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ORIGINAL PAPER

Investigation of the Parameters Affecting the Cetane Number of Biodiesel

Kapila Wadumesthrige · Jeremiah C. Smith · John R. Wilson · Steven O. Salley · K. Y. Simon Ng

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Abstract The cetane number is the most significant property for measuring the ignition quality of fuels for compression ignition diesel engines. In this study, the derived cetane number (DCN) of several types of biodiesel, biodiesel components and ultra-low sulfur diesel (ULSD) was determined using an Ignition Quality Tester (IQT^{TM}). The chemical structure of FAME leads to a higher cetane number of biodiesel compared to ULSD. The contribution to DCN from minor components present in biodiesel is not significant. Oxidation of biodiesel samples results in higher DCN values while depending on the conditions of oxidation. A greater than 25% increase was observed when oxidation was carried out in a way to retain volatile oxidative products such as carboxylic acids and aldehydes. Accelerated oxidation of cotton seed oil (CSO) biodiesel at 110 °C and 10 L/min air flow rate after 210 min resulted in a loss of 14% of the FAME content, of which 10% can be attributed to the oxidation of methyl linoleate (C18:2), whereas oxidation of soy bean oil (SBO) biodiesel resulted in a loss of 21% total FAME after 210 min. A significant amount of methyl linolenate (C18:3) remained un-reacted after 210 min of oxidation. Ambient oxidation of distilled biodiesel samples resulted in a very high cetane number. Oxidative products such as aldehydes, hydroperoxides and oligomers of FAME are probably responsible for this higher DCN. This study enhances the understanding of the effect of composition on the cetane number of biodiesel as well as the effect of oxidative aging on both biodiesel composition and the resultant DCN.

Keywords Biodiesel · Derived cetane number · Ignition quality tester · Minor components · Antioxidants · Biodiesel oxidation · Oxidative products

K. Wadumesthrige · J. C. Smith · S. O. Salley · K. Y. S. Ng (✉)
Department of Chemical Engineering and Materials Science, Wayne State University, 5050 Anthony Wayne Drive, Detroit, MI 48202, USA
e-mail: sng@wayne.edu

J. R. Wilson
National Biofuels Energy Laboratory, NextEnergy, Detroit, MI 48202, USA

Introduction

Diesel engines have been widely used for industrial machinery, generators, trucks, automobiles, and shipping equipment because of their excellent durability and thermal efficiency [1]. At the same time, diesel engines significantly contribute to various types of air pollutant emissions such as oxides of nitrogen (NOx), particulate matter (PM), and other harmful compounds [1]. With the increasing concern for environmental protection and more stringent government regulation on exhaust emissions, reduction in engine emissions becomes a major consideration in engine development.

Similarly, the development of alternative and renewable fuels has become a very intense research area in the last decade. Among alternative diesel fuels, use of biodiesel derived from the transesterification of vegetable oils, animal fats and waste frying oils has increased significantly in many countries around the world including the United States. Biodiesel is technically competitive with conventional, petroleum-derived diesel fuel and requires virtually no changes in the fuel distribution infrastructure. Other advantages of biodiesel compared to petrodiesel include reduction of most exhaust emissions, biodegradability, higher flash point, inherent lubricity [2] and the fact that it

is of domestic origin. Some technical problems facing biodiesel include the reduction of NOx exhaust emissions [3], the improvement of cold-flow properties and oxidative stability, among others.

Exhaust emissions are determined by the combustion behavior of the components of the fuel under the conditions in the combustion chamber. The cetane number (CN) is a non-linear dimensionless parameter representative of the ignition delay (ID) time of a diesel fuel upon injection into the combustion chamber. The CN has an inverse relationship to the ID. Higher CN has been correlated with reduced NOx emissions [4], although this may not always hold for all types of engine technologies. Diesel fuels with a poor cetane number and hence poor ignition quality are associated with diesel knock, misfiring, engine deposits, piston tarnishing, hard starting in cold weather and increased exhaust emissions [5].

The CN has been included as a fuel quality specification in biodiesel standards, with a minimum of 47 prescribed for neat biodiesel or B100 in the United States using American Society for Testing and Materials (ASTM) D 6751-07a, and a minimum of 51 in some European countries (e.g., European standard EN 14214:2003). However, engine manufacturers specify their own cetane number requirements depending on the engine design and operating condition. For example, the Powertech 5030H diesel engine manufactured by John Deere Corp. requires a cetane number >45; and for temperatures below −20 °C or elevations above 1,500 m, a cetane number >50 is preferred [6]. There is no apparent benefit to using a higher cetane fuel than is specified by the engine's manufacturer.

It has been reported that biodiesel derived from various feedstocks has a CN range of 48–67, mainly depending on the fatty acid composition of the base oil but also on several parameters such as oil processing technology and climate conditions where vegetable oil is collected [7]. The chemical structure of the FAMEs contributes significantly to the cetane number. The degree of saturation, chain length and branching of the fatty compounds will influence the CN to varying degrees. A study by Knothe reported that the CN would generally increase as larger branched esters are produced from different alcohols of increasing chain length [8].

The number of double bonds in a given FAME indicates the degree of unsaturation within that compound. As unsaturation is decreased (fewer double bonds), the CN will increase [9]. Likewise, the location(s) of the double bond within FAMEs will also influence the CN. Szybist altered the fatty acid composition of soy-derived fuels by increasing the methyl oleate (C18:1) from 23 to 76% while decreasing the methyl linoleate (C18:2) from 52.1 to 6.7% to achieve a very modest increase of the DCN from 48.2 to 50.4 [10].

High temperatures as well as oxygen rich atmospheres are known contributors to increase the natural CN of biodiesel [11]. Moreover, FAMEs can be oxidized under ambient conditions, leading to the formation of various oxidative products over time [12] and may contribute to a greater cetane number. Other components such as impurities and secondary oxidative products have also been reported to have an effect on the cetane number of biodiesel [13].

