Epoxidation of waste used-oil biodiesel: Effect of reaction factors and its impact on the oxidative stability

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Abstract−Epoxidation of waste used-oil biodiesel (WUO-B) was performed to test the feasibility of properties improvement. The effects of the reaction temperature (30-50 °C) and time (2-12 h), molar ratio of H_2O_2 : HCOOH (1 : 7 to 1 : 1) and the stirring rate (100-300 rpm) on the level of unsaturated carbon bond conversion and the epoxy compound selectivity were identified using a 2^k (two levels) factorial design. Besides epoxy biodiesel as the main product, only one by-product, hydroxyl-biodiesel, was generated. The conversion of unsaturated carbon bonds was positively affected by the molar ratio of H_2O_2 : HCOOH and the stirring rate, while the reaction temperature and time had no significant affect (in the investigated ranges). In contrast, with respect to the epoxy compound selectivity, the stirring rate had a positive effect, while both the reaction temperature and time each had a negative effect. The oxidative stability (OS) of the epoxy waste used-oil biodiesel (EWUO-B) revealed a linear relationship to the unsaturated carbon bond conversion level, but no significant relationship to the epoxy compound selectivity. EWUO-B prepared from a 1 : 1 molar ratio of H_2O_2 : HCOOH at 50 °C with stirring at 300 rpm for 12 h exhibited a higher OS (around 37.85 h) than that of the WUO-B. Except for the cold flow properties and methyl ester content, all other key properties of the EWUO-B were within the specifications of the EN14214 standard set by the Department of Energy Business.

Key words: Waste Used-oil Biodiesel, Epoxidation, Factorial Design, Oxidative Stability

INTRODUCTION

Biodiesel, which is widely recognized as an alternative renewable diesel fuel, is derived from the transesterification of vegetable oils, or other feedstocks containing triglycerides, with a monohydric alcohol in the presence of an acid or base catalyst. It has clear advantages relative to petroleum-derived diesel fuel that include an inherent lubricity, high cetane number, relatively low emission of particulates, NO_x, SO_x, CO and hydrocarbons, a low toxicity, a higher safety due to its relatively high flash point, a lower lifecycle of CO_2 and a high degree of biodegradability [1,2]. In addition, it is compatible with the existing fuel distribution infrastructure, is potentially sustainably renewable and can be of domestic origin [3]. Nonetheless, the commercialization and utilization of biodiesel in automotive applications is currently limited to blends of less than 20% (v/v) with petroleum-derived diesel fuel, due to its relatively poor low-temperature properties and insufficient OS [4]. These negative properties of biodiesel are associated with various biodiesel components, including the residual alcohol and, especially, the fatty acid chain, which are derived from the fatty acid prole of the feedstock. Most commonly used biodiesel feedstocks are commodity vegetable oils, such as soybean, palm, rapeseed/canola and animal fats. To lower the cost of biodiesel production and remove the conflict between crop production for food or biodiesel, the use of waste cooking oil

is an alternative promising source for biodiesel production. However, these feedstocks consist mainly of the common C16 and C18 fatty acids (palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2) and linolenic acids C18:3)), and so the resultant biodiesel derived from them will face the problems of a low cold flow properties or a poor OS or both [5].

To improve the properties of biodiesel with respect to its fatty ester structure, two principal strategies can be carried out: the use of additives and the alteration of the fatty ester composition. The addition of additives to biodiesel is probably the simplest method. However, the problem of additive compatibility and the unintended effects on other fuel properties are of concern [3]. Therefore, the alteration of the fatty ester composition is often preferred and might be better.

The partial hydrogenation of unsaturated vegetable oils results in their simple reduction [6], as well as in migration and isomerization of the *cis* double bonds into the *trans* configuration [7]. Similar results have been observed for catalytic hydrogenation, where the total saturated fatty acid content was increased from 29.3% to 76.2% after 2 h. However, although the obtained biodiesel showed a higher oxidation stability and higher cetane number, it retained the relatively poor cold flow properties [8].

By using catalytic epoxidation reactions, high conversion and selectivity to oxirane was observed. Among the inorganic catalyst, the order of effectiveness of catalysts was found to be $H_2SO_4 > H_3PO_4 > HNO_3 > HCl$ [9]. The use of CH_3COOH as oxygen carrier was found to be more effective than HCOOH for either cottonseed oil [9] or

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sunflower oil [10] epoxidation. The presence of high inorganic acid at high temperature could help to reduce the reaction time needed to reach the maximum conversion [11]. By using the solid catalyst, the use of tungsten containing catalyst called "Tetrakis" led to a rather complete and selective transformation of *cis* methyl oleate into *cis* epoxide at low operating temperature [12]. The use of bis[3,5-bis(trifluoromethyl) diphenyl] diselenide in combination with fluorinated alcohols as solvents or co-solvents demonstrated a total cis-selectivity of fatty methyl esters and their mixtures as presented in biodiesel with excellent epoxide yields of around 87-93% [13]. In addition, the utilized catalyst had ability to reuse up to seven reaction cycles. By using the combined hydroxylation and epoxidation reactions, a decrease in the unsaturated fatty acid methyl ester (FAME) fraction of around 44 and 39%, respectively, was obtained [8]. The addition of hydroxyl groups to the unsaturated regions of the fatty acid chain can promote better properties of the biodiesel, including cold flow properties, lubricity and OS [8].

In addition, the epoxy biodiesel had a higher OS, higher cetane number and better cold flow properties compared with that for the original biodiesel. Moreover, the alkoxylation of biodiesel, derived from canola oil under mild conditions, altered the cloud point value of the alkoxylated biodiesel, with a slight increase upon alkoxylation being observed with the methyl ($-2\,^{\circ}$C to 4 $^{\circ}$C) and ethyl ($-3\,^{\circ}$C to 0 $^{\circ}$C) fatty ester based biodiesels, and a slight decrease ($-3\,^{\circ}$C to $-4\,^{\circ}$C) for butyl biodiesel [2,14].

