AN ENTIRELY RENEWABLE BIOFUEL PRODUCTION FROM USED PALM OIL WITH SUPERCRITICAL ETHANOL AT LOW MOLAR RATIO

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Abstract – The biofuel production from used palm oil (UPO) using supercritical ethanol (SCE) at low molar ratio was investigated in order to produce an entirely renewable fuel. The effects of the reaction time and ethanol to oil molar ratio were considered from 0.5 to 10 min and 6:1 to 18:1, respectively. The optimal parameters were 10 min and a 12:1 molar ratio, representing a remarkable reduction from 42:1 for the conventional SCE process. Because of the high operating temperature, the triglycerides conversion rate reached 99%, and the glycerides content met the international specification for biodiesel. However, an ester content of 70% was obtained at optimal conditions. The side reaction between glycerol and ethanol demonstrated a positive effect in increasing fuel yield by 8.15%. The product can be considered an alternative biofuel instead of biodiesel.

Keywords: biofuel, supercritical ethanol,vegetable oil, used palm oil, low molar ratio

INTRODUCTION

The depletion of non-renewable petrochemical resources combined with concerns over global warming has focused the world's attention on the search for alternative sources of renewable energy. Biofuels synthesized from lipid-based biomass, especially biodiesel, offer a promising alternative substitute for petroleum-based fuels.

Biodiesel has potential utility as a sustainable, renewable fuel for transportation without requiring engine modification (Carraretto *et al.*, 2004). In addition, biodiesel is an environment-friendly energy source, producing less air pollution compared with fossil fuels and trace emission of sulfur oxides. It also contributes to climate change mitigation by reducing net CO_2 emissions from the transportation sector (Cetinkaya *et al.*, 2005).In general, biodiesel is synthesized through the transesterification of vegetable oils with a short-chain alcohol. The commercial biodiesel production facilities mostly employ methanol (derived from fossil sources) as the reacting alcohol

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because of its low cost and favorable chemical and physical properties (Ma and Hanna, 1999). In contrast, ethanol is a renewable source; because it can be produced from biomass by fermentation and has similar chemical and physical properties, it has been proposed as a reacting alcohol in place of methanol (Rodrigues *et al.*, 2009). Therefore, using ethanol provides a 100% renewable basis for biodiesel production feedstocks.

Used cooking oil is one interesting feedstock, with costs typically two or three times lower than that of virgin vegetable oil (Math *et al.*, 2010). It has been reported that0.7 to 1 and 0.2 million tons of used cooking oilis annually produced in European countries and the United Kingdom, respectively (Hamze *et al.*, 2015). China and Japan generates about 4.5 and 0.6 million tons of used cooking oil per year, respectively (Diya'uddeen *et al.*, 2012; Balat and Balat, 2010).This suggests the ready availability of used cooking oil to meet the future demand for biodiesel production. However, because of its high content of free fatty acid (FFA) and water resulting from the frying process, the conventional catalytic process, especially an alkali-catalytic process, is unsuitable for the conversion of used cooking oil as a feedstock because the alkaline catalysts react with FFA to form soaps, significantly reducing the biodiesel yield. The supercritical alcohol (SCA) process is an alternative route to resolve those problems without using catalysts. It has been reported that the presence of water and FFA in the feedstock, up to 36 and 30 wt. %, respectively, does not affect the progress of transesterification in SCA (Tan *et al.*, 2010; Kusdiana and Saka, 2004; Silva and Oliveira, 2014). These FFA can be esterified and converted into biodiesel. Hence, the SCA process carries the additional advantage that it can utilize low-quality feedstocks such as used cooking oil and crude palm oils as a source of triglyceride without encountering saponification problems.