Several previous studies discuss the effect of individual FAMEs on cetane number. Knothe et al. reported the DCN of some of the individual fatty esters present in biodiesel using an Ignition Quality Tester (IQT^{TM}) instrument [8]. The influence of simulated unsaponifiable matter as a whole (a mixture of mostly sterols and tocopherol) had been discussed by Van Gerpen and coworkers previously. They concluded that there was no effect of unsaponifiable matter on cetane number [14]. The effect of oxidation on biodiesel cetane number also studied in this work. However, the effects of other individual minor components in biodiesel such as free fatty acids, unreacted or partially reacted triglycerides have not been reported. There are few reports on the variation of cetane number of biodiesel with aging and the composition change during aging. Van Gerpen et al. discussed the influence of biodiesel oxidation on performance and emissions of diesel engines [15, 16]. Knothe et al. investigated the FAME composition of biodiesel change during oxidation and correlated this with contact area with air [17]. However no correlation was given with FAME composition, oxidation time and cetane number in this study. The objective of this study, therefore, is to identify the factors such as minor and major components and oxidative products, affecting the ignition quality or cetane number of various types of biodiesel under different treatment conditions and to correlate the composition of FAME with oxidation time and cetane number.

Experimental

Materials

Biodiesel produced from Soybean Oil (SBO), Cotton Seed Oil (CSO), Poultry fat (PF) and Yellow Grease (YG) were obtained from Biodiesel Industries, (Denton, Texas) and were stored at 4 °C in sealed, dark glass bottles in order to minimize natural air oxidation. Another soybean oil based biodiesel (SBO II) was obtained from G. F. Wacker, Inc (Manchester, Michigan). This biodiesel was used for accelerated oxidation studies.

Certification #2 ultra low sulfur diesel (ULSD) was obtained from Haltermann Products (Channelview, Texas). A sample of synthetic aviation fuel (S-8) produced by Syntroleum Corporation, (Tulsa, Oklahoma) was provided by National Automotive Center, US Army, Warren, Michigan.

Distillation of Biodiesel

Five hundred milliliter of each type of biodiesel were distilled under reduced pressure (3×10^{-3} torr) at about 130–150 °C. Analysis of the distillates using a PerkinElmer (Shelton, CT) Clarus 500 gas chromatograph equipped with a flame ionization detector (GC-FID) indicated that they contained only FAMEs. Once distilled, they were stored at 4 °C.

Sample Preparation

All samples were filtered prior to IQT™ testing using a threaded syringe fitted with a disposable 5 μm hydrophobic fluoropore (PTFE) filter (Millex®-LS, Millipore, Bedford, MA).

FAME Composition

The fatty acid composition of each type of biodiesel both before and after distillation was determined using a Perkin-Elmer (Shelton, CT) Clarus 500 GC–MS with a split automatic injector and a Rtx-WAX (Restek, Bellefonte, PA) column (length: 60 m; ID: 0.25 mm, coating: 0.25 μm). Fifteen mg of biodiesel was dissolved in 5 mL of heptane. Twenty microliter of ethyl arachidate (C20:0) was added as an internal standard. This mixture was injected into the column using an auto sampler. The column was held at 120 °C for 1 min and then ramped to 240 °C at 20 °C/min, and it was then held at 240 °C for 13 min. The transfer line between GC and MS was kept at 240 °C. Helium (99.9999%, Cryogenic Gases, Detroit, MI) was used as the carrier gas with a flow rate of 1.5 mL/min. Total Ion Count (TIC) was used for the quantification of each component.

FTIR and UV-Visible Spectroscopy

FTIR spectra were obtained using a Perkin-Elmer (Shelton, CT) Spectra 400 FTIR spectrometer. UV-Visible spectra were obtained using a Thermo-Fisher Scientific (Hanover Park, IL) Evolution spectrophotometer using hexane as a solvent in sample preparation or the samples were left in neat biodiesel form especially for visible spectra data collection.

Total Acid Number (TAN)

The total acid number of oxidized biodiesel was measured according to ASTM D 664 using a Brinkmann/Metrohm 809 Titrando (Westbury, NY).

Accelerated Oxidation of Distilled Biodiesel Samples

Accelerated oxidation was carried out by two different methods. In the first method, a Rancimat (Metrohm 873 Biodiesel Rancimat, Brinkmann Instruments, Westbury, NY) was used. Several Rancimat test tubes, each with 30 mL of distilled biodiesel were oxidized for predetermined time periods at 110 °C and an air flow rate of 10 L/hr. Samples were withdrawn at regular time intervals and immediately placed in an ice bath to quench further oxidation.

In the second oxidation method, 500 mL of distilled biodiesel were oxidized under reflux conditions in order to minimize or prevent the loss of volatile oxidative products. The temperature was kept between 110 and 113 °C with an air flow rate of 10 L/hr. Similar to the Rancimat method above; 30 mL samples were withdrawn at regular time intervals and immediately placed in an ice bath to quench further oxidation. The quenched samples were kept at 4 °C until DCN measurements and all analyses were made. Oxidized biodiesel was further analyzed using FTIR and UV-Vis spectroscopic techniques in order to have a better understanding of the oxidative products.

Ignition Delay and DCN Measurements

The DCN was determined with the IQT™ (Advanced Engineering Technology, Inc, Ottawa, Canada). A complete sequence comprised 15 preliminary cycles to provide equilibrium operating conditions and 32 further test cycles. The ignition delays for the last 32 cycles were averaged to produce the ID result. Each test consumes about 10 mL of sample volume. The IQT™ system software has its own list of test methods definitions (including DCN correlation equations) that is used when analyzing its test results. For fuels with ignition delays between 3.3 and 6.4 ms the following equation is used as given by ASTM 6890 (7b):

$$\mathrm{DCN_{IQT}} = 4.46 + (186.6/\mathrm{ID})$$

Outside this range the following correlation equation is used.

$$\mathrm{DCN_{IQT}} = 83.99 \times (\mathrm{ID} - 1.512)^{-0.658} + 3.547$$

The standard deviation of the 32 combustion events was also calculated. The IQT™ was calibrated with hexadecane and heptane as primary reference fuels. An analysis of variance with students '*t*' test was used to determine significant differences.

