass hermetically sealed pan (Part No. 901670901, TA Instruments, New Castle, DE) was selected for analyses with a sample mass of 2 - 3 mg. A purge gas of ultra-high purity nitrogen with a flow rate of ~50.00 ml/min was regulated by a mass flow controller. Cooling and heating scans for biodiesel were conducted with the following program: (1) equilibrate at 20 °C, cool at 5 °C/min to -80 °C, and hold isothermally for 5 min; (2) heat at 5 °C/min to 20 °C, and hold isothermally for 5 min; (3) repeat step (1) and (2). The step (3), repeated cooling and heating scan, is conducted to ensure that the pan is well sealed and the curve is repeatable. The procedure provides crystallization peaks that are more convenient to integrate than the fusion peaks because the baseline of the cooling scan is more stable and it is easier to distinguish the start and end points of phase transition peaks. The cooling scan was analyzed to determine the crystallization onset temperature (FO), the maximum peak temperature (FP) and enthalpy of crystallization (ΔH_{cry}).

Storage and Oxidative Stabilities

The ASTM D4625 [30], and modified D5304 [31] and D2274 [32] methods were employed to test the storage and oxidation stabilities of biodiesel. ASTM D4625 and D5304 were both originally developed to evaluate the storage stability of middle distillate petroleum fuel [37-40]. ASTM D4625 requires that fuel be stored at 43 °C for 24 weeks with samples analyzed every 4 or 6 weeks to quantify the amount of filterable and adherent insolubles present. For this method, one week of storage at 43 °C is roughly equivalent to a month of storage at ambient temperatures, 21 °C. This method has been expanded to evaluate the storage stability of distilled and undistilled biodiesels [9-11, 21, 25, 41, 42]. ASTM D5304 is an accelerated method compared to ASTM D4625. The storage stability of the fuel is evaluated after 16 h subjected to an oxygen atmosphere at 90 °C and 800 kPa. The 16 h test is expected to yield approximately

the same amount of insolubles as 27 months of storage at 20 °C, 101.325 kPa air pressure. ASTM D5304 has also been employed to study the storage stability of biodiesels [27, 43, 44]. ASTM D2274 is an accelerated method developed to quantify the oxidation stability of distillate fuel oil [37-39]. This method also requires an elevated temperature, 95 °C, and continuous exposure to 3L/h, bubbled flow of pure oxygen at ambient pressure. As with ASTM D4625 and D5304, this method has also been employed for biodiesel samples [9-11, 25, 42, 45].

ASTM methods D4625, D5304 and D2274 quantify the amount of insolubles formed under controlled test conditions. The total insolubles include filterable and adherent insolubles – the filterable insolubles are solid particles formed during storage which can be removed by filtration and the adherent insolubles are gums formed during storage that remain tightly attached to the walls of the test vessel. All three test methods call for stressing the fuel followed by cooling for 60 ± 5 min in the dark at room temperature. In all cases, filterable insolubles of the aged samples were quantified using two nylon membrane filters (Whatman, 47 mm diameter, 0.8 μ m pore size, Cat. No. 09 902 13, Fisher Scientific) . Adherent insolubles were removed from the oxidation cell or storage bottle and associated glassware with trisolvent (an equal molar mixture of acetone, methanol, and toluene). Depending on the ASTM method, the solvent was evaporated at 135 °C or 160 °C to obtain the adherent insolubles.

RESULTS AND DISCUSSION

Physicochemical Properties

The GC/MS scan of biodiesel derived from waste cooking oil had five dominant peaks ranging in retention time from 35 to 49 min, as shown in Figure 1. The results indicate biodiesel consists of five main components, i.e. methyl palmitate, methyl oleate, methyl linoleate, methyl stearate, and methyl linolenate, with retention times at 35.396, 46.642, 46.944, 47.751 and 48.163 min, respectively. These five substances are the most common compounds present in biodiesel [2]. The molar concentrations were calculated to be 26.3% methyl palmitate, 27.8% methyl oleate, 30.4% methyl linoleate, 8.9% methyl