In our previous study, a laboratory batch reactor was used in successful biofuel production from refined palm oil (RPO) using the SCA process at 400°C and 15 MPa (Sawangkeaw *et al.*, 2011). This novel process was employed to resolve the problem of the high alcohol to oil molar ratio (>40:1) in the SCA process, which generated an environmental impact from the large energy input of preheating and recovering the alcohol (Kiwjaroun *et al.*, 2009). The alcohol to oil molar ratio can be reduced to 12:1 and 18:1 for the supercritical methanol (SCM) and supercritical ethanol (SCE) processes at 400°C and 15MPa, respectively. As proposed in some studies (Marulanda *et al.*, 2010; Marulanda *et al.*, 2009), the increase of the operating temperature to 350 °C–400 °C dramatically reduced the molar ratios from 40:1–42:1 to 6:1–12:1 at moderate pressures of 10.0–15.0 MPa. Moreover, this process also resulted in important advantages, most importantly an increase of approximately 5%–10% in fuel yields and a reduction in the alcohol to oil molar ratio. In addition, the

lower proportion of alcohol required is reflected in a lower energy requirement for alcohol preheating, pumping, and recovery compared with conventional SCA processes with a 42:1 alcohol to oil molar ratio (Sawangkeaw *et al.*, 2012). Thus, this work selected reaction conditions of 400 °C and 15 MPa to reduce the employment of alcohol for biofuel production from used palm oil (UPO) with SCE. The effects of the reaction time and ethanol to oil molar ratioswere investigated to explore the utility of the SCE process and its potential for scale-up to a continuous process.

EXPERIMENTAL

Materials

The UPO in this study was collected from a local restaurant near Chulalongkorn University, Bangkok, Thailand. The RPO was supplied from Morakot Industries Co., Ltd. Analytical grade ethanol and glycerol supplied by Fisher.To measure the ethyl ester content in the biofuel products, analytical grade methyl heptadecanoate (99.5%) was used as an internal standard, and *n*-heptane (99.5%) was used as an analytical solvent, supplied by Fluka and Fisher, respectively.

Experimental set-up and procedure

The reactions of UPO and glycerol with SCE were investigated in a constant-volume batch reactor. The batch reactor was constructed from stainless steel tubing (closed at both ends) of 9.52-mm outside diameter, 1.24-mm thickness, and 110-mm length with a volume of 4-mL. The reactor vessel was heated in a fluidized sand bath using a k-type thermocouple and a proportional-integral-derivative controller (PID controller) to monitor and control the temperature, respectively.

The reactor was then charged with UPO and ethanol in amounts calculated using the Redlich–Kwong equation of state to obtain the desired pressure of 15 MPa, including the amount of ethanol and glycerol at the molar ratio of 9:1. Because the total volume of reactants was commonly higher than 3-mL, the effect of the initial air in the 4-mL reactor, which could cause oxidation at 400 °C, could be neglected. The reaction times ranged from 0.5–10 min. The testing reactor was immersed into a fluidized sand bath at the desired temperature and shaken manually from time to time to ensure uniform mixing. Note that the heating rate of this reactor is 30 °C/s as reported in our previous work (Sawangkeaw et al., 2010). At the end of the reaction, the reactor was then quenched in a water bath to stop the reaction. Excess ethanol was removed by rotary evaporation at 50 °C and 15 mbars (1.5 kPa) for 30 min. The biofuel products were collected for analysis by gas chromatography (GC), from which the triglyceride conversion level (X_{TG}) was obtained.

Feed and product analysis

The UPO was filtered to remove food residues before examining its properties. The physical properties of the UPO sample were analyzed using standard testing methods, including the water content (EN ISO 12937), iodine value (ASTM D5554), and acid value (ASTM D664). In determining the distribution of fatty acid, the American Oil Chemists' Society standard (AOCS Ce2-97) was applied to prepare an ethyl ester (FAEE) sample. The ethyl ester content in the FAEE sample was measured based on the peak area obtained from GC, Shimadzu GC-14B, equipped with a capillary column (DB-WAX) and a flame ionization detector. The temperatures of the injector and detector were set at 250 °C. The column temperature was set at 180 °C, with a holding time of 8 min, and then increased to 200 °C at a heating rate of 10 °C/min.