The addition of alkoxy side-chains with methanol, butanol or *n*-propanol to butyl biodiesel cannot improve the cold flow properties, while the addition with alcohols larger than butanol can promote a decrease in the cloud points of around 5 $^{\circ}$C compared to that for the methyl biodiesel. Of the metal oxide catalysts, Mo_x/α-Al_2O_3 at 15% (w/w) was reported to exhibit the highest catalytic activity and a high selectivity in the epoxidation reaction, but did not attain the complete decomposition of *tert*-butyl hydroperoxide or oxidative cleavage of carbon-carbon double bonds [15]. The winterization technique [16] was used to remove unfavorable long-chain saturated compounds (arachidic or C20:0, behenic or C22:0, and lignoceric or C24:0 acid methyl esters) from peanut oil derived biodiesel. These authors [16] reported that winterization with methanol reduced the cold filter plugging point from 17 $^{\circ}$C to $-8\,^{\circ}$C for only a small (8.93%) biodiesel yield loss.

As mentioned previously, the raw material for biodiesel production is usually virgin vegetable oils, such as those from rapeseed, soybean and sunflower. However, the price of these materials is high, resulting in the high cost of biodiesel. In addition, the use of food oils for biodiesel production is of arguable ethics and economics [17]. Thus, waste used-oil (WUO) is an alternative raw material for biodiesel production because it does not compete with the food market, recycles waste oils or fats that otherwise have some environmental concern and so reduces the production costs and therefore increases the economic competitiveness [18]. However, due to the presence of non-favorable fatty acid profiles in waste cooking oils, the WUO derived biodiesel (WUO-B) obtained from this type of feedstock will face the problem of insufficient OS or poor cold flow properties. Thus, we attempted to modify the fatty ester composition of oil based WUO-B by epoxidation with *in situ* peroxy-formic acid generation to form the epoxy-WUO-B (EWUO-B). The effect of the epoxidation factors on the conversion level of unsatur-

ated carbon bonds (C_{unsat}) and the epoxy compound selectivity (S_{epox}) was identified using a 2^k factorial design. Finally, the impacts of both these response factors on the OS of the resultant EWUO-B were explored.

EXPERIMENTAL

1. Materials

WUO as spent oil from a fried food process was collected from a local restaurant. Phosphoric (H_3PO_4) and sulfuric (H_2SO_4) acids at 98% AR grade, plus AR grade sodium hydroxide (NaOH), potassium hydroxide (KOH) and anhydrous sodium sulphate (Na_2SO_4) were from Merck. AR grade sodium hydrogen carbonate ($NaHCO_3$), methanol (CH_3OH; 99.8%), formic acid (HCOOH; 98.0%) and 30% (v/v) aqueous hydrogen peroxide (H_2O_2) were from Fisher Scientific.

2. Experimental Procedures

2-1. Synthesis of WUO-B

The spent oil was initially filtered to separate the residual food at atmospheric pressure. Prior to use of the WUO as a feedstock for biodiesel production, it was pretreated in a de-gumming process to remove the contaminating phospholipids (phosphorus-containing lipids composed of diacylglycerol and a simple organic molecule). To this end, 500 g WUO was mixed with 0.35 ml H_3PO_4 and 5 ml de-ionized water in a three-necked round bottom glass flask connected with a condenser and immersed in a water bath at 80-100 $^{\circ}$C for 1 h with constant stirring at 200 rpm. The mixture was then left for a while without stirring until phase separation was observed, where with the de-gummed WUO (D-WUO) containing upper phase was harvested, leaving the lower solid phase containing the removed gum. The harvested D-WUO was then acid treated to convert the free fatty acid content to FAMEs. In this process, 500 g D-WUO was mixed with 100 g CH_3OH in a three-necked round bottom glass flask connected with a condenser and immersed in a water bath. The system was then agitated at a constant stirring rate of 200 rpm while the temperature was increased gradually from room temperature ($\sim$30 $^{\circ}$C) to 60 $^{\circ}$C, whereupon it was held at this temperature and 5 ml of H_2SO_4 was added and left for 4 hr. The de-gummed and de-fatty-acid treated WUO (DD-WUO) was then separated from the mixture, washed with excess de-ionized water and vacuum dried at 50 $^{\circ}$C to eliminate any excess acid and alcohol.

The transesterification reaction was carried out in a 1-L three-necked glass flask connected with a reflux condenser, using tap water to condense the methanol vapor, and a thermocouple probe. A 500 g aliquot of DD-WUO was agitated at a constant stirring rate of 200 rpm and slowly heated from ambient temperature to 60 $^{\circ}$C, whereupon 5 g of NaOH dissolved in 100 g of CH_3OH was added into the DD-WUO solution and the reaction was maintained at 60 $^{\circ}$C for 1 hr. The mixture was left until a phase separation was observed, that is the FAME or WUO-B in the upper phase and glycerol in the bottom phase. The upper WUO-B containing phase was harvested and rinsed several times with de-ionized water until the color of the rinsed water was clear. Finally, the obtained WUO-B was vacuum dried at 50 $^{\circ}$C for 24 hr.

2-2. Characterization of the EWUO-B Synthesis

A 2^k factorial design was carried out to explore the effects of the temperature (30-50 $^{\circ}$C), mole ratio of H_2O_2 : HCOOH (1 : 7-1 : 1), stirring rate (100-300 rpm) and reaction time (2-12 hr) on the level

Table 1. Physical properties of the WUO and DD-WUO raw materials and the obtained WUO-B and EWUO-B biodiesels

Quality	EN 14214	Raw material[a]		Biodiesel[a]	
		WUO	DD-WUO	WUO-B	EWUO-B[b]
Methyl ester (% wt)	>96.5			85.86±0.29	83.02±0.27
Density at 15 ºC (g/cm³)	0.86-0.9			0.893±0.002	0.897±0.008
Flash point (ºC)	>120	266±1.4	228.5±2.1	187±2.8	194±2.0
Viscosity at 40 ºC (cSt)	3.5-5.0	62.7±0.1	32.3±0.01	4.6±0.03	4.1±0.85
Cloud point (ºC)				12±1	15±1
Pour point (ºC)		24±1	17±1	7±1	8±1
OS (hr)	>10			0.69±0.014	38.52
Iodine value (g I$_2$/100 g)	<120	131.2±1.4	127.0±1.2		
Acid value (mg KOH/g)	<0.5	3.66±0.07	1.66±0.07	0.46±0.036	0.45±0.013
Saponification number (mg KOH/g)		199.5±4.6	192.9±2.7		
Higher heating value (MJ/kg)				39.12±0.17	37.70±0.04