165 stearate, and 6.6% methyl linolenate. The amount of unsaturated esters with bis-allylic sites accounts for
166 over 35% of the biodiesel, which highly influences the stability of the fuel sample. The second column of
167 Table 2 lists the physicochemical properties of the biodiesel. The five measured properties of this waste
168 cooking oil derived biodiesel meet the ASTM D6751 specification, — kinematic viscosity (ν) in the range
169 of 1.9 - 6 mm² s⁻¹ at 40 °C and acid value (AV) < 0.5 mg of KOH/g. The measured heat of combustion
170 (HHV) of this waste cooking oil derived biodiesel, 39.1707 ± 0.0422 MJ kg⁻¹, is lower than petroleum
171 diesel, e.g. the HHV of marine diesel NATO F-76 [46] and ultra-low sulfur diesel (ULSD) are 44.8292 ±
172 0.0733 and 44.9569 ± 0.1840 MJ kg⁻¹, respectively.

173 Low temperature properties of the biodiesel were also investigated using DSC. Figure 2 shows three
174 distinct peaks during both the cooling and heating cycle scans. Dunn investigated the crystallization
175 process of pure methyl palmitate, methyl stearate, and methyl oleate and reported that their crystallization
176 onset temperature (FO) values are 24.4, 33.7 and -40.6 °C, respectively [47]. Crystallization temperatures
177 of methyl linoleate and methyl linolenate have not been reported in the literature; melting temperatures
178 were reported to be -35, and -45.5 °C, respectively [48]. The first crystallization peak in the cooling scan
179 (the maximum peak temperature (FP) at ~5 °C) spans a wider temperature range, approximately 37 °C,
180 compared to the ~12 °C width observed for the -50 and -65 °C peaks. This appears to be the result of
181 crystallization of saturated esters in the presence of methyl oleate. Similar wide peak phenomena were
182 also observed in biodiesel derived from palm and peanut [49]. Peaks 2 and 3 correspond to the phase
183 change of unsaturated esters, i.e. methyl oleate, methyl linoleate, and methyl linolenate, and possibly
184 some low molecular weight impurities that were not characterized by GC/MS. Table 3 presents the
185 crystallization FO, FP, and enthalpy of crystallization (ΔH_{cry}) of the biodiesel sample based on the cooling
186 curve. From these results, this biodiesel derived from waste cooking oil is expected to have inferior cold-
187 flow properties compared to biodiesel derived from rapeseed, sunflower and soybean biodiesel (FO
188 values < 0 °C) [49], but better cold flow properties than palm and peanut based biodiesels (FO = 7.6 and
189 15 °C, respectively) [49]. These differences between biodiesels result from their varied contents of

saturated long chain esters which account for >35 % of the waste cooking oil biodiesel. Note that the enthalpy of crystallization data could be used for modeling the cold-flow properties of biodiesel.

Storage Stability

A fuel's storage stability is highly affected by its aromatic content, sulfur content, and fuel oxidative and thermal stabilities. [50] ASTM D4625-04 (2009) is one of the most widely established methods for testing the storage stability of middle distillate petroleum fuels and has been employed for characterizing the storage stability of biofuels [9-11, 21, 25, 41, 42, 51]. Biodiesel samples were subjected to long-term storage tests, i.e. ASTM D4625 for 24 weeks with replicated analyses occurring at 0, 4, 8, 12, 16, 20, and 24 weeks. Figure 3 shows the amounts of filterable and adherent insolubles formed in the biodiesel samples increased with storage time, which agrees with the results reported by McCormick and Westbrook [25], and Westbrook and Stavinoha [42]. The physicochemical properties of biodiesel were also affected by the long term storage as shown in Table 2. The density, kinematic viscosity, PV, HHV and AN all increased after 24 weeks of storage. The differences in AN, density, and HHV values for the samples were statistically significant, but for the latter two quantities differences were small. The kinematic viscosity and AN of the stored samples remained within ASTM D6751 specifications.