The biofuel products were analyzed for their ester content and triglyceride conversion using a GC, Varian Technology Model CP3800, equipped with a capillary column (Rtx®-65TG, 30-m length, 0.250-mm I.D.) and a flame ionization detector. The temperatures of the injector and detector were set at 360 °C. The column temperature was set at 150 °C, with a holding time of 3 min, and then increased to 370 °C at a heating rate of 15 °C/min. The GC chromatogram of an incomplete conversion sample is shown in Figure 1. The determination of %FAEEs of each biofuel sample followed the European standard method EN 14103:2003 and employed methyl heptadecanoate as the internal standard. To quantify unreacted triglyceride in synthesized biofuel, 5-level solutions of palm oil in n-heptane were used in the external calibration. In addition, the triglyceride conversion level (%X_{TG}) was calculated using Equation 1.

$$X_{TG}(\%) = 100 \times (1 - \frac{TG_{Unreact}}{TG_{Initial}}) \qquad (1)$$

where X_{TG} is the % triglyceride conversion level, $TG_{Unreact}$ is the unreacted triglyceride level (g/L) in the resultant biofuel (measured by GC), and $TG_{Initial}$ is the initial triglyceride level (g/L) in the UPO reactant (also measured by GC).

The compounds in the biofuel and the ethanol–glycerol samples were identified by gas chromatography–mass spectroscopy (GC–MS), Shimadzu, model GCMS-QP2010, equipped with a capillary column (Agilent J&W DB-5 ms, 20-m length × 0.1-mm o.d. × 0.1-µm film thickness). For the biofuel samples, the column was started at 60 °C (held for 2 min), ramped to 270 °C at 20 °C/min, and then held at the final temperature at 270 °C for 2 min. The temperature program for the ethanol–glycerol reaction products started at 60 °C (held for 2 min), ramped to 115 °C (held for 1 min) at 5 °C/min, and then ramped to 220 °C (held for 20 min) at 10 °C/min.

The distillation (volatility) characteristics of the biofuel samples were analyzed by distillation gas chromatograph
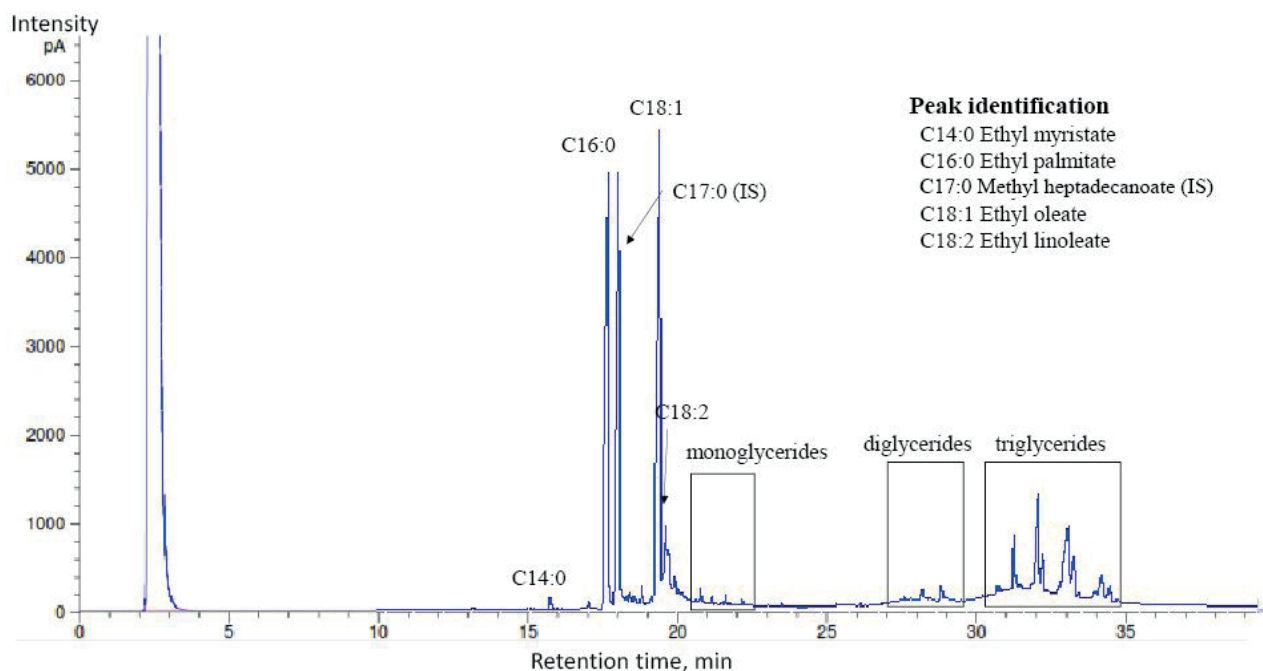