Results and Discussion

Effect of FAME Composition and Biodiesel Age on DCN

Derived cetane numbers for SBO, CSO, PF and YG based biodiesels stored under ambient conditions, stored at 4 °C or distilled are shown in Fig. 1a. As a comparison the DCN

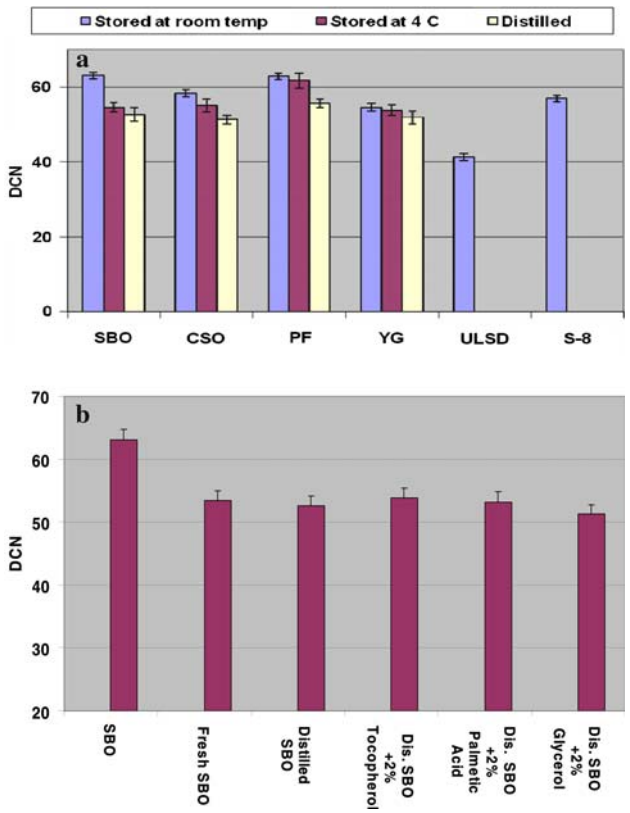

Fig. 1 **a** Derived cetane numbers of various biodiesels stored at ambient conditions, stored at 4 °C, and distilled biodiesel. Storage time, after receipt of SBO biodiesel is 9 and 4 months for all other biodiesel samples. DCN of ULSD and S8 also included for comparison. The DCN differences of each condition are significant in SBO, CSO and PF, but not significant in YG biodiesel. **b** Derived cetane number of distilled SBO biodiesel with added minor components. There were no significant contributions from these minor components on the cetane number of biodiesel

of certification number 2 Ultra Low Sulfur Diesel (ULSD) and Synthetic Aviation (Jet) fuel (S-8) are also included. The ULSD and S-8 did not contain any cetane "improvers" and were stored under ambient conditions. The storage time for SBO based biodiesel was 9 months and that of other biodiesels was about 4 months when DCN measurements were performed. As seen in Fig. 1a, the DCN of all biodiesel types are significantly higher than that of ULSD. The lower DCN value of ULSD can be attributed to the presence of aromatic hydrocarbons and branched chain hydrocarbons, (the composition of ULSD according to the certificate of analysis provided by manufacturer is aromatics 17–25%, saturated hydrocarbons 70–80% and olefins 3–6% by weight). The relatively higher DCN of synthetic aviation fuel can be attributed to primarily straight long chain hydrocarbons and lack of aromatic components in S-8 (100% C7-18 alkanes according to the certificate of analysis provided by the manufacturer). The DCN of SBO and PF based biodiesel stored at room temperature were significantly higher than the other types of biodiesel. Although PF biodiesel had a relatively shorter storage time compared to SBO, its DCN was almost the same. The DCN of CSO and YG were significantly lower than those of SBO and PF.

The DCN for undistilled CSO, SBO and YG stored at low temperature were not significantly different from one another while that of PF was significantly higher. The higher DCN of this PF biodiesel can be attributed to the presence of higher amounts of oxidative products due to the lack of natural antioxidants in PF biodiesel.

The DCN of distilled biodiesel is also included in Fig. 1a. Based on GC–MS and GC-FID analysis, no detectable levels of antioxidants, sterols, triglycerides or glycerol were found in distilled biodiesel samples, and thus these samples were used as the control to study the effect of major and minor components, and oxidative products on DCN. It should be noted that the GC-FID conditions used here cannot detect the oxidative products in biodiesel. Once distilled, samples of each type of biodiesel were kept at 4 °C to minimize natural oxidation. The differences in DCN between different types of distilled biodiesel are due only to the FAME compositions and the structural difference (degree of unsaturation and chain length) of the FAMEs. The t tests performed for the data set of distilled biodiesel revealed that the DCN of CSO biodiesel is significantly lower than the DCN of SBO, PF, and YG. Also the DCN of YG is significantly lower than that of PF, but there are no significant DCN difference between SBO and PF biodiesel. On the other hand, the DCN difference between undistilled biodiesel stored at room temperature and the distilled biodiesel for all biodiesel types except YG are statistically significant. The percent DCN changes between these two sets comparing distilled and undistilled, room temperature stored samples are 19.8, 13.6, 13.0 and 5.2 for SBO, CSO, PF and YG, respectively. SBO, with the highest storage time, has the highest percent DCN change. In contrast, the DCN difference between distilled and undistilled biodiesel stored at 4 °C are significant for CSO and PF but not significant for SBO and YG.