Oxidation Stability

A modified ASTM D5304 method was employed to investigate the oxidation process of biodiesel under pure oxygen at 90 ± 1 °C, and 800 ± 10 kPa pressure. Although not recommended in testing the stability of biodiesel owing to the oxygen absorption of some biodiesels [6], the modified method allows investigation of the biodiesel oxidation process by monitoring the oxygen consumption rate in the pressurized vessel, rather than just investigating the formation of insolubles and fuel property change. The oxygen consumption rate is calculated based on the pressure change of the vessel. Figure 4 shows the oxygen consumption of biodiesel after 16 and 40 h tests. The oxygen consumption is relatively slow in the first 8 h owing to the added BioExtend™ 30 antioxidant, after which the rate is accelerated. Similar phenomena were also observed by Stavinoha and Howell [6], but the oxygen consumption rate of their

samples accelerated after 1 h. Approximately 50% of the initial O₂ pressure remains in the vessel after 16 h and all of the oxygen was consumed after about 35 h. The amount of insolubles formed after the 16 and 40 h tests was also measured and are shown Figure 5. The total amount of insolubles formed after 16 h is similar to that formed after the 24 week ASTM D4625 test. The filterable and adherent insolubles formation significantly increased after 40 h, especially the filterable insolubles. The amount of filterable insolubles increased by more than an order of magnitude in the 24 h following the 16 h ASTM D5304 test, corresponding to the period of rapid O₂ consumption shown in Figure 4.

Changes in fuel composition and physicochemical properties were also investigated after the modified ASTM D5304 tests. Figure 6 illustrates the composition change of the five major components, i.e. methyl palmitate, methyl oleate, methyl linoleate, methyl stearate, and methyl linolenate, after stressing the biodiesel samples for 8, 16 and 40 h. The concentration of methyl palmitate, methyl linoleate, methyl stearate, and methyl linolenate in the biodiesel increases slightly with oxidation time, whereas the methyl oleate concentration decreases. This indicates that the oxidation and degradation rates of methyl oleate are faster than the other four compounds during the ASTM D5304 test. This composition change was also reflected by the physicochemical properties after stressing the samples. Table 2 summarizes the biodiesel properties before and after the modified ASTM D5304 tests. Fuel density decreased approximately 10% after 8 h owing to the formation of small molecular weight substances, such as acids, aldehydes, alcohols, ketones, and peroxides, [28] through oxidation reaction. The density of the biodiesel increased after the 16 and 40 h tests, which may result from the formation of highly stable conjugated structures by the Diels-Alder reaction between the conjugated diene groups in the chain and polyunsaturated olefinic groups from nearby chains. [4] This was also reflected by the significant increase of kinematic viscosity after stressing the biodiesel samples. The formation of acids and peroxides induced by stressing the sample for 40 h was also demonstrated by increases in peroxide values and acid numbers, approximately 60 and 10 fold, respectively. Note that the heat of combustion was not affected, and that the peroxide value of samples after stressing for 40 h was lower than that after testing for 16 h, indicating that the

biodiesel reached the termination stage of the oxidation process between 16 and 40 h. Figure 7 shows the influence of biodiesel oxidation on the low temperature properties of the fuel. The FO of crystallization at Peak 1 after 8, 16, and 40 h of ASTM D5304 test conditions is 6.14, 6.24 and 6.35 °C, respectively, and the changes are not significant compared to the untreated biodiesel. The shift and change of Peak 3, which represents the phase change of unsaturated esters, is significant. Peak 3 completely disappears after 40 h of testing.

Extended duration ASTM D2274 tests were also conducted to investigate the oxidation process of the waste-oil biodiesel, i.e. instead of merely oxidizing the biodiesel for 16 h, the biodiesel was oxidized for 16, 40, 64, 88 and 112 h to study the impact of oxidation time on oxidation stability. Figure 8 illustrates the relationships between the insoluble formation and the oxidation time of the biodiesel samples. Generally, formation of filterable and adherent both increases with the oxidation time. The amount of filterable insolubles increases linearly with oxidation time, while the amount of adherent insolubles increases exponentially, i.e. the total insolubles formation is dominated by the formation of adherent insolubles when oxidation time exceeds 40 h. However, the total amount of insolubles formed by this waste cooking oil derived biodiesel is lower than the values reported by Waynick [11], 12.4 mg/100ml, after 40 h of testing, and the values reported by McCormick et al. [23], Stavinocha and Howell [6], and McCormick and Westbrook [25] after 16 h of testing.