[a]Data are shown as the mean±1 SD and are derived from three repeats
[b]Epoxidation was performed at 50 ºC with a H_2O_2 : HCOOH mole ratio of 1 : 1, a stirring rate of 300 rpm and a reaction time of 12 hr

of unsaturated carbon bond conversion and epoxy compound selectivity of EWUO-B. The epoxidation reaction was performed in a 1-L three-necked round bottom glass flask placed in a water bath, equipped with a 2 cm-diameter six bladed glass turbine impeller and a reflux condenser. A 300 g aliquot of WUO-B was placed in the reactor at the desired stirring rate and to this was added the required amount of HCOOH and slowly followed by 170 ml of H_2O_2 (30% (v/v) aqueous solution). H_2O_2 was added dropwise at room temperature (~30 ºC) and was completed within 15-20 min. The reaction was continued at the desired reaction time and temperature. When the reaction was over, the mixture was left for a moment (~30 min) until phase separation was complete. The upper phase (EWUO-B) was collected and then washed twice with 5% (w/w) NaHCO$_3$ and then with de-ionized water to eliminate any excess acid. Consequently, it was dried under vacuum at 40 ºC until a clear biodiesel was obtained. Finally, the residual water content in EWUO-B was eliminated by the addition of 30 g anhydrous Na$_2$SO$_4$, and subsequently filtered.

3. Analytical Procedures

The structure of the WUO-B and EWUO-B preparations was characterized by ^{1}H-NMR using a Mercury 300, FTNMR spectrometer (Varian), as previously described [19]. The FAME contents in the WUO-B and EWUO-B were measured by gas chromatography (GC-14 B SPL, Shimadzu) according to the European standard EN 14103 with a DB-Wax (polyethylene glycol) capillary column and a flame ionization detector detector. The density of each biodiesel was measured at 15 ºC using a pycnometer in tempering bath. The flash points of raw materials and biodiesels were analyzed according to ASTM D 93 by the Pensky Martens closed tester (Pensky Martens PMA4, Petrotest, Germany). The viscosity at 40 ºC was determined following ASTM D 445 using a glass capillary viscometer (Cannon-Fenske Routine viscometer CFRV, Petrotest, Germany). The cold flow properties, evaluated in terms of the cloud and pour points, were measured according to and ASTM D 2500 and D 97, respectively. The OS was derived from monitoring the oxidation level of WUO-B and EWUO-B, which was determined according to the EN 14112 procedure with a Rancimat instrument (Rancimat 743, Metrohm). The chemical properties of the raw materials and

resultant biodiesels, including the iodine value, acid value and saponification number, were analyzed chemically as follows. The iodine number was measured by volumetric titration using Wijs reagent, according to the European standard EN 14111. The acid and saponification values were analyzed by the volumetric titration with KOH according to the ASTM D 664 and ASTM D 94 standards, respectively. The heating values of WUO-B and EWUO-B were measured using an adiabatic bomb calorimeter (Parr 6200, Parr Instrument Company, USA).

RESULTS AND DISCUSSION

1. Properties of WUO and WUO-B

Table 1 shows the physical properties of the raw materials (WUO and DD-WUO) utilized in this work and the derived WUO-B and EWUO-B biodiesels. The original WUO had a high flash point, viscosity, iodine value, acid value, pour point and saponification number, and also solidified at 15 ºC. The acid value was related to the free fatty acid content in the WUO samples and could be disadvantageous for the alkali-catalyzed transesterification process. The high viscosity and iodine value indicated the presence of a high level of unsaturated fatty acid chains or gums in the WUO. However, after de-gumming and removal of the free fatty acids, all the measured properties of the obtained DD-WUO were improved. This is because the contaminated phospholipids were eliminated during the de-gumming process and the fatty acids were converted to ester in the de-acid process. The properties of biodiesel (WUO-B) derived from the DD-WUO including density, flash point, viscosity and acid value were in the acceptable range, as designed by EN 14214 and the pour point decreased significantly from the original value of the raw material. On the other hand, a low methyl ester content by 11% (w/w) compared with standard was obtained. Nevertheless, the methyl ester content of this WUO-B preparation was still some 8% (w/w) higher than that of the commercial biodiesel derived from WUO (77.98% wt [20]). The low OS of WUO-B was obtained at around 0.69 hr, which was significantly lower than the standard value of around 14.5-fold. This might due to the effect of the utilization of waste used-oil as raw material, because the waste used-oil con-
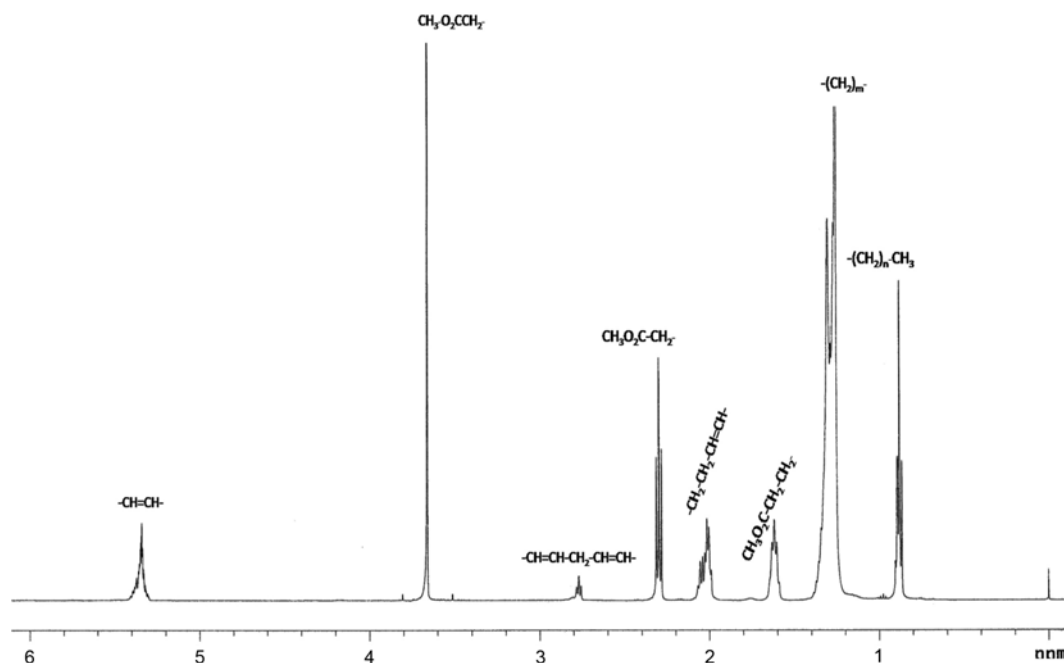
Fig. 1. Representative ^{1}H-NMR spectra of WUO-B derived from the transesterification of waste used-oil (WUO).
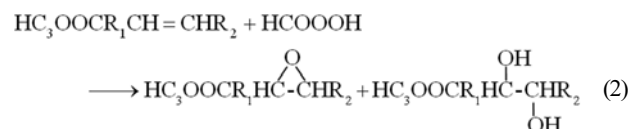
tains water, food particles and particularly to free fatty acid. Although, pretreatment was carried out to eliminate free fatty acid. This process can not eliminate free fatty acid completely, resulting in the contamination of fatty wastes in the obtained biodiesel. This fatty waste generally is more susceptible to oxidation because they vary in level of unsaturation, resulting in the formation of low OS properties.

