Effect of Accelerated High Temperature on Oxidation and Polymerization of Biodiesel from Vegetable Oils

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Abstract: Oxidation of biodiesel (BD) obtained from the decomposition of biomass can damage the fuel injection and engine parts during its use as a fuel. The excess heating of vegetable oils can also cause polymerization of the biodiesel. The extent of BD oxidation depends on its fatty acid composition. In this study, an accelerated oxidation test of BDs at 95 °C was investigated according to ASTM D 2274 by applying a long-term storage test for 16 weeks. The density, viscosity, and total acid number (TAN) of BDs increased because of the accelerated oxidation. Furthermore, the contents of unsaturated fatty acid methyl esters (FAMEs), C18:2 ME, and C18:3 ME in BDs decreased due to the accelerated oxidation. The ^{1}H-nuclear magnetic resonance spectrum of BDs that were obtained from the accelerated high temperature oxidation at 180 °C for 72 h differed from that of fresh BDs. The mass spectrum obtained from the analysis of the model FAME, linoleic acid (C18:2) methyl ester, which was oxidized at high temperature, indicated the formation of dimers and epoxy dimers of linoleic acid (C18:2) methyl ester by a Diels-Alder reaction.

Keywords: biodiesel; fatty acid methyl ester; free fatty acids; oxidation stability; antioxidant

1. Introduction

The use of biomass for the production of biofuels has been encouraged because of the severe global issues that are related to climate change and energy security [1,2]. Biodiesel (BD), a mixture of fatty acid methyl esters (FAMEs) extracted from vegetables or animal fats, is a renewable fuel that can be used for diesel engines [3–5]. BD can be used directly or after blending with petroleum diesel (PD) without the need to significantly modify conventional diesel engines. The emissions of particulate matter and exhaust gas, such as hydrocarbons, sulfur dioxide, and carbon monoxide, can also be reduced by blending PD with BD with the decrease of smoke opacity [6–9].

Bai et al. [10] reported the relationship between the blending ratio of BDs in diesel fuel and their effects in engine and environmental aspects and recommended to mix 20–50% of BDs to provide the environmental and technical advantages. High pressure (e.g., 180 MPa) pumping is applied to modern light duty diesel engines to provide short injection, good spray, and air mixing of diesel fuels [11]. The excess fuel is returned to the fuel tank by the recirculation system, which houses the fuel injectors. Owing to fuel recirculation, the oil can be partially oxidized and mixed with fresh oil in the tank after

it cools the fuel injection system. The temperature of the recirculating oil can rise to 60–150 °C, while it cools the hot injection system and makes contact with high temperature air [12–16].

BD, obtained from common biomass feedstocks, is a mixture of FAMEs consisting of fatty acid chains having different numbers of carbon atoms (16 or 18) and double bonds (0~3). The oxidation of FAMEs forms peroxy radicals and it is initiated by the formation of free radicals at the allylic position and the reaction with oxygen [17–19]. The peroxy radicals formed are converted to hydroperoxides and alkyl radicals via intramolecular isomerization or by the extraction of hydrogen from other fatty acid chains. The hydroperoxides can be converted to hydroxyl and alkoxy radicals, which can decompose to alkyl aldehydes and alkyl radicals, produce acids via oxidation, or undergo polymerization by reacting with other alkenes [20–25].

The content of unsaturated fatty acids in BD is directly related to the extent of oxidation of BD, because the rate of oxidation increases with the number of double bonds in fatty acid chains [26]. Owing to the importance of fuel stability during its use as a fuel [23], the use of BD with high contents of double bonds (e.g., linolenic acid (C18:3) or linoleic acid (C18:2); Figure 1) in FAMEs is being limited, even though they can provide excellent cold flow properties.
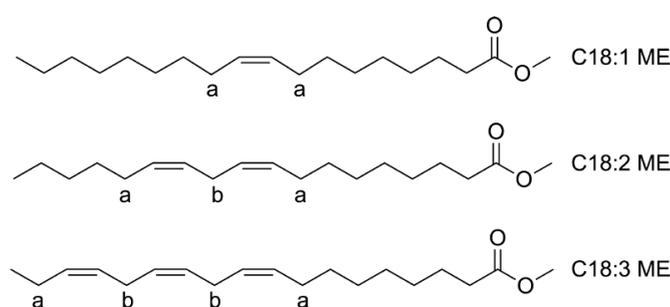

Figure 1. Common unsaturated C18 methyl esters in biodiesel: C18:1 ME, oleic acid methyl ester, C18:2 ME, linoleic acid methyl ester, and C18:3 ME, linolenic acid methyl ester, with (**a**) allylic positions and (**b**) bis-allylic positions.