The FAME composition of distilled BD is shown in Table 1a, where the abbreviation CX: *Y* is used and where *X* is the number of carbon atoms in the fatty acid chain and *Y* is the number of double bonds present in the fatty acid chain. Vegetable oil based biodiesels mainly consist of 14–25% methyl palmitate (methylhexadecanoate C16:0), 18–33% methyl oleate (methyl-9*Z*-octadecenoate C18:1), and 49–55% methyl linoleate (methyl-9*Z*, 12*Z*-octadecadienoate C18:2). SBO and YG biodiesel have a higher percentage of unsaturated FAME. There was no methyl linolenate (methyl-9*Z*, 12*Z*, 15*Z*-octadecatrienoate C18:3) observed in the CSO based biodiesel.

The degree of unsaturation and the chain length distribution of each biodiesel together with corresponding DCN

Table 1 (a) FAME composition of distilled biodiesel samples measured by GC–MS. FAME profiles of soybean oil based biodiesel obtained from different producers show slight differences. (b) Percentage of unsaturated and saturated FAME and profile of FAME composition based on chain length together with the DCN values for different types of biodiesel

	SBO	SBO II	CSO	PF	YG
(a)					
C14:0	0.0%	0.0%	0.8%	1.0%	0.1%
C16:0	14.1%	11.0%	24.7%	21.8%	16.0%
C16:1	0.7%	0.0%	0.4%	3.7%	0.01%
C18:0	5.2%	4.2%	2.7%	7.6%	3.9%
C18:1	25.3%	22.6%	18.5%	36.6%	32.7%
C18:2	48.7%	55.0%	53.0%	27.0%	45.0%
C18:3	6.1%	7.2%	0.00%	1.8%	2.1%
C20:0	0.0%	0.0%	0.00%	0.00%	0.3%
C22:1	0.0%	0.0%	0.00%	0.40%	0.0%
(b)					
ΣUHC	80.8%	84.8%	71.8%	69.5%	79.8%
ΣSHC	19.2%	15.2%	28.2%	30.5%	20.2%
C14	0.0%	0.0%	0.8%	1.0%	0.14%
C16	14.8%	11.0%	25.1%	25.5%	16.0%
C18	85.2%	84.8%	74.1%	73.0%	83.6%
DCN	52.6	43.3	51.3	55.6	51.8

are presented in Table 1b. It was reported that the cetane number of FAME increases with decreasing amount of unsaturated hydrocarbon (UHC) and with increasing chain length (number of carbon atoms) in the fatty acid chain [8]. Considering only the % of UHC, one would expect the DCN varies as PF $\sim$ CSO $>$ SBO $\sim$ YG. On the other hand, DCN order of SBO $\sim$ YG $>$ CSO $\sim$ PF should be expected considering the amount of C18 FAMEs. However, the actual measured values of DCNs, as shown in Table 1b, do not coincide with these trends. This is due to the fact that the effects of unsaturation and chain length on cetane number act contrary to each other. These results indicate that although the FAME profile is the major determining factor for CN, other factors such as the presence of oxidative products can affect CN significantly.

Effect of Minor Components on Biodiesel DCN

The presence of minor components in biodiesel can affect some of the fuel properties. For example, trace amounts of transition metals (e.g., Cu) [18], can reduce the oxidation stability significantly; and polar minor components (e.g., free fatty acids and monoglycerides) increase the lubricity of biodiesel [19]. In general, biodiesel contains more than 98% FAME. The remaining 2% are antioxidants, free fatty acids, unreacted triglycerides or partially reacted mono or diglycerides, unrecovered methanol, and by-products of transesterification such as glycerol. In order to investigate the effect of minor components on DCN, 2% tocopherol, palmitic acid, and glycerol were added to distilled biodiesel samples, respectively. The DCN of these are given in Fig. 1b. The DCN of 9 month old and fresh SBO-based biodiesel is also included in the figure for comparison. Based on these results, the DCN of distilled biodiesel with added minor components are not significantly different from that of fresh biodiesel.

Effect of Oxidation Products on Biodiesel Cetane Number

As described earlier, the cetane number of biodiesel varies with storage conditions and storage time. Also, storage of biodiesel under ambient conditions resulted in higher cetane number as a function of storage time (Fig. 1a). This higher cetane number of aged biodiesel samples may be due to the oxidative products. Fatty acid oxidation is a complex process [20], and occurs via formation of hydroperoxides. These hydroperoxides are often called primary oxidative products. The formation of hydroperoxides involves hydrogen abstraction from a carbon atom. The most easily abstracted hydrogens are generally the ones that are involved in hydrogen bonded to carbons allylic to olefinic unsaturation [21]. Carbons that are simultaneously allylic to two olefinic groups (bis-allylic) will be the most susceptible to hydrogen abstraction. The methylene groups that interrupt the multiple olefinic unsaturation in FAME in biodiesel are examples of carbons that are bis-allylic, hence very susceptible to the formation of hydroperoxides [20–22].

Once fatty oil hydroperoxides are formed, they will further decompose to form aldehydes such as hexenals, heptenals, and propanal [23]. These aldehydes then oxidize into carboxylic acids. Increased acidity is always a result of oxidation of fatty oils and biodiesel [24, 25], due to the formation of shorter chain fatty acids. Moreover, as hydroperoxides decompose, oxidative linking of fatty acid chains can occur so as to form species with higher molecular weights, i.e., oxidative polymerization. Such polymeric species rarely become larger than trimers or tetramers [24].