2. Epoxidation Mechanism

Representative ^{1}H-NMR spectra obtained from the unmodified (WUO-B) are shown in Fig. 1. WUO-B shows the main signals of methyl esters, including the signals at 0.85-0.95 ppm associated with the terminal methyl group of fatty acids ($-(CH_2)_n$-CH_3), sharp peaks at 1.2-1.4 ppm assigned to the methylene protons on the saturated carbon atoms ($-(CH_2)_m$), signals at 1.6-1.7 ppm of by the β-methylene protons from the carbonyl carbon (CH_3O_2C-CH_2-CH_2-), peaks at 1.95-2.1 ppm related to the allylic methylene protons ($-CH_2$-CH_2-$CH=CH$-), peaks at 2.25-2.35 ppm attributed to the α-methylene protons from the carbonyl carbon (CH_3O_2-CH_2-), signals at 2.75-2.80 ppm assigned to the bis-allylic methylene protons ($-CH=CH$-CH_2-$CH=CH$-) and very sharp peaks at 3.5-3.8 that are from the presence of the terminal methyl group of the ester and peaks at 5.3-5.5 ppm assigned to the olefinic protons ($-CH=CH$).

With regards to the ^{1}H-NMR spectra of the EWUO-B (Figure not shown), all the representative biodiesel peaks seen in the WUO-B were still observed in the EWUO-B, plus in addition, signals at 1.4-1.6 ppm, 2.8-3.0 ppm and 3.0-3.2 ppm were observed. The signals at 1.4-1.6 ppm are ascribed to the methylene protons adjacent to the oxirane carbon ($-CH_2CHOCHCH_2$-) and those at 2.8-3.0 ppm indicate the presence of the methine protons of the oxirane carbon ($-CHOCH$-). This emphasizes that an oxygen atom in formic acid can join to an olefinically unsaturated bond of the biodiesel resulting in the formation of EWUO-B, as reported before [8]. In addition, the signals at 3.0-3.2 ppm represent the presence of the methine protons of the hydroxy carbon. Thus, it can be speculated that two products

were generated in our epoxidation reaction, which are the EWUO-B as the main product and hydroxyl-biodiesel as a by-product. Based on the epoxidation reactions listed by Goud et al. [21], then it is likely that here the *in-situ* epoxidation of WUO-B with peroxyformic acid (reaction (1)) was followed by the epoxy ring formation (reaction (2)).

$$HCOOH + H_2O_2 \xrightarrow{H^+} HCOOOH + H_2O \qquad (1)$$

$$HC_3OOCR_1CH = CHR_2 + HCOOOH$$

$$\longrightarrow HC_3OOCR_1\overset{O}{\overset{|}{HC}\text{-}CHR_2} + HC_3OOCR_1\overset{OH}{\underset{OH}{\overset{|}{HC}\text{-}CHR_2}} \qquad (2)$$

From the ^{1}H-NMR spectra, the level of the unsaturated carbon conversion (C_{unsat}) and the selectivity of the epoxide compound (S_{epox}) can be calculated according to Eqs. (3) and (4), as reported previously [19].

$$C_{unsat}(\%) = \frac{I_x + I_y}{I_x + I_y + I_z} \times 100 \qquad (3)$$

$$S_{epox}(\%) = \frac{I_x}{I_x + I_y} \times 100 \qquad (4)$$

where I_x, I_y and I_z are the intensity of the signals of the oxirane carbon protons at 2.8-3 ppm, the methine protons of hydroxy carbon at 3-3.2 ppm and the olefinic protons at 5.3-5.5 ppm, respectively.

3. Analysis of Variance (ANOVA) and Obtained Regression Model

The application of a 2^k factorial design analysis provides an empirical relation between the four independent variables related to the epoxidation conditions (A: reaction temperature, B: mole ratio of $H_2O_2 : HCOOH$, C: stirring rate and D: reaction time) and the two selected response factors of the unsaturated carbon bond level and the epoxy compound selectivity. The 2^4 factorial design was con-

Table 2. The two responses (% C_{unsat} and % S_{epox}) derived from the 2^4 factorial design trial for variations in the four indicated independent variables

Run no	A	B	C	D	C_{unsat} (%)	S_{epox} (%)	Variables	(−1)	(+1)	(0)
1	−1	−1	−1	−1	13.87	100.00	A: temperature (°C)	30	50	40
a	+1	−1	−1	−1	28.79	63.58	B: mole ratio of H_2O_2 : HCOOH	1 : 7	1 : 1	1 : 4
b	−1	+1	−1	−1	37.54	87.08	C: stirring rate (rpm)	100	300	200
ab	+1	+1	−1	−1	25.98	61.27	D: reaction time (hr)	2	12	7
c	−1	−1	+1	−1	58.97	79.91				
ac	+1	−1	+1	−1	28.52	77.09				
bc	−1	+1	+1	−1	50.13	78.38				
abc	+1	+1	+1	−1	79.29	70.57				
d	−1	−1	−1	+1	24.67	57.66				
ad	+1	−1	−1	+1	57.48	73.92				
bd	−1	+1	−1	+1	27.07	60.49				
abd	+1	+1	−1	+1	42.80	76.89				
cd	−1	−1	+1	+1	24.06	73.55				
acd	+1	−1	+1	+1	48.44	70.96				
bcd	−1	+1	+1	+1	94.88	69.60				
abcd	+1	+1	+1	+1	95.84	69.04				
Center	0	0	0	0	61.92	73.80				
Center	0	0	0	0	61.92	73.80				
Center	0	0	0	0	61.92	73.80				

Table 3. ANOVA results for the analysis of the unsaturated carbon bond conversion levels