In addition, the presence of oxygenates (e.g., acids, alcohols, aldehydes, and peroxides) in BD causes the accumulation of deposits and gum, as well as an increase in the fuel darkness, which decreases BD stability during long-term storage [27,28]. The presence of air, moisture, heat, and other contaminants can also decrease the stability of BD, because they can cause air oxidation, thermal oxidation, wet hydrolysis, microbial degradation, etc. [11–13], which can drastically change fuel properties [29,30]. Among various kinds of reactions, oxidation is considered to be the most significant contributor to the instability of BD, because of the ease with which it occurs during long-term storage of BD. Excessive degradation of BD can increase the contents of high molecular insoluble polymers, which can not only have negative effects (e.g., coking, clogging, and contamination deposits) on many vehicle parts (e.g., injector, fuel filter, fuel lines, and the engine), but also cause incomplete combustion [17,31].

Biodiesel stability tests can be classified by their purpose into the thermal stability test (ASTM D6468-08), storage stability test (ASTM D4625-16, ASTM D5304-15 and EN 15751), and oxidation stability tests (ASTM D2274, ASTM D7545-14, and EN 14112) [20,28–30,32].

In this study, the oxidation stability of commercial grade BDs was examined using ASTM D2274 by applying accelerated oxidation conditions normally at 95 °C during long-term storage for 16 weeks to provide the handling guidelines on the production, use, and storage of BDs. The accelerated high temperature oxidation at 180 °C for 72 h was also investigated to know the polymerization of fresh and oxidized unsaturated FAMEs.

2. Materials and Methods

Figure 2 shows the experimental procedure for the accelerated oxidation and polymerization of BD and linoleic acid methyl esters and product analysis methods. The change in total acid number (TAN), density, kinematic viscosity, and C18 FAME content during the accelerated oxidation were measured to evaluate the BD quality. Linoleic acid (C18:2) methyl ester was also used as a model FAME, because it can be polymerized at high temperatures. After polymerization at 180 °C (72 h), the polymerized linoleic acid methyl ester and the oxidized BDs were purified by flash chromatography to the polymerized FAME products and were evaluated using ^{1}H-nuclear magnetic resonance (NMR, Bruker, Billerica, MA, USA) spectroscopy and normal phase high performance liquid chromatography-atmospheric pressure chemical ionization mass spectrometry (HPLC-APCI MS, Thermo Fisher Scientific, Bannockburn, IL, USA).
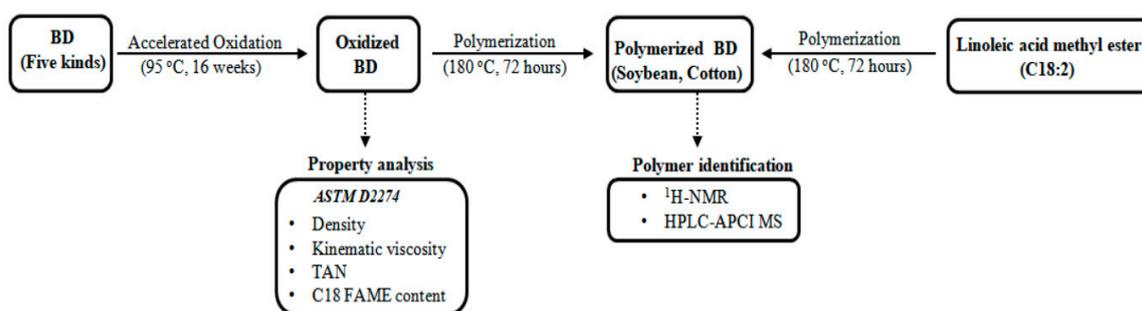

Figure 2. Experimental procedure for the accelerated oxidation and polymerization of biodiesel (BD) and linoleic acid methyl esters and product analysis methods.

2.1. Materials

Five kinds of commercial grade BD having no antioxidant, namely soybean oil, waste cooking oil, rapeseed oil, cottonseed oil, and palm oil, extracted from different types of biomass were purchased from Dansuck Co., Ltd. In Korea to give the guidelines on the production, use, and storage of commercialized BDs with their oxidation characteristics. High-purity linoleic acid methyl ester (C18:2 ME) was purchased from Sigma-Aldrich Co.

2.2. Fuel Properties of Biodiesels

Table 1 shows the properties of the BDs that were analyzed in this study before the accelerated oxidation. The physical and chemical properties of the fresh BDs, except oxidation stability, satisfy Korean and European standards for fuels that can be used for compression-ignition diesel engines [33]. The lower oxidation stability of the BDs can be explained by the absence of antioxidants [34,35]. Among the five BDs analyzed in this study, the BD that was extracted from palm revealed the longest oxidation stability time (4.48 h), followed by that from soybean (3.16 h), rapeseed (3.05 h), waste cooking oil (1.24 h), and cottonseed (1.03 h). The FAME compositions of five BDs are enumerated in Table 2. All BDs had FAMEs consisting of C18 as the main component. However, the unsaturated FAME contents differed depending on the biomass species. Rapeseed BD revealed the highest unsaturated FAME content (89.39%), followed by soybean BD (83.23%), waste cooking BD (79.02%), cottonseed BD (70.03%), and palm BD (49.16%). Owing to the high content of palmitic acid (16:0) methyl ester, palm BD had the lowest unsaturated FAME content.