Figure 1. GC chromatogram of biofuel sample synthesized from UPO in SCE at 400 °C. C17:0 (IS) is an internal standard (methyl heptadecanoate).

(DGC), followed ASTM D2887-14, Agilent Technology Model 6890 N, equipped with a capillary column (5-m length × 0.53-mm o.d. × 0.09-μm film thickness, SIMDIS HT750, Analytical Controls) and a flame ionization detector. The temperature program was held at 30 °C and was then increased to 320 °C at 10 °C/min. The holding time at the final temperature (320 °C) was 20 min. The boiling ranges of biofuel sampleprecisely determined based on the calibration curve between boiling point of normal aliphatic hydrocarbon standard and retention time. For example, the boiling ranges of gasoline (C4–C12) is 100–180°C which represent as retention time of 0-5 min, kerosene (C12–C16) is 180–250°C which represent as retention time of 5-10 min and so on. The %mass recovery was calculated from summation of peak area between those represented retention times.

RESULTS AND DISCUSSION

Properties of RPO and UPO

A comparison of the physical and chemical properties of the RPO and UPO samples is presented in Table 1. The UPO differs in physical properties from RPO, especially in the acid value, because of the higher level of FFA produced from the hydrolysis reaction during the cooking process (Bastida and Sanchez-Muniz, 2002). The acid value is directly related to the levels of FFA in the samples that can be determined by calculation following ASTM D664. Therefore, the %FFA can be derived as 4.50 wt. % from the acid value of 9.62 mg KOH/g. According to alkali-catalyzed biodiesel production, a feedstock requires FFA levels below 0.50 wt.%. Thus, it is clear that a pre-treatment process would be required to use UPO as a feedstock because the FFA can react with the alkali-catalyst to form soaps, which reduces ester yield in the product (Encinar et al., 2011). However, the FFA do not significantly affect the supercritical transesterification with methanol and ethanol (Kusdiana and Saka, 2004; Tan et al., 2010; Vieitez et al., 2012). Under supercritical conditions, the FFA can be esterified to produce fatty acid alkyl ester, increasing the ester yield and process efficiency (Sawangkeaw et al., 2011). Furthermore, the amount of FFA in the feedstocks, approximately 10%, shows the catalytic activity, which results in higher conversions in SCM and SCE processes (Minami and Saka, 2006; Vieitez et al., 2012).The fast reaction rates of the simultaneous transesterification and esterification reactions were also reported in the biodiesel production from *Jatropha curcas* L. oil (>10% FFA) in SCE at the lowered operating conditions (Silva et al., 2014).

The water content in the feedstocks could affect the conversion in the transesterification reaction using the conventional acid-catalyzed method, as reported in a previous study (Kusdiana and Saka, 2004). However, the water contents in RPO and UPO are very low, as indicated in Table 1; thus, the effect of water is negligible in this study.

The UPO mainly comprises 35.33% palmitic acid, 38.50% oleic acid, and 11.51% linoleic acid, which can be transesterified to a main product, i.e., fatty acid ethyl esters (FAEEs) in biofuel. Fatty acid ester derived from

Table 1. The physical and chemical properties of RPO and UPO samples.