Source of variation	Sum of squares	Degrees of freedom	Mean square	F_0	P-value
Model	6293.51	3	2097.84	8.58	0.0018
B	1779.36	1	1779.36	7.28	0.0173
C	3078.31	1	3078.31	12.59	0.0032
BC	1435.84	1	1435.84	5.87	0.0295
Curvature	628.63	1	628.63	2.57	0.1311
Residual	3422.03	14	244.43		
Pure error	0.00	2	0.00		
Lack of fit	3422.03	12	285.17		
Total	10344.17	18			

ducted with three center points (Table 2). To minimize errors due to possible systematic trends in the variables, all trials were performed with a completely randomized design. Statistical analysis was then done for all the experimental values, and the effects of main factors and their interaction on the chosen responses were calculated with the main effects and interactions for the conversion of unsaturated carbon with a confidence level of 95% shown in Table 3. The mole ratio of H_2O_2 : HCOOH, stirring rate, and their interaction had a significant effect on the conversion of unsaturated carbon. Also, the P-value of the curvature, defined as the difference between the average of the centre point responses and the average of the factorial points, was higher than the critical value, suggesting that the curvature had no effect on the conversion of unsaturated carbon. Consequently, the experimental results were fitted with the linear regression model and expressed in terms of a first-order model along with the interaction in Eq. (5):

$$C_{unsat} = 46.15 + 10.55B + 13.87C + 9.47BC \tag{5}$$

where B and C are the molar ratio of H_2O_2 : HCOOH and the stirring

rate (rpm), respectively.

A high coefficient of determination (R^2=0.9526) from the normal probability plot of the residuals was obtained (Fig. 2(a)), while the residuals of the developed model (Eq. (5)) did not follow any trend with regard to the predicted variables (Fig. 2(b)). This structureless distribution indicates that the developed regression model can be used to represent the data over the experimental range.

According to the linear regression model (Eq. (5)) and the plot of the main factor effects as demonstrated in Fig. 3(a), the H_2O_2 : HCOOH mole ratio and the stirring rate had a positive effect on the unsaturated carbon bond conversion. This might be attributed to the fact that high concentrations of H_2O_2 can promote a high production rate of peroxyformic acid (HCOOOH) that consequently reacts with the double carbon bonds in WUO-B, resulting in the reduction in the level of unsaturated double carbon bonds. Also, the positive effect of stirring on the unsaturated carbon bond conversion is likely to be because a high stirring rate might help to give a good contact between the liquid-liquid interphases [21] and also help to eliminate the effect of the mass-transfer limitation between the peroxy-
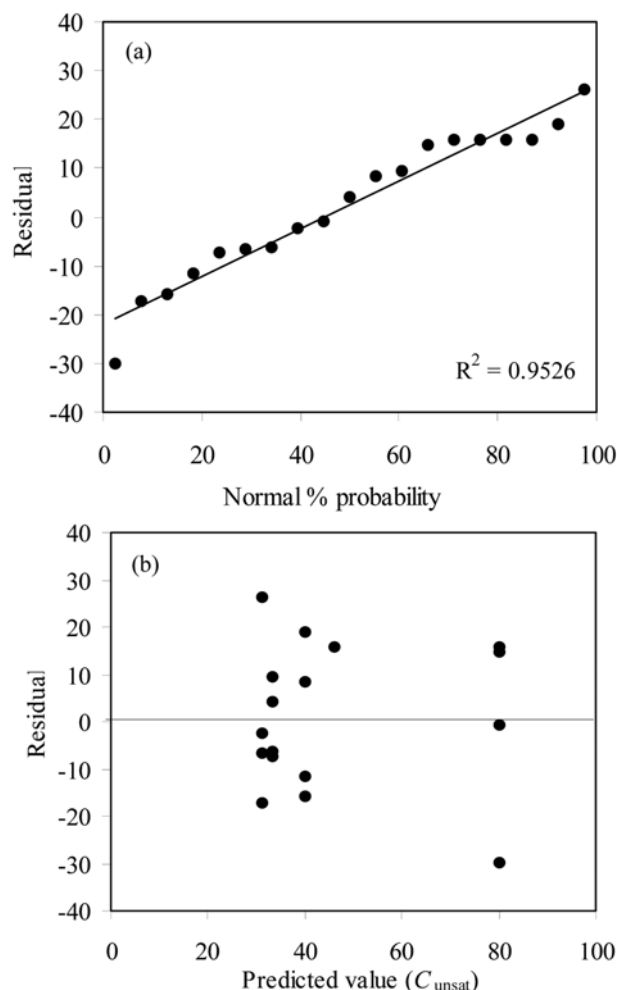
Fig. 2. Plots of (a) the normal probability and (b) the predicted value (C_{unsat}) versus the residuals of the unsaturated carbon bond conversion level.
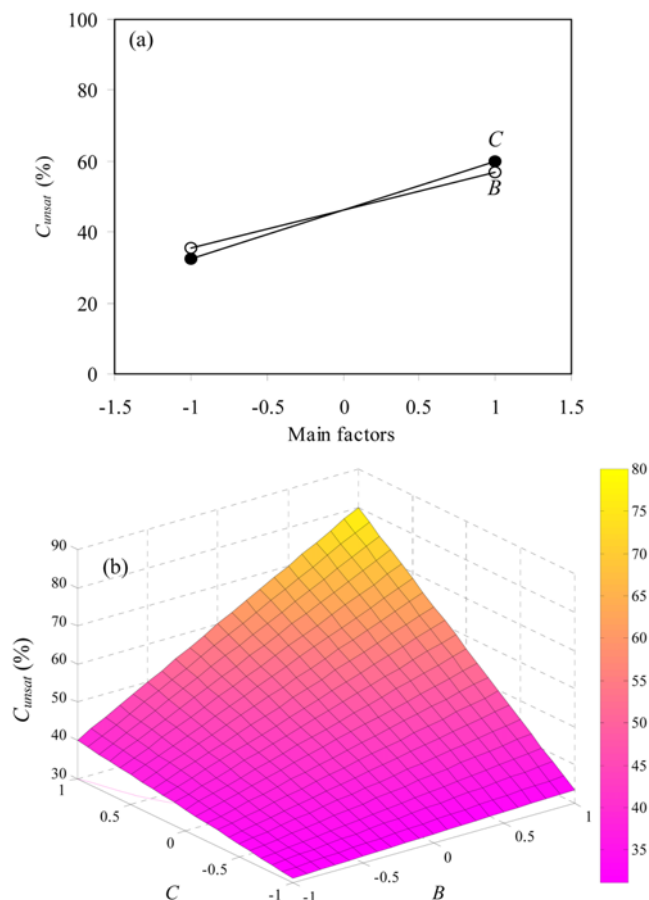