Table 1. Physicochemical characteristics of BD samples.

Item	Korean Limit	EN 14214 Limit	Soybean	Waste Cooking	Rapeseed	Cottonseed	Palm
FAME content (wt. %)	96.5 min.	96.5 min.	98.20	97.59	97.35	98.56	97.68
Kinematic viscosity (40 °C, mm²/S)	1.9~5.0	3.5~5.0	4.03	4.16	4.43	4.04	4.53
Sulfur content (mg/kg)	10 max.	10 max.	0.7	1.5	2.0	1.1	1.1
Flash point (°C)	120 min.	120 min.	177	177	183	173	171
Carbon residue (wt. %)	0.1 max.	0.3 max.	0.02	0.03	0.02	0.02	0.03
Total contamination (mg/kg) [a]	24 max.	24 max.	5.1	13.0	7.6	10.0	8.9
Density (15 °C, kg/m³)	860~900	860~900	886	884	885	882	876
Water content (mg/kg)	500 max.	500 max.	133	105	183	80	272
Oxidation stability (110 °C, h) [b]	6 min.	6 min.	3.16	1.24	3.05	1.03	4.48
Total acid number (mg KOH/g)	0.50 max.	0.50 max.	0.24	0.32	0.36	0.15	0.30
Iodine number	-	120 max.	133	113	108	105	50
Total glycerol (wt. %)	0.24 max.	0.25 max.	0.13	0.13	0.11	0.10	0.15
CFPP (°C)	0	-	−3.0	−2.0	−11.0	7.0	>10.0
Cloud point (°C)	-	-	0.0	3.0	−3.0	9.0	16.0
Monoglyceride (wt. %)	0.80 max.	0.80 max.	0.45	0.40	0.10	0.24	0.45
Diglyceride (wt. %)	0.20 max.	0.20 max.	0.00	0.00	0.01	0.05	0.18
Triglyceride (wt. %)	0.20 max.	0.20 max.	0.00	0.00	0.00	0.00	0.04
Free glycerol (wt. %)	0.02 max.	0.02 max.	0.01	0.02	0.00	0.02	0.00
Phosphorus content (mg/kg)	10 max.	10 max.	0.08	0.35	0.07	0.06	0.19

[a] 10% of sample, [b] No addition of antioxidant.

Table 2. Fatty acid methyl ester (FAME) compositions of BD samples.

FAME (wt. %)	Soybean	Waste Cooking	Rapeseed	Cottonseed	Palm
C14:0	0.08	0.31	0.06	0.96	1.01
C14:1	0.01	0.05	-	-	-
C16:0	10.35	14.22	5.58	25.32	44.39
C16:1	0.12	0.93	0.25	0.59	0.22
C18:0	4.53	4.09	1.94	2.79	4.28
C18:1	21.39	30.37	55.11	15.91	38.48
C18:2	54.20	42.96	26.24	51.94	9.99
C18:3	7.22	4.31	6.76	1.05	0.29
C20:0	0.42	0.44	0.64	0.18	0.39
C20:1	0.21	0.34	1.01	0.10	0.16
C22:0	0.38	0.21	0.32	0.10	0.08
C24:0	0.16	0.09	0.17	0.03	0.09
C24:1	0.08	0.06	0.02	0.44	0.02
Not identified	0.85	1.62	1.9	0.59	0.6
Sat. FAME	15.92	19.36	8.71	29.38	50.24
Unsat. FAME	83.23	79.02	89.39	70.03	49.16

2.3. Accelerated Oxidation

The accelerated oxidation of BDs was performed according to the ASTM D 2274 method using the heat and aeration that were reported in previous studies [36,37]. For this, 1 L of BD in a brown glass tube was aerated at 95 °C in a thermal oven under 100 mL/min of zero-grade air for 16 weeks. The temperature of the oil condenser was maintained at 20 °C. The sampling of aged BD was performed once a week, and the sampled BD was kept in a dark container (4 °C) in a nitrogen atmosphere until analysis.