In order to investigate the effect of secondary oxidative products on DCN, an accelerated oxidative aging test using the Rancimat apparatus (110 °C, 10 L/min Air flow) was performed on distilled CSO biodiesel. The conductivity of volatile oxidative products dissolved in the Rancimat conductivity cell and DCN of each corresponding aged biodiesel at specified oxidation times is plotted in Fig. 2. Both DCN and conductivity increase linearly with increasing oxidation time. DCN increased from 48.1 initially to 55.6 and conductivity from 0.05 to 12 μs, after a

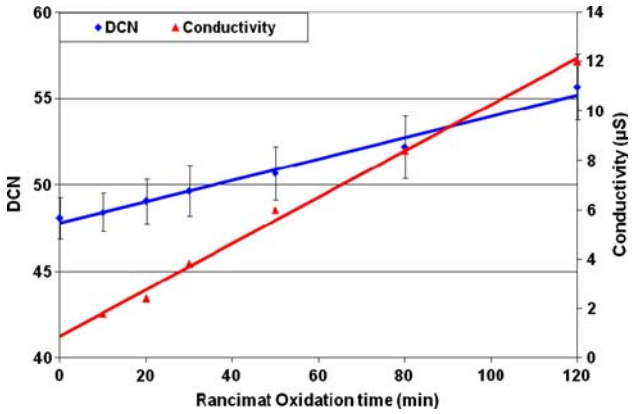

Fig. 2 Derived cetane number and rancimat conductivity of distilled CSO biodiesel samples as a function of reaction time. The conductivity increase with oxidation time is due to the accumulation of volatile oxidative products in conductivity cell

total oxidation time of 120 min. Figure 3 shows the DCN of accelerated oxidation of CSO and SBO biodiesel samples under reflux conditions. Oxidizing biodiesel by refluxing prevents the escape of volatile oxidative products. Comparing Figs. 2 and 3, oxidation under reflux conditions resulted in even higher cetane numbers than Rancimat oxidation at each time interval. For example, after 120 min of reflux oxidation the cetane number is about 25% more than under Rancimat oxidation. This 25% increase can be attributed to the volatile oxidative products such as aldehydes and carboxylic acids retained in the reflux-oxidized samples. Interestingly, the DCN of CSO biodiesel stored at ambient conditions for 4 months has a DCN of 58.3 ± 1.2.

The FAME composition of distilled CSO biodiesel oxidized under reflux condition was analyzed using GC–MS. A GC–MS total ion current chromatogram of CSO biodiesel oxidized for 210 min is given in Fig. 4a. Under the GC–MS experimental conditions described earlier, all

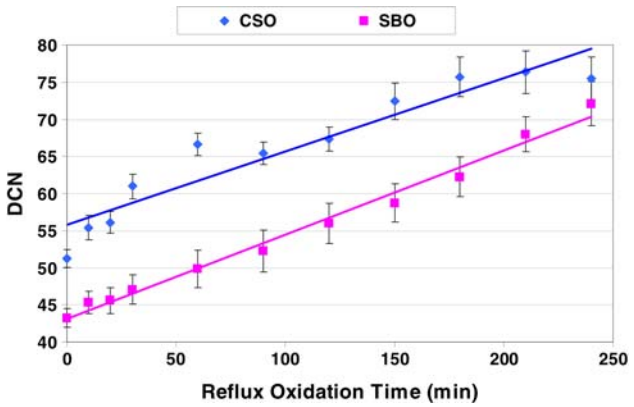

Fig. 3 Derived cetane number of distilled CSO and distilled SBO biodiesel samples as a function of oxidation time under reflux conditions. Relatively higher DCNs were observed for oxidized SBO biodiesel even though SBO contains about 6% of C18:3

the peaks appear in the chromatogram are due to FAME. The amounts of C18:2 and C16:0 together with total FAME amounts are shown in Fig. 4b. The unsaturation percent of distilled CSO biodiesel is about 68% as measured by GC–MS. Among these unsaturated compounds C18:2 with a bis-allylic carbon atom ($-CH_2$) are the easiest to oxidize. The C18:2 compositions changed from 53.0 to 47.8% of total FAME composition within 210 min of oxidation. Moreover, the total FAME amount decreased from 100 to 86.0%. Based on this result about 14% of distilled CSO biodiesel after 210 min of accelerated oxidation was converted to oxidative products. This shows that the absolute amount of C18:2 decreases with oxidation time but the amount of C16:0 does not change. The total acid number (TAN) of distilled SBO biodiesel increased as a function of oxidation time. The observed TAN values are 5.5, 8.6, 13.9, 9.7 and 4.2 mg KOH/g for 20, 30, 60, 90 and 120 min of accelerated oxidation, respectively. These high TAN numbers and the FTIR data presented in Fig. 5a and b suggest that this fraction of compounds contain carboxylic acids. The area of IR absorption peak at 3,450 cm^{-1}, attributed to the O–H stretching of carboxylic acids, increases with increasing oxidation time (Fig. 5a). Moreover, the IR absorption peak at 2,888 cm^{-1}, which is due to the C–H stretching frequency of sp^2 C, (inset of Fig. 5a)

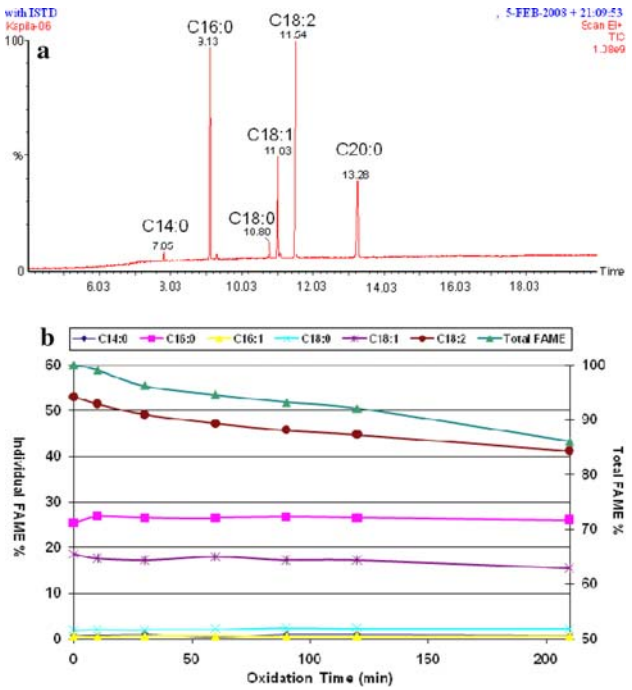

Fig. 4 **a** GC–MS chromatogram of a oxidized distilled CSO biodiesel. C20:0 is used as the internal standard. **b** Total and individual FAME compositions of CSO biodiesel as a function of oxidation time. The amounts of unsaturated FAME such as C18:2 decreases with time while the composition of saturated FAME does not change with time