Fig. 3. The (a) main effect and (b) response surface plots of the unsaturated carbon bond conversion level as a function of the (B) mole ratio of H_2O_2 : HCOOH and (C) the stirring rate.

formic acid and the unsaturated chain of WUO-B. To acquire a fuller understanding of the potential interactions, a three-dimensional contour response surface plot was drawn. The lowest unsaturated carbon bond conversion level was observed in the presence of a low mole ratio of H_2O_2 : HCOOH (1 : 7) and a low stirring rate (100 rpm). Increasing either of these factors alone then results in a slightly increased conversion of the unsaturated carbon bonds, but this was dramatically more marked if both factors were increased together, where up to 80% conversion of the unsaturated carbon bonds was found at a 1 : 1 molar ratio of H_2O_2 : HCOOH and a 300 rpm stirring rate (Fig. 3(b)).

With regards to the epoxy compound selectivity, the reaction temperature and time and their interactions significantly affected the epoxy compound selectivity (data not shown). The curvature had no influence on the selectivity and the regression model should thus be expressed by Eq. (6).

$$S_{epox} = 73.12 - 2.71A - 4.11D + 6.40AD - 5.46ACD \qquad (6)$$

where A, C and D are the temperature (°C), stirring rate (rpm) and reaction time (h), respectively.

However, the relatively low statistical support for a linear rela-

tionship ($R^2 = 0.8988$) of the normal probability plot of the residuals (Fig. 4(a)), and the observation that the plot of residuals versus fitted values is in an outward-opening funnel shape (Fig. 4(b)), both indicate that the assumption of a constant variance is unsatisfied. One common approach for dealing with a non-constant variance system is to use a variance-stabilizing transformation. In this case, the inverse transformation was carried out and an analysis of variance on the transformed data was then performed, with the results shown in Table 4. The reaction temperature, reaction time and the stirring rate, as well as the temperature-time and temperature-time-stirring rate interactions all significantly affected the epoxy compound selectivity. Also, the P-value of the curvature was higher than the critical value, suggesting that the curvature had no effect on the epoxy compound selectivity.

Eq. (7) shows the relationship between the influential factors and the inversion of the epoxy compound selectivity.

$$1/S_{epox} = 0.0139 + 0.0004A - 0.0003C + 0.0007D \\ - 0.0012AD + 0.0010ACD \qquad (7)$$

where A, C and D are the temperature (°C), stirring rate (rpm) and reaction time (hr), respectively.

This equation provided the best-fitting of the experimental data with a high R^2 value (0.9545) and structureless residuals (Fig. 5), indicating that the developed regression model is sufficient to repre-
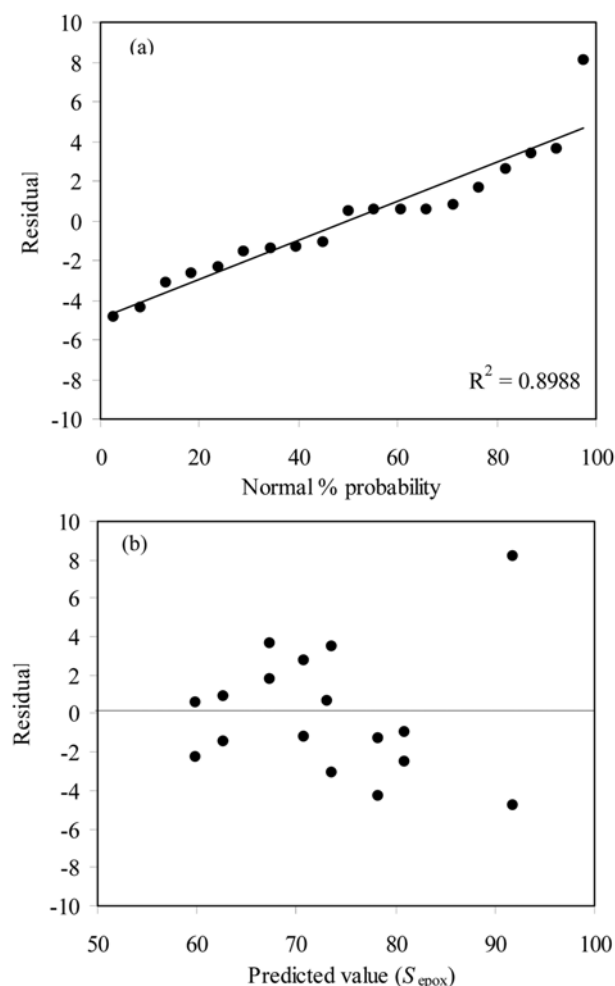
Fig. 4. Plots of (a) the normal probability and (b) the predicted value (S_{epox}) versus the residuals of the epoxy compound selectivity.
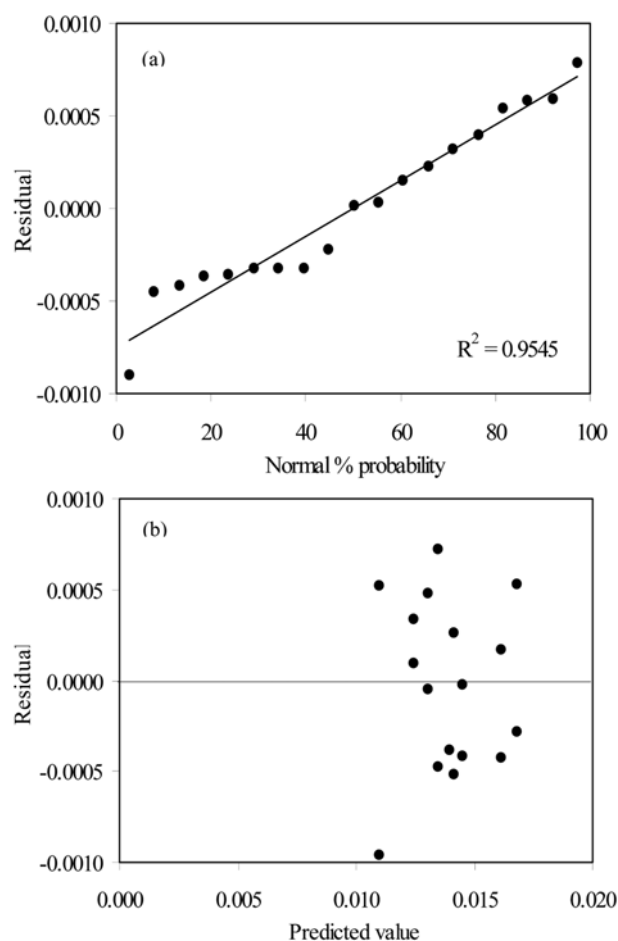

Fig. 5. Plots of the transformed data for (a) the normal probability and (b) the predicted value (C_{unsat}) versus the residuals of the transformed epoxy compound selectivity.

sent the data over the experimental range.