2.4. Property Analysis of Oxidized BD

The quality of the aged BDs was evaluated by measuring their FAME content, density, kinetic viscosity, and TAN values. The composition of FAMEs in BD was analyzed by a gas chromatography/flame ionization detector (7890 A, Agilent Technology) using a fused silica capillary

column (30 m length × 0.25 mm inner diameter × 0.2 μm film thickness; SP-2380, Supelco) for the separation of FAMEs and methyl heptadecanoate-heptane as an internal standard. The density and kinematic viscosity of BD were evaluated according to KS M 2014 while using a digital density meter (DA300, Koto Electronics) and an automated kinematic viscometer (CAV-2100F, Cannon instrument), respectively. The TAN value of BD was measured according to KS M ISO 6245 using an 809 Titrando instrument (Brinkman Metrohm).

2.5. FAME Polymerization

Linoleic acid methyl ester (C18:2 ME; 3 g) and 10 g of oxidized soybean and cotton BDs during 16 weeks were heated in a sealed tube in air at 180 °C for 72 h. After polymerization, they were purified by flash chromatography to yield the oxidation product as a brown oil (R_f 0.35, SiO_2, 10% $MeOH$-CH_2Cl_2).

2.6. Property Analysis of Polymerized Samples

The NMR spectra of polymerized soybean BD were obtained on a Bruker Avance 500 (Billerica, MA, USA) spectrometer operating at 500 MHz with $CDCl_3$ as the solvent. High speed LC connected to a LTQ orbitrap XL mass spectrometer equipped with APCI ionization (Thermo Fisher Scientific, Bannockburn, IL, USA) was performed using a HPLC-APCI-MS according to the method that was developed by Holcapek and Jandera [38,39]. For this, 5 μL of linoleic acid (C18:2) methyl ester was separated with a Hypersil GOLD (100 mm × 2.1 mm, 1.9 μm) using a mobile phase consisting of methanol (solvent A) and acetonitrile (Solvent B), pumped at 0.5 mL/min. A mobile phase flow gradient was applied to provide effective separation (75% A + 25% B to 5 min; 90% A + 15% B to 35 min; and 100% A to 45 min) using isocratic elution.

3. Results and Discussion

3.1. Fuel Properties of Accelerated Oxidation

Figures 3 and 4 show the change in the TAN, density, and kinematic viscosity of BDs during the accelerated oxidation. Although the TAN values of BDs gradually increased by increasing the oxidation time, the TAN values were below the threshold specified in the Korean and European standards (0.5 mg KOH/g until three weeks). Moreover, the TAN values of the BDs increased from four weeks to 16 weeks. After accelerated oxidation for 16 weeks, the TAN value was the highest (5.0 mg KOH/g) for cottonseed BD and lowest (2.3 mg KOH/g) for soybean BD. The sudden increase in TAN values can be explained by the oxidation of the FAMEs in the BDs. During the oxidation of FAMEs, free radicals are formed by the abstraction of hydrogen from the methylene groups in the allylic positions of the unsaturated FAMEs. By further reaction with atmospheric oxygen, these free radicals can be converted to hydroperoxides, causing the TAN value of the BDs to increase. Therefore, the rapid increase in TAN value after four weeks indicates that the rate of hydroperoxide formation is accelerated after four weeks during the accelerated oxidation test. The density values of BDs also increased gradually until four weeks; thereafter, they increased rapidly up to 16 weeks. However, except for the density values of cottonseed BD obtained after oxidation for 14 weeks, the BD density values remained below the thresholds that were specified in the Korean and European standards (900 kg/m^3 at 15 °C) after 16 weeks of accelerated oxidation. The kinematic viscosity values of BDs also showed a change trend that was similar to that of the TAN and density during the accelerated oxidation test, exhibiting the rapid increase after four weeks. This indicates that the increase in density and kinematic viscosity are closely related to the change in TAN values during BD oxidation. The presence of unsaturated FAMEs causes the additional polymerization of BD, producing compounds with higher molecular weights and increasing the density and kinematic viscosity values of BDs during long-term accelerated oxidation. Interestingly, the rates of increase of TAN, density, and kinematic viscosity of cottonseed BD were much higher than those of the other BDs tested in this study. This indicates that the structural properties of FAMEs in cottonseed BD underwent more profound changes those in other BDs.
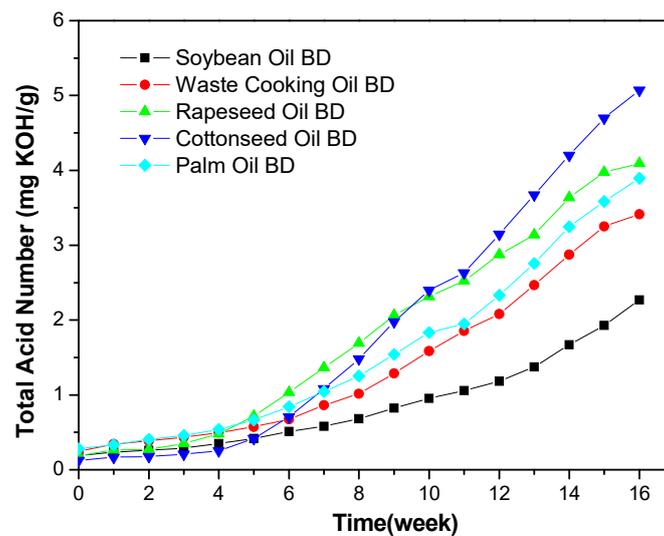
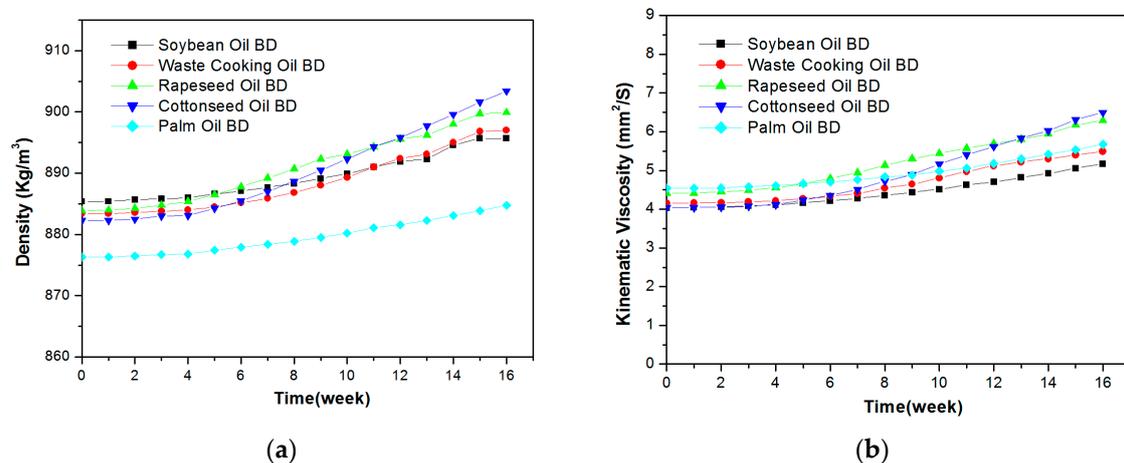**Figure 3.** Change in total acid number (TAN) values of BDs during accelerated oxidation.