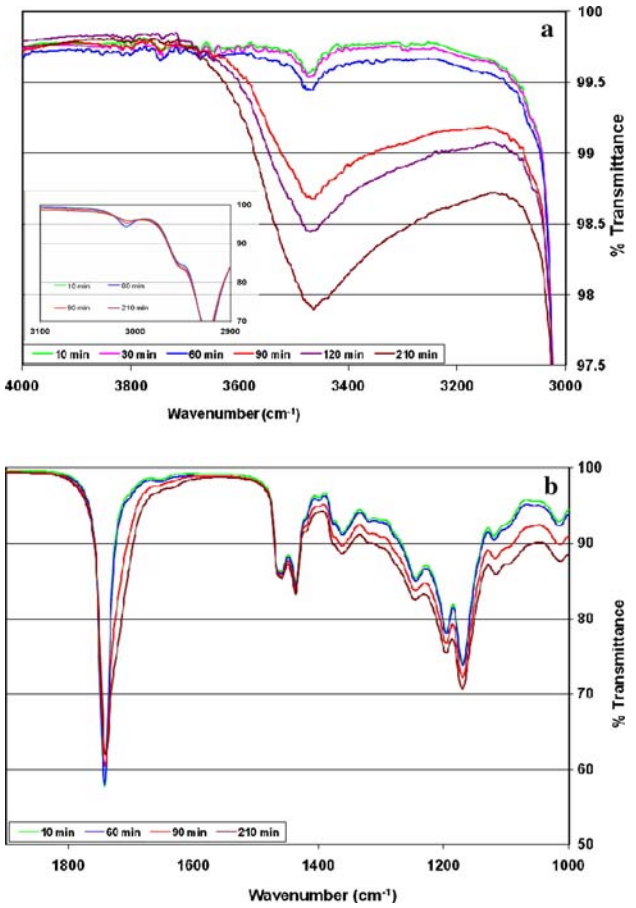

Fig. 5 FTIR spectra of distilled CSO biodiesel oxidized under reflux conditions. **a** Expanded region of wave number range from 3,000 to 3,700 cm^{-1} of oxidized samples at 10, 30, 90, 120 and 210 min. Inset shows the variation of peak at 2,888 cm^{-1} with oxidation time. **b** Broadening and shifting of carbonyl absorption region indicates the formation of aldehydes with oxidation time

and 724 cm^{-1} (out-of-plane bending) decreases with oxidation time, indicating the decrease in unsaturation number. This implies that the formation of secondary products such as aldehydes, carboxylic acids and any polymeric products formed via breaking of carbon-carbon double bonds. A major increase in intensity and broadening can be seen in the carbonyl region of 1,740–1,680 cm^{-1} and C–O stretching region around 1,100 cm^{-1} region (Fig. 5b). The strong sharp peak at 1,742 cm^{-1} of unoxidized biodiesel is due to the carbonyl group ester band of FAME. Broadening and shifting toward lower energy can be attributed to the formation of aldehydes and carboxylic acids. In particular low energy shoulders are observed at 1,724 and 1,695 cm^{-1} on the strong ester band at 1,742 cm^{-1}. The peak at 1,724 cm^{-1} can be assigned to the carbonyl band in aldehydes and the 1,695 cm^{-1} peak can be assigned to hydrogen bonded carbonyl groups. The area of the two peaks at 1,459 and 1,435 cm^{-1}, (Fig. 5b) which are due to the asymmetric and symmetric bending vibrations of C–H bonds in methyl group (in CH_3COO), remained unchanged during oxidation. This is attributed to the fact that the ester group in biodiesel is intact during accelerated oxidation. It should be noted that the CSO biodiesel oxidized under Rancimat conditions does not show the presence of significant carboxylic acids (based on FTIR data, not shown). This confirms the earlier assertion that carboxylic compounds were carried away by the air bubbled into the conductivity cell of the Rancimat.

As shown in Table 1a, CSO biodiesel does not contain any C18:3 fatty acid methyl esters, but SBO biodiesel contains 6–7% of C18:3 components. In order to investigate the effects of C18:3 methyl esters on biodiesel oxidation and subsequently on DCN, distilled SBO II biodiesel was oxidized under reflux conditions, with the resulting DCN values as a function of oxidation time shown in Fig. 3. For both the CSO and SBO II biodiesel, the cetane number increased with increasing oxidation time.

The FAME composition of individual components and total FAME of distilled SBO II biodiesel as a function of oxidation time is given in Fig. 6. About a 21% decrease in total FAME composition was observed. This amount consists of 3.9% of C18:1, 15% of C18:2 and 1.7% of C18:3. The amounts of saturated FAME such as C16:0 and C18:0 did not change during the accelerated oxidation. This tells us that the hydroperoxides or any other free radicals formed do not participate in any carbon chain breaking in saturated FAME. It is interesting to note here that the C18:3 which has two bis-allylic carbon atoms did not react completely during the oxidation process.