Fig. 6 illustrates the effect of the three main factors (reaction temperature and time and the stirring rate) on the epoxy compound selectivity. The reaction temperature and time had a positive effect on the inverse epoxy compound selectivity, while the stirring rate had a negative effect. Generally, higher temperatures lead to the formation of more peroxyformic acid (Eq. (1)), as a direct proportional relationship [21]. However, a high temperature not only results in a more rapid oxirane or epoxy compound formation reaction, but also in a higher oxirane cleavage rate [22], resulting in a lower epoxy compound selectivity. With regards to the effect of the reaction time, it had a smaller negative effect on the epoxy compound selectivity

Table 4. ANOVA results for the analysis of the transformed data for the epoxy compound selectivity

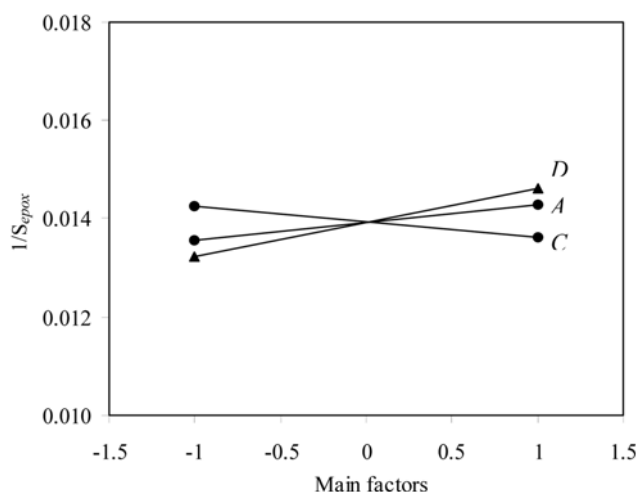| Source of variation	Sum of squares	Degrees of freedom	Mean square	F_0	P-value
Model	5.1E-05	5	1.0E-05	36.61	7.3E-07
A	2.0E-06	1	2.0E-06	7.25	2.0E-02
C	1.6E-06	1	1.6E-06	5.53	3.7E-02
D	7.6E-06	1	7.6E-06	26.92	2.3E-04
AD	2.3E-05	1	2.3E-05	81.70	1.1E-06
ACD	1.7E-05	1	1.7E-05	61.67	4.5E-06
Curvature	3.7E-07	1	3.7E-07	1.30	2.8E-01
Residual	3.4E-06	12	2.8E-07		
Pure error	0.0E+00	2	0.0E+00		
Lack of fit	3.4E-06	10	3.4E-07		
Total	5.5E-05	18			

Fig. 6. Main effect plot of the (A) reaction temperature, (B) molar ratio of H_2O_2 : HCOOH and (C) stirring rate on the epoxy compound selectivity.

in comparison to that of when changing the reaction temperature. A long reaction time can promote the epoxide ring opening or oxirane
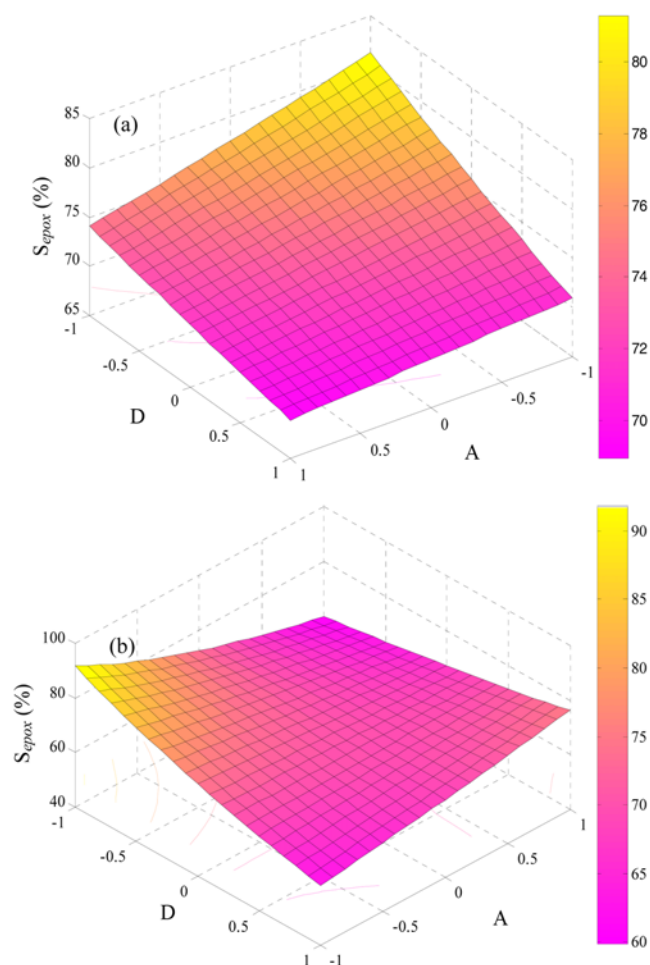
cleavage reaction, leading to a decrease in the epoxy compound selectivity. Conversely, the epoxy compound selectivity was enhanced by increasing the stirring rate, at least over the investigated range of 100-300 rpm, similar to that seen for the unsaturated carbon bond conversion level. Again, this is because the higher stirring rate facilitates a good liquid-liquid interphase contact and also reduces the mass-transfer limitation between the peroxyformic acid and the unsaturated chain of WUO-B. In addition, the main effect lines of all factors were traverse, indicating an interaction between all three influential factors on the epoxy compound selectivity. Fig. 7 demonstrates the response surface plot of the reaction temperature and time on the epoxy compound selectivity at a low (100 rpm) and high (300 rpm) stirring rate, where in both cases the lowest level of selectivity was observed in the presence of a high reaction temperature (50 °C) and time (12 hr) (Fig. 7(a)), while the highest epoxy compound selectivity was achieved in the presence of a low reaction temperature (30 °C) and time (2 hr) (Fig. 7(b)). This is consistent with the obtained regression model and the effect of these three main factors (Fig. 6).