(**a**)

(**b**)

Figure 4. Change in (**a**) density and (**b**) kinematic viscosity of BDs during accelerated oxidation.

Figure 5 shows the change in contents of typical unsaturated FAMEs, C18:2 ME, and C18:3 ME, which accounted for the largest fraction of fresh BDs during accelerated oxidation. The contents of both unsaturated FAMEs decreased as the oxidation time increased, indicating the oxidation and/or polymerization of unsaturated FAMEs by oxidative aging. The C18:2 ME content in the palm BD, rapeseed BD, cottonseed BD, waste cooking BD, and soybean BD decreased to 51.6%, 40.7%, 27.7%, 19.9%, and 8.4%, respectively, after 16 weeks of accelerated oxidation. The content of C18:3 ME also decreased to 5.2% for soybean BD and to values lower than 2% for other BDs. Among the five BDs, the cottonseed BD, which exhibited the largest increase in TAN, density, and kinematic viscosity (Figure 5), showed the largest decrease in both unsaturated FAMEs. This confirms that a rapid decrease in unsaturated FAMEs increases the TAN, density, and kinematic viscosity of BDs by oxidation and polymerization. Frankel et al. [24] and Cosgrove et al. [40] also indicated that an auto-oxidation chain reaction is initiated from di-and tri-unsaturated fatty acids due to their high reactivity.
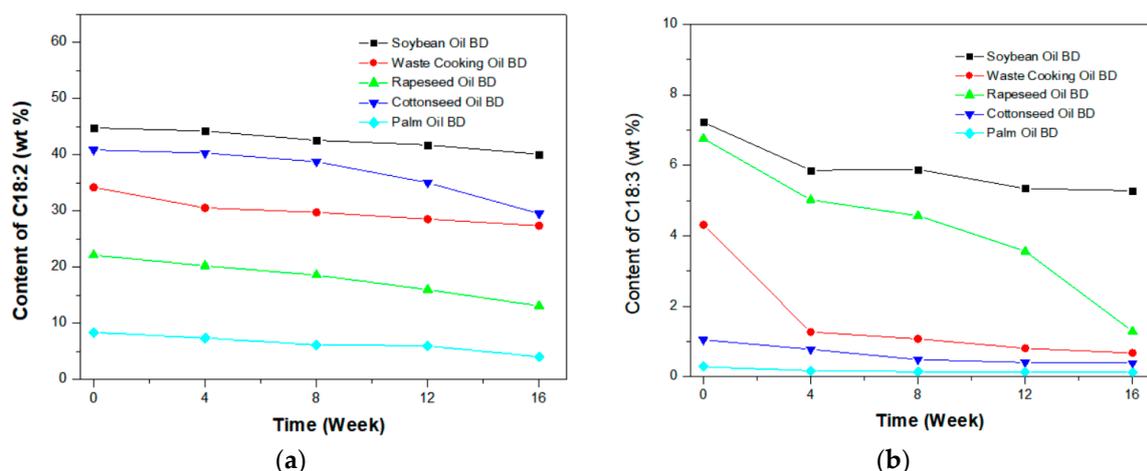
Figure 5. Change in C18 FAMEs contents in BDs during accelerated oxidation. (**a**) C18:2 ME; (**b**) C18:3 ME.