The influence of oxidation time on biodiesel composition and low temperature properties was also investigated. Figure 9 shows the biodiesel composition of the degrading biodiesel over the extended duration ASTM D2274 tests. As expected, the composition of unsaturated esters, i.e. methyl oleate, methyl linoleate, and methyl linolenate decreased with oxidation time owing to the breaking of double bonds. The mole fractions of methyl linoleate and methyl linolenate were reduced to 0 % after 64 and 112 h, respectively. In addition, the degradation rate of the methyl linoleate was faster than the methyl oleate. This demonstrates that polyunsaturated esters are more susceptible to oxidation than monounsaturated esters owing to the presence of additional bis-allylic methylene groups [4, 13]. The trend in composition

changes obtained after the extended time ASTM D2274 tests is different from that obtained after the ASTM D5304 tests shown in Figure 6, where the composition change of the five dominate compounds is mainly induced by the more rapid oxidation of methyl oleate. This difference is the likely result of the initial high pressure condition required by the ASTM D5304 method. Figure 10 shows the DSC cooling scan of untreated and stressed biodiesel samples after extended duration ASTM D2274 tests. In general, the oxidized biodiesel samples exhibit inferior low-temperature qualities compared to the untreated biodiesel samples. The FO of Peak 1 increases with oxidation time, from 5.56 to 12.40 °C, owing to the formation of high molecular weight compounds through the Diels-Alder reaction of polyunsaturated methyl esters. This could affect the utilization of biodiesel in colder climates. Changes of methyl linoleate and methyl linolenate content in the stressed biodiesel samples were also reflected by the DSC scans, with both low-temperature peaks disappearing after 88 h.

Figure 11 (A)-(C) displays the influence of ASTM D2274 oxidation time on biodiesel physicochemical properties. Overall, the ASTM D2274 tests had significant impact on fuel properties owing to the high temperature and the continuous supply of pure oxygen. The kinematic viscosity, density and AN (Figure 11 (A) and (C)) increased with oxidation time, while the heat of combustion decreased with oxidation time (Figure 11 (C)) and the peroxide value fluctuates (Figure 11 (B)). After 112 h, changes induced by these conditions include ~10% increase of density, a greater than 4-fold increase of kinematic viscosity, more than an order of magnitude increase of AN and PV, as well as a 15% decrease of HHV. The PV in Figure 11 (B) reaches a maximum after approximately 30 h of extended D2274 testing, marking the oxidation reaction's transition from the induction and exponential stages before ~30 h, to the termination stage thereafter. This is in good agreement with the oxidation mechanism of polyunsaturated fatty acid esters proposed by Christensen and McCormick [5].

CONCLUSION

The influence of long-term storage and oxidation on properties of B100 derived from waste cooking oil was investigated by monitoring insoluble formation, oxygen consumption rate, viscosity, density, peroxide value, acid number, heat of combustion, and phase behavior. Similar to other commercial biodiesel, this B100 consists of five primary compounds, i.e. methyl palmitate, methyl oleate, methyl linoleate, methyl stearate, and methyl linolenate. Unsaturated esters account for >60% of liquid volume and approximately 60% of the unsaturated esters contain bis-allylic sites which highly affect the B100 stability. Owing to the mild conditions of slightly increased temperature and atmospheric pressure, the long-term storage tests, ASTM D4625, did not have significant impacts on fuel properties. Total insolubles formed after 24 weeks of ASTM D4625 test conditions were similar to those formed after 16 h of ASTM D5304 tests. ASTM D5304 test conditions of elevated temperature and pressure under a pure oxygen head space, however, produced significant changes in physicochemical properties (viscosity, density, AN, PV, HHV, and phase behavior). The ASTM D2274 tests had greater impact on B100 properties compared to the D5304 tests due to the continuous supply of pure oxygen. The oxidation process of B100 reached the termination of the peroxide propagation stage after ~30 h of ASTM D2274 test conditions, as reflected by changing shape of PV curve. In addition, DSC measurements indicate that oxidation negatively impacts the low-temperature quality of B100, which would limit the use of B100 in cold climates.