4. Impact of Conversion of Unsaturated Carbon and the Epoxy Compound Selectivity on the OS of the EWUO-B

As reported previously [23,24], the degree of unsaturation of the FAME chain significantly affects the OS of the biodiesel. Fig. 8(a)

Fig. 7. Response surface plot of the epoxy compound sensitivity at a (a) low (100 rpm) and (b) high (300 rpm) stirring rate (C) as a function of the reaction (A) temperature and (D) time.
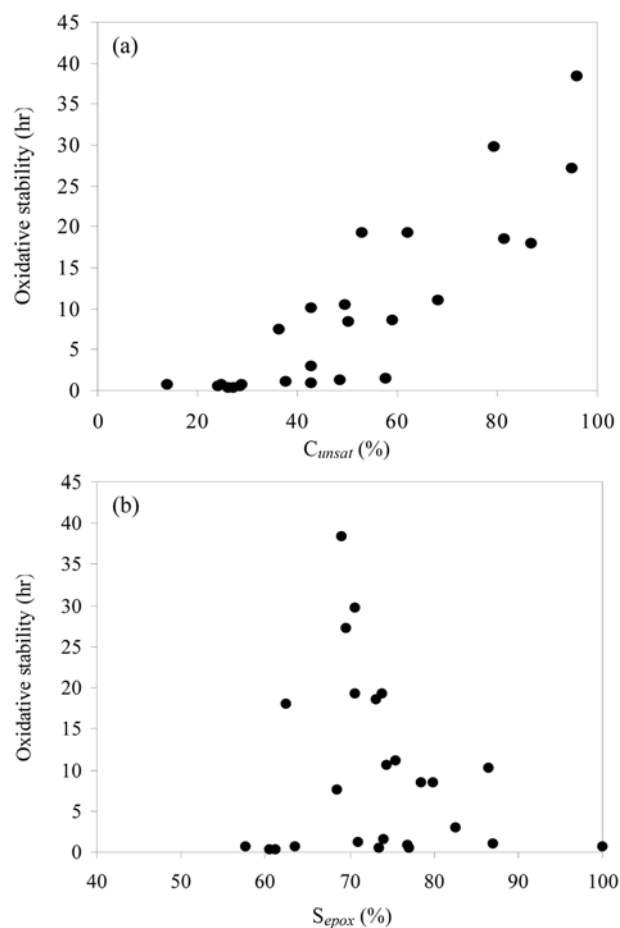

Fig. 8. Changes in the OS of EWUO-B as a function of (a) the unsaturated carbon bond conversion level and (b) the epoxy compound selectivity.

shows the variation in the OS of these EWUO-B preparations as a function of the unsaturated carbon bond conversion level. The OS increased as a function of the unsaturated carbon bond conversion level, indicating that the OS of EWUO-B depends significantly on the amount of carbon double bonds in the biodiesel, consistent with results of Knothe [25]. However, it does not appear to relate to the epoxy compound selectivity, as demonstrated in Fig. 8(b).

From these results, the maximum OS of EWUO-B was obtained at a high reaction temperature (50 °C), time (12 hr) and stirring rate (300 rpm) with a 95.8% unsaturated carbon bond level and a 69.0% selectivity (an epoxy content of 66.2%). The key physical properties of the EWUO-B formed under this set of optimal conditions were then measured and compared with those for WUO-B, as summarized in Table 1. Compared to that for the WUO-B, the methyl ester content, viscosity and heat of combustion (higher heating value) of the EWUO-B were slightly reduced, at around 1.03-, 1.12- and 1.04-fold, respectively, which might be attributed to the presence of mixed species between unsaturated-, epoxidized- and hydroxyl-methyl esters in the EWUO-B. In addition, the peroxyformic acid (HCOOOH) reacted selectively at the unsaturated bond of methyl group of ester compound as demonstrated in Eq. (2), resulting in not significant alternation of methyl ester content in EWUO-B. Although epoxidation of WUO-B did not enhance the cold flow properties or the methyl ester content, all other key properties were within the specification of the EN14214 standard (Table 1). The cold flow temperatures of the EWUO-B increased, as seen in terms of the 3 °C and 1 °C increase in the cloud and pour points, respectively. This might be attributed to the fact that the cold flow properties of biodiesel increase as the degree of carbon bond saturation and chain length increase [3]. The epoxidation reaction causes the unsaturated carbon bonds to be substituted by the epoxy group, resulting in a decreased unsaturated fatty acid content. Besides, the presence of both unsaturated-, epoxidized- and hydroxyl-methyl esters may facilitate a closer packing arrangement and promote the side-by-side parallel packing of the molecules, which would also result in an increase in both the cloud significantly increased the flash point and OS of EWUO-B. That is, the flash point and OS increased around 7 °C (1.04-fold) and 38 hr (55.8-fold), respectively. It had a higher proportion of saturated methyl esters compared to UWO-B [26,27]. As the present form, the EWUO-B is still not suitable to be used as an alternative diesel fuel. However, it can be used as a raw material in oleochemistry applications.

CONCLUSION

The epoxidation of oil based WUO-B resulted in EWUO-B as the main product and hydroxyl-biodiesel as a by-product. The mole ratio of H_2O_2 : HCOOH and the stirring rate had a positive effect on the unsaturated carbon bond conversion level, while the reaction temperature and time had no significant effect within the studied ranges. However, both the reaction temperature and time each had a significant negative effect on the epoxy compound selectivity, while the stirring rate had a positive effect. The maximum conversion of unsaturated carbon bonds of EWUO-B (95.8%) was obtained at a high level of the key factors (reaction temperature and time of 50 °C and 12 hr, 300 rpm stirring rate and a 1 : 1 mole ratio of H_2O_2 : HCOOH), while the maximum epoxy compound selectivity (100%)

was obtained with a low level of the same factors (30 °C, 2 hr, 100 rpm and a 1 : 7 mole ratio). With regards to the impact of the epoxidation reaction on the biodiesel properties, a decreased unsaturated carbon bond level in the fatty ester chain can enhance the OS of the biodiesel but revealed no relationship between the OS and the epoxy compound selectivity.

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