Visible spectra of oxidized biodiesel were obtained and compared to the original biodiesel. In contrast to oxidized CSO biodiesel, oxidized SBO II biodiesel shows an absorption maximum at about 450 nm. Figure 7a compares

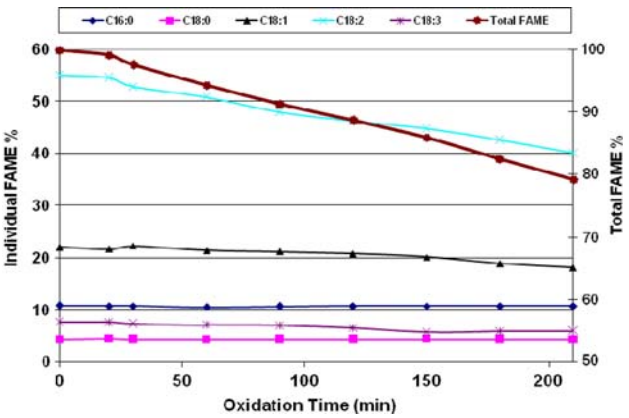

Fig. 6 Total and individual FAME compositions of SBO biodiesel as a function of oxidation time. About 21% of total FAME lost during 210 min of oxidation. Significant amount of C18:3 remain unreacted even though C18:3 has two bis-allylic carbon atoms

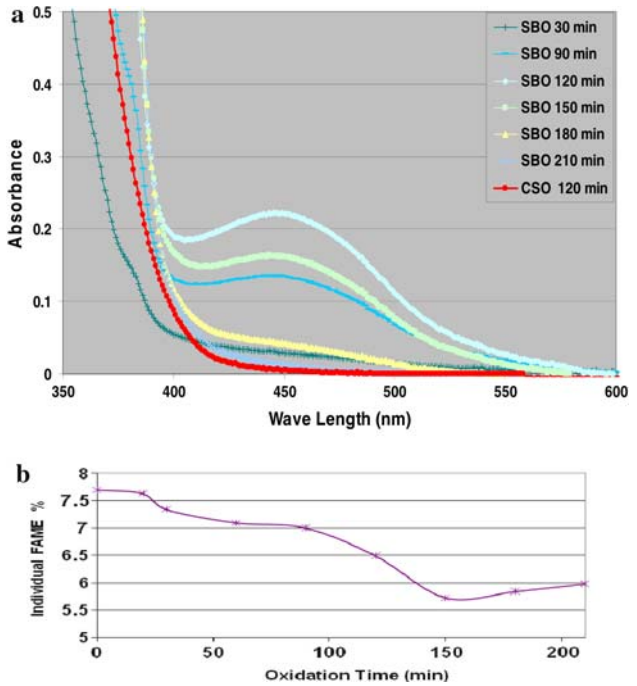

Fig. 7 **a** Visible spectra of distilled SBO biodiesel as a function of oxidation time. Oscillation of the absorption maxima at 450 nm was observed. Absorption spectra of CSO biodiesel sample at $t = 120$ min included for comparison. **b** Variation of o C18:3 amount on distilled SBO biodiesel as a function of oxidation time

the visible spectra of oxidized SBO II based biodiesel at different time intervals. The intensity of maximum absorption changes with time as 120 min > 150 min > 90 min > 180 min > 30 min > 210 min. Maximum absorption was observed at 120 min of oxidation time and 210 min of oxidation decreases the absorption even lower than that at 30 min oxidized sample. The oscillation of the 450 nm peak as a function of time roughly related to the amounts of C18:3 reacted with oxidation time as indicated in Fig. 7b. The absorption maxima at 450 nm can be attributed to the rearrangement of methylene-interrupted 3 olefinic double bonds in C18:3(9Z, 12Z, 15Z) into conjugated C18:3(9Z, 11Z, 13Z), and further oxidation to conjugated dienal. It should be noted that a conjugated arrangement of multiple olefinic unsaturation is the most thermodynamically stable arrangement, due to the partial stabilization imparted by delocalization of the pi electrons. However, spontaneous rearrangement of a methylene-interrupted configuration to a conjugated configuration does not occur at ordinary temperatures due to the high activation energy associated with the breaking and reforming of pi bonds. However oxidized CSO biodiesel did not show any absorption at this wavelength, because there is no observable C18:3. Visible absorption spectrum of CSO biodiesel oxidized for 120 min is included for comparison in Fig. 7a.

Table 2 FAME composition and DCNs of distilled CSO biodiesel after ambient oxidation. Highest overall DCN change observed under these conditions

	Fresh	2 months	4 months
C14:0	0.8%	0.7%	0.05%
C16:0	24.7%	25.2%	23.2%
C16:1	0.4%	0.4%	0.2%
C18:0	2.7%	2.4%	2.0%
C18:1	18.5%	18.6%	14.1%
C18:2	53.0%	48.5%	5.8%
C18:3	0.00%	0.0%	0.0%
C20:0	0.00%	0.0%	0.0%
%FAME	100.0%	95.8%	45.2%
DCN	51.3 ± 1.2	66.1 ± 1.6	130 ± 3.2

As a control experiment, a sample of distilled CSO biodiesel was kept at ambient conditions and DCN and FAME compositions were measured at 2 and 4 months (Table 2). The DCN increased significantly from 48 to more than the upper limit of the cetane scale, 100, within 4 months of aging. It should be noted that the ASTM D6890 works best for the cetane range 34–61. Deviations are greater for shorter ignitions delays. However, the observed DCN for this sample is 130. This distilled biodiesel sample is very susceptible to oxidation even under ambient conditions because of the lack of any natural antioxidants. The higher DCN values compared to accelerated oxidation at 110 °C may be due to the retention of both primary and secondary oxidative products at room temperature. FTIR spectra and high TAN indicate the presence of carboxylic acids, aldehydes and HNMR (proton nuclear magnetic resonance) data (not shown) indicate formation of some polymeric materials. Relatively larger broadening and shifting of the sharp peak at 1,724 cm^{-1} toward lower energy indicates the formation of aldehydes and carboxylic acids. This relatively higher DCN of ambient biodiesel compare to Rancimat oxidized biodiesel may be due to presence of these volatile oxidation products.