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Figure Captions

FIGURE 1. GC/MS chromatogram of B100 from waste cooking oil.

FIGURE 2. DSC heating and cooling curve of B100 from waste cooking oil.

FIGURE 3. Insolubles formed in the B100 determined by ASTM D4625 for 24 weeks. Each data point is average of two samples.

FIGURE 4. Oxygen consumption of B100 samples during ASTM D5304 test.

FIGURE 5. Insolubles measured in B100 after 16 and 40 h ASTM D5304 tests.

FIGURE 6. B100 composition change after ASTM D5304 tests.

FIGURE 7. DSC cooling curve after stressing B100 for different test durations using ASTM D5304 techniques.

FIGURE 8. Insolubles formed in B100 subjected to ASTM D2274 test methods for up to 112 hours.

FIGURE 9. B100 composition change after extended duration ASTM D2274 tests lasting up to 112 hours.

FIGURE 10. DSC cooling curve after stressing B100 using ASTM D2274 method for up to 112 hours.

FIGURE 11. Physicochemical properties of biodiesel after extended ASTM D2274 tests for up to 112 hours: (A) kinematic viscosity at 40°C and density at 15°C; (B) peroxide value; (C) high heating value and acid number. The PV between 16 and 34 h was measured by sampling ~30 ml biodiesel every 2 h from the oxidation cell.

451 Table 1. Five most common fatty acid methyl ester compounds in the biodiesel. [2]

Common Name	Formal Name	CAS. No.	Molecular	Molecular	Molecular Structure
Methyl palmitate	Hexadecanoic acid, methyl ester	112-39-0	$C_{17}H_{34}O_2$	270.45	
Methyl stearate	Octadecanoic acid, methyl ester	112-61-8	$C_{19}H_{38}O_2$	298.50	
Methyl oleate	9-Octadecenoic acid (9Z)-, methyl ester	112-62-9	$C_{19}H_{36}O_2$	296.49	
Methyl linoleate	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	112-63-0	$C_{19}H_{34}O_2$	294.47	

Methyl linolenate	9,12,15-Octadecatrienoic acid (Z,Z,Z)-, methyl ester	301-00-8	$C_{19}H_{32}O_2$	292.45	

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454 Table 2. Physicochemical properties of B100 before and after ASTM D4625 and modified D5304 tests.

Properties	As-purchased	D4625 24weeks	D5304 8 h	D5304 16 h	D5304 40 h
ρ at 15°C (g cm ⁻³)	0.8778 ± 0.0001	0.8781 ± 0.0001	0.8003 ± 0.0001	0.8799 ± 0.0001	0.8865 ± 0.0002
ν at 40°C (mm ² s ⁻¹)	4.3725 ± 0.0016	4.3787 ± 0.0065	4.4590 ± 0.0027	4.4489 ± 0.0778	5.0034 ± 0.0120
PV (mg kg ⁻¹)	16.59 ± 0.49	17.36 ± 1.83	422.18 ± 10.87	1139.74 ± 8.70	1053.96 ± 23.52
HHV (MJ kg ⁻¹)	39.1707 ± 0.0422	39.3074 ± 0.0291	39.3419 ± 0.2924	39.2502 ± 0.1681	38.9834 ± 0.2000
AN (mg of KOH/g)	0.23 ± 0.01	0.32 ± 0.01	0.61 ± 0.04	0.88 ± 0.02	2.62 ± 0.03

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456 Table 3. Summary DSC heating and cooling curve data for B100 in Figure 2.

Peak Number	FO/°C ^{a,b}	FP/°C ^{b,c}	$\Delta H_{\text{cry}}/\text{J g}^{-1}$ ^d
Peak 1	5.56	3.97 and 5.28	41.05
Peak 2	-49.72	-52.01	23.93
Peak 3	-63.06	-66.15	12.38

457 ^a FO = crystallization onset temperature

458 ^b The uncertainty of the temperature measurement is ± 0.10 °C

459 ^c FP= crystallization peak temperature

460 ^d ΔH_{cry} = enthalpy of crystallization

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483 Figure 11a

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