3.2. Polymerization of FAMEs

The FAMEs that are polymerized due to oxidation can be decomposed and they can be re-polymerized by additional polymerization reactions with other FAMEs and oxidized FAMEs. Owing to the negative effect of polymerized FAMEs in BD on the vehicle, the polymerization of BD is being regulated on its use. Although FAMEs can be polymerized by the thermal aging that accompanies the rapid decrease in unsaturated FAMEs, the thermal polymerization of BDs is difficult to monitor because they are not stored at high temperatures, which cause changes to the structure of FAMEs. However, polymerization of BDs in actual vehicles can occur by the repeated heating of the engine before combustion, which results in instability in the BDs [39].

To identify the chemical properties of polymerized FAMEs, the accelerated oxidation of soybean and cotton BDs were additionally performed at 180 °C for 72 h. For reference, the accelerated oxidation of linoleic acid (C18:2) methyl ester was also performed under the same condition. After the accelerated oxidation, the polymerized FAMEs were purified using flash chromatography and identified using ^{1}H-NMR and HPLC-APCI MS because it is difficult to study the polymerized chemicals using GC technologies. Figure 6 shows the ^{1}H-NMR spectra of purified soybean BD before and after the accelerated oxidation at 180 °C for 72 h. When compared to the non-oxidized BD, the oxidized BD revealed broader spectra and decreased intensities for the olefinic protons (-CH=CH-) of the double bonds at 5.45–5.49 ppm, suggesting the polymerization of FAMEs and the decrease in double bonds in these polymerized FAMEs [41]. Chuck et al. [13] also explained that the oxidation BDs had the decreased intensities of unsaturated fatty acids by increasing the oxidation temperature and time.
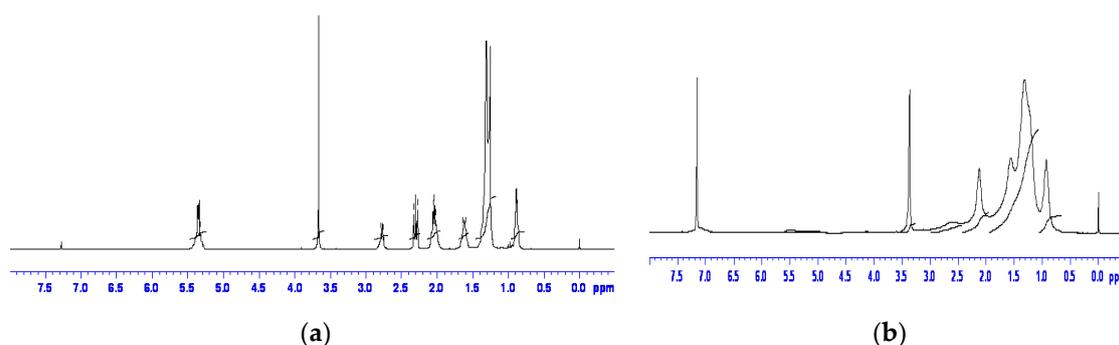

Figure 6. Change in the ^{1}H-NMR spectrum of soybean BD by accelerated oxidation at 180 °C for 72 h. (**a**) Fresh BD; (**b**) Oxidized BD.