The FAME composition of distilled CSO biodiesel kept under ambient conditions changed significantly as shown in Table 2. There is only 45% FAME remaining after 4 months under ambient oxidation. The C 18:2 composition decreased from 53 to 12.6% within 4 months. The rest of the cetane number increase is due to the formation of oxidative products from FAME. As shown in Fig. 8, a linear relation can be obtained for the % increase DCN with reacted FAME percentage. This oxidation process does not require high temperatures. The very high DCN of these ambient oxidized samples compared to 110 °C accelerated oxidation samples are due to the collective effect of primary oxidative products (hydroperoxides) and

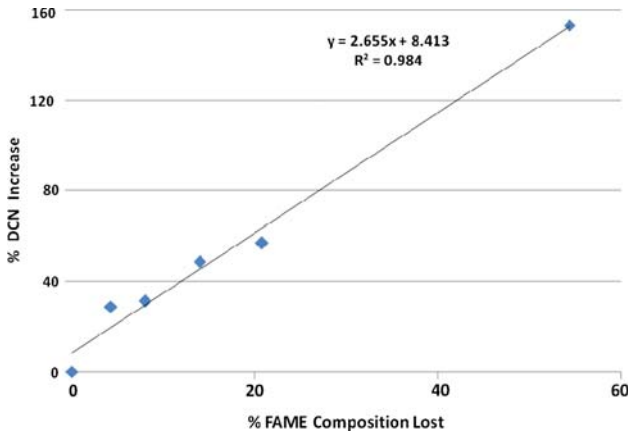

Fig. 8 Variation of % DCN increase with % FAME lost during oxidation

secondary oxidation products such as aldehydes, carboxylic acids and polymers of FAME. However the presence of hydroperoxides were not confirmed with the techniques utilized in this study. Among these components aldehydes may contribute to a higher cetane number, based on the results of NREL report on cetane number of several compounds [25]. The decrease of unsaturation number during oxidation also suggests the formation of polymeric materials. However, no deposit formation was observed under any of above oxidation conditions which suggest that the polymerization does not occur beyond dimers or trimers. The results obtained here can be useful in designing cetane improvers for modern diesel fuel. As an example, moderate biodiesel additions or cetane improvers derived from biodiesel can be used to improve the cetane number of ULSD, most of which hardly meets current US ASTM standards and does not make it under current EU or Engine Manufacturers Association standards. Since biodiesel helps with lubricity and thus, if the usual low-temperature problems can be avoided, it can make a very useful multi-purpose fuel additive.

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References

1. Heywood JB (1988) Internal combustion engine fundamentals. McGraw-Hill, New York
2. Haas MJ, Scott KM, Alleman TL, McCormcik RL (2001) Engine performance of biodiesel fuel prepared from soybean soapstock: a high quality renewable fuel produced from a waste feedstock. Energy Fuels 15:1207–1212
3. McCormick RL, Graboski MS, Alleman TL, Herring AM (2001) Impact of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy-duty engine. Environ Sci Technol 35:1742–1747
4. Ladommatos N, Parsi M (1996) The effect of fuel cetane improver on diesel pollutant emissions. Fuel 75:8–14
5. Tao Y, Operation of a cummins N14 diesel on biodiesel: performance, emission and durability. National Biodiesel Board, Ortech Report No. 95-E11-B004524
6. Operators Manual, Powertech^{TM} 2.4 L & 3.0 L 4024 and 5030 OEM Diesel Engines, OMRG34851, Issue 13 Oct 04, John Deere Power System, Moline
7. Ramadas AS, Jayaraj S, Muraleedharan C, Padmakumari K (2006) Artificial neural networks used for the prediction of the cetane number of biodiesel. Renew Energy 31:2524–2533
8. Knothe G, Matheaus A, Ryan III T (2003) Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester. Fuel 82:971–975
9. Knothe G, Bagby M, Ryan III T (1998) Precombustion of fatty acids and esters of biodiesel. A Possible Explanation for differing cetane numbers. J Am Oil Chem Soc 75(8):1007–1013
10. Szybist J, Boehman A (2005) Evaluation of formation strategies to eliminate the biodiesel NOx effect. Fuel Process Technol 86:1109–1126
11. Conceicao MM, Fernandes VJ, Araujo AS, Farias MF, Santos IMG, Souza AG (2007) Thermal and oxidative degradation of castor oil biodiesel. Energy Fuels 21:1522–1527
12. Quantification and improvement of the long term storage stability of biodiesel and biodiesel blends (1997) NBB Project No. 96207–1, Final Report, December 1
13. Matthaus, Bertrand W (1996) Determination of the oxidative stability of vegetable oils by rancimat and conductivity and chemiluminescence measurements. J Am Oil Chem Soc 73(8):1039–1042
14. Van Gerpan JH, Hammond Y, Monyem A (1997) Determining the influence of contaminants on biodiesel properties. SAE Technical Paper Series, 971685
15. Monyem A, Van Gerpen JH (2001) The effect of biodiesel oxidation on engine performance and emissions. Biomass Bioenergy 20:317–325
16. Monyem A, Van Gerpen JH, Canakci M (2001) The effect of timing and oxidation on emissions from biodiesel-fueled engines. Trans ASAE 44:35–42
17. Knothe G (2006) Analysis of oxidized biodiesel by H-NMR and effect of contact area with air. Eur J Lipid Sci Technol 108:493–500
18. Meyer- Pittroff OFR (2004) The effect of fatty acid composition on biodiesel oxidative stability. Eur J Lipid Sci Technol 106:837–843
19. Knothe G, Steidley KR (2005) Lubricity of components of biodiesel and petrodiesel. The origin of biodiesel lubricity. Energy Fuels 19:1192–1200
20. Frankel EN (2005) Lipid oxidation, 2nd edn edn. The Oily Press Ltd, Bridgewater
21. Miyashita K, Takagi T (1986) Study of the oxidative rate and prooxidant activity of free fatty acids. J Am Oil Chem Soc 63(10):1380–1384
22. Dunn RO (2005) Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel). Fuel Process Technol 86:1071–1085
23. Dunn RO (2002) Effect of oxidation under accelerated conditions on fuel properties of methyl soyate. J Am Oil Chem Soc 79:915–920
24. Neff WE, El-Agaimy MA, Mounts TL (1994) Oxidative stability of blends and interesterified blends of soybean oil and palm olein. J Am Oil Chem Soc 71(10):1111–1116
25. Murphy MJ, Taylor JD, McCormick RL (2004) Compendium of experimental cetane number data, NREL Report, NREL/SR-540-36805