HPLC-APCI MS analysis of the oxidized linoleic acid (C18:2) methyl ester at 180 °C for 72 h in a sealed tube in air was performed to study the polymerization of FAMEs in BDs, because linoleic acid (C18:2) methyl ester accounts for high fractions in soybean (54.20%) and cottonseed (51.94%) BDs, and it can be polymerized by the Diels-Alder reaction at high temperatures [32,42,43]. Figure 7 shows the mass spectra for the fresh and oxidized linoleic acid (C18:2) methyl ester. The fresh linoleic acid (C18:2) methyl ester, shown in Figure 7a, revealed typical ions, m/z 265.2526 and 297.2788. However, the oxidized one, as shown in Figure 7b, had large molecular ions, such as m/z 557.49, 587.50, 589.51, and 603.49, indicating its polymerization due to the accelerated oxidation. The possible structural information for the polymerized linoleic acid (C18:2) methyl ester that was suggested by the isotopic cluster for these ions (Figure 7c) is shown in Table 3. Figure 8 shows the possible reaction pathways for the formation of dimers and epoxy-dimers of linoleic acid (C18:2) methyl ester. For the thermal oxidation process, one of the conjugated diene groups in the chain can react with the olefinic group from the nearby fatty acid chain and form a substituted cyclo-ring, as part of the Diels-Alder reaction. The formation of these dimers and oxidized dimers of linoleic acid (C18:2) methyl ester can be explained by thermal polymerization during the Diels-Alder reaction [30,44]. When linoleic acid (C18:2) methyl ester was oxidized, the epoxy dimer of linoleic acid (C18:2) methyl ester could be formed by the Diels-Alder reaction between the oxidized and fresh linoleic acid (C18:2) methyl esters. These results indicate that the high temperature oxidation of BDs increase the contents of dimers and epoxy dimers of unsaturated FAMEs in BDs via their oxidation and polymerization.
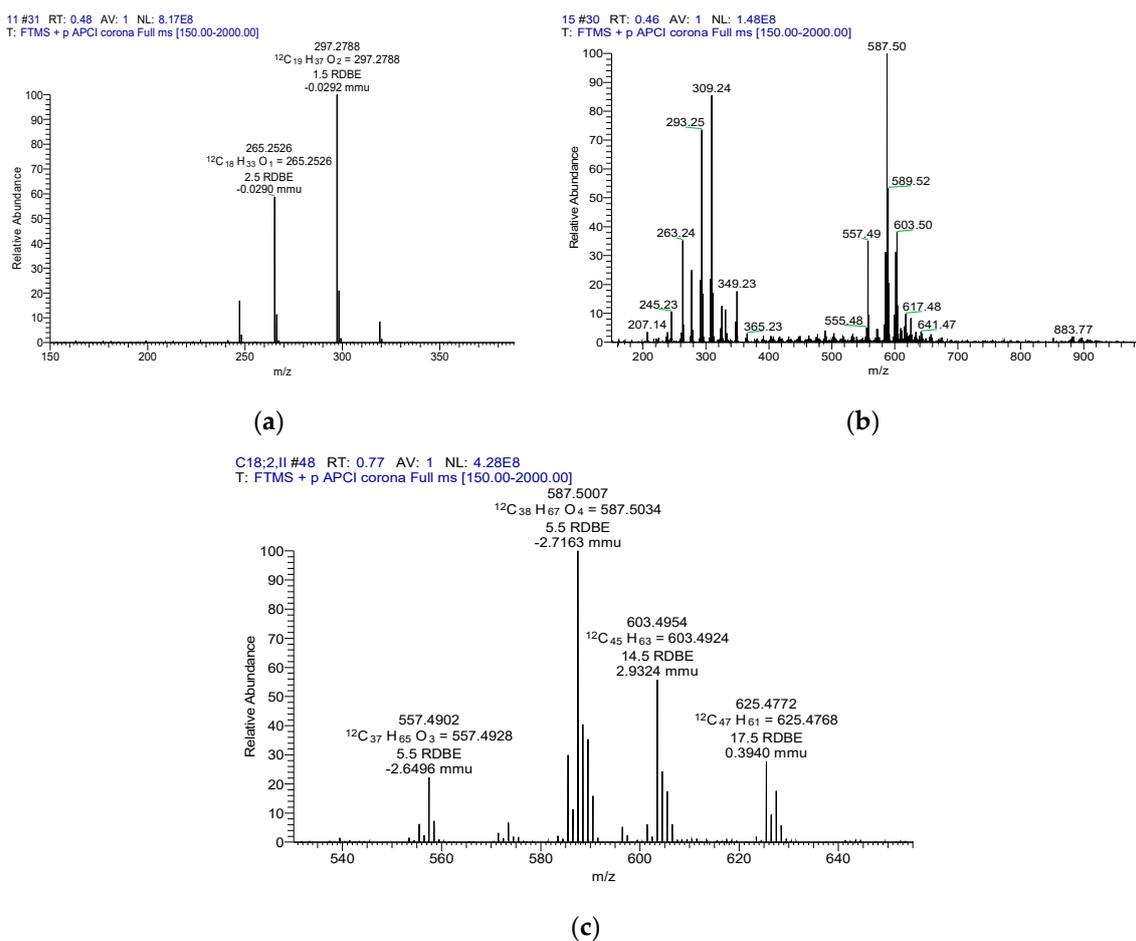

(a)

(b)

(c)

Figure 7. High performance liquid chromatography-atmospheric pressure chemical ionization mass spectrometry (HPLC-APCI MS) spectra for the fresh and polymerized linoleic acid (C18:2) methyl ester. (**a**) Fresh linoleic acid (C18:2) methyl ester; (**b**) Polymerized linoleic acid (C18:2) methyl ester; and, (**c**) Expanded spectrum for polymerized linoleic acid (C18:2) methyl ester.

Table 3. Identification by HPLC-APCI MS detection of FAME polymer from C18:2 ME.

Ion Fragment(m/z)	Theo. Mass	Elemental Composition	Proposed Structure
557.4902	557.4928	C37H65O3	-
587.5007	587.5034	C38H67O4	Dimer
589.5159	589.5190	C38H69O4	Dimer
603.4954	603.4957	C38H67O6	Epoxy-dimer
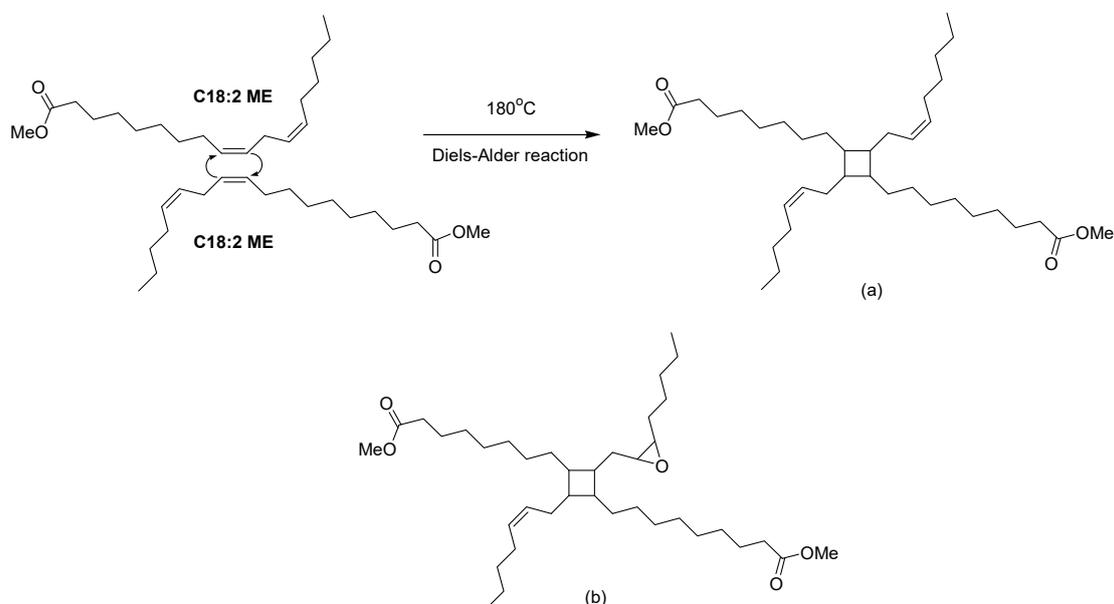
Figure 8. Diels-Alder reaction from C18:2 ME: (**a**) dimer of linoleic acid (C18:2) methyl ester; (**b**) epoxy-dimer of linoleic acid (C18:2) methyl ester.

4. Conclusions

The oxidation of BDs that were obtained from the decomposition of biomass can damage the fuel injection and engine parts during its use as a fuel. The excess heating of BDs can also cause polymerization of the biodiesel. In this study, the stability and polymerization of BDs by the accelerated oxidation were investigated. High unsaturated FAME contents in BDs led to a reduction in oxidation stability as compared to that of BDs with high saturated FAME contents. During the 16 week accelerated oxidation test at 95 °C, the TAN, density and kinematic viscosity of BDs decreased gradually until three weeks, and the decreased rapidly until 16 weeks. The unsaturated FAME contents in BDs showed similar change trends, decreasing slowly until three weeks and then rapidly until 16 weeks, indicating the occurrence of structural changes to the unsaturated FAMEs as a result of the oxidation. The accelerated high temperature oxidation at 180 °C for 72 h results in the polymerization of fresh and oxidized unsaturated FAMEs via the Diels-Alder reaction. The polymerized products that were obtained by the oxidation of unsaturated FAMEs at high temperature were identified as the dimers and epoxy dimers of FAMEs through the Diels-Alder reaction between the FAME and oxidized FAME molecules. The formation of these dimers and oxidized dimers of linoleic acid (C18:2) methyl ester can be explained by thermal polymerization. This study will provide the important basic data on the oxidation and polymerization of BDs, which can be used to know their effects on diesel vehicles and give the guideline on their production, use, and storage.

Conflicts of Interest: The authors declare no conflict of interest.

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