Fatty acid composition	Carbon number	Degree of unsaturation	Samples	
			RPO[a] (wt. %)	UPO (wt. %)
Lauric acid	12	0	0.45 ± 0.1	5.72 ± 2.5
Myristic acid	14	0	1.10 ± 0.2	4.41 ± 1.6
Palmitic acid	16	0	46.14 ± 2.4	35.33 ± 3.6
Stearic acid	18	0	4.43 ± 0.1	4.42 ± 0.9
Total saturated fatty acids			52.12 ± 2.8	49.88 ± 8.6
Palmitoleic acid	16	1	N/D	N/D
Oleic acid	18	1	37.12 ± 4.6	39.96 ± 1.5
Linoleic acid	18	2	11.10 ± 1.0	11.51 ± 1.4
Linolenic acid	18	3	0.21 ± 0.1	0.34 ± 0.2
Total unsaturated fatty acids			48.43 ± 5.7	51.81± 3.1
Acid value (mg KOH/g)			0.21 ± 0.05	9.62 ± 1.5
Water content (g/100g)			0.04 ± 0.05	0.14 ± 0.04
Iodine value (g/100g)			53.60 ± 5	68.47 ± 5
Molecular weight			840	858

[a]Obtained from Morakot Industries Co., Ltd.; N/D is not detected.

oleic acid has been proposed as a suitable candidate for improving fuel properties because of its high oxidation stability compared with other fatty acids containing two or three double bonds (Knothe, 2008). Studies of ethyl oleate, especifically on its fuel properties, are not available; but the same results as for methyl oleate would be expected. In addition, UPO contained higher levels of lauric acid (C12:0) and myristic acid (C14:0) than that RPO, most likely resulting from the decomposition of high-molecular-weight fatty acids, especially polyunsaturated fatty acids. As reposted in the literature, the lauric acid and myristic acid contents in palm oil are naturally present in the range of 0.1–0.4 wt.% and 0.9–1.4 wt.%, respectively (Lee and Ofori-Boateng, 2013).

Effect of reaction times

The effect of reaction time was investigated from 0.5 to 10 min, and the variation of the levels of FAEEs with reaction time at an ethanol to oil molar ratio of 18:1 is shown in Figure 2. The total FAEEs content increases steadily with reaction times up to 8 min and then tends to decrease because of the decrease of ethyl palmitate (C16:0), ethyl oleate (C18:1), and ethyl linoleate (C18:2). Ethyl palmitate (C16:0) and ethyl oleate (C18:1) were observed as the main components, which corresponded to the primary composition in Table 1. This observation indicates that the initially formed FAEEs can degrade with excessive reaction times at high temperature, as previously reported in the literature (Sawangkeaw et al., 2011; Imahara et al., 2008). In addition, it is evident that ethyl linoleate (C18:2) is more rapidly degraded, with a decline starting at 5 min

of reaction time. As a polyunsaturated fatty acid containing two double bonds, ethyl linoleate (C18:2) is increasingly unstable at higher temperatures compared with the mono-unsaturated and saturated ones. A similar behavior was likewiseobserved in the biodiesel production of soybean with SCE (Vieitez et al., 2011), ethyl linoleate (C18:2) and ethyl linolenate (C18:3) drastically reduce relative to ethyl palmitate (C16:0) at the highest temperature of 370 °C. The thermal cracking products are comprised of small compounds, i.e., alkane hydrocarbons in the range of C9-C10 as shown in Table 4 (see Section Reaction between glycerol and supercritical ethanol). Although the decomposition of FAEEs is not desirable in biodiesel production, some products, such as small hydrocarbons (C7-C14), could improve cold flow properties, density and viscosity, which was suggested for an additive for biofuel (Sawangkeaw et al., 2011).

As mentioned earlier, the transesterification and/or esterification reactions are the main reactions in SCE at 400 °C. Therefore, the effect of reaction time on the triglyceride conversion ($\%X_{TG}$) was also investigated to establish the optimal reaction time for the process. In addition, due to the decomposition of FAEEs observed at this reaction temperature (400 °C), the FAEEs yield could not be maximized to meet the 96.5% of the biodiesel standard value. The conversion of triglyceride was observed to minimize the glycerides content as specified by The European Standard (EN 14214) (see Section Effect of molar ratio). The data indicate that $\%X_{TG}$ increased rapidly at the beginning of the reaction, reaching a plateau of approximately 99% at a reaction time of 10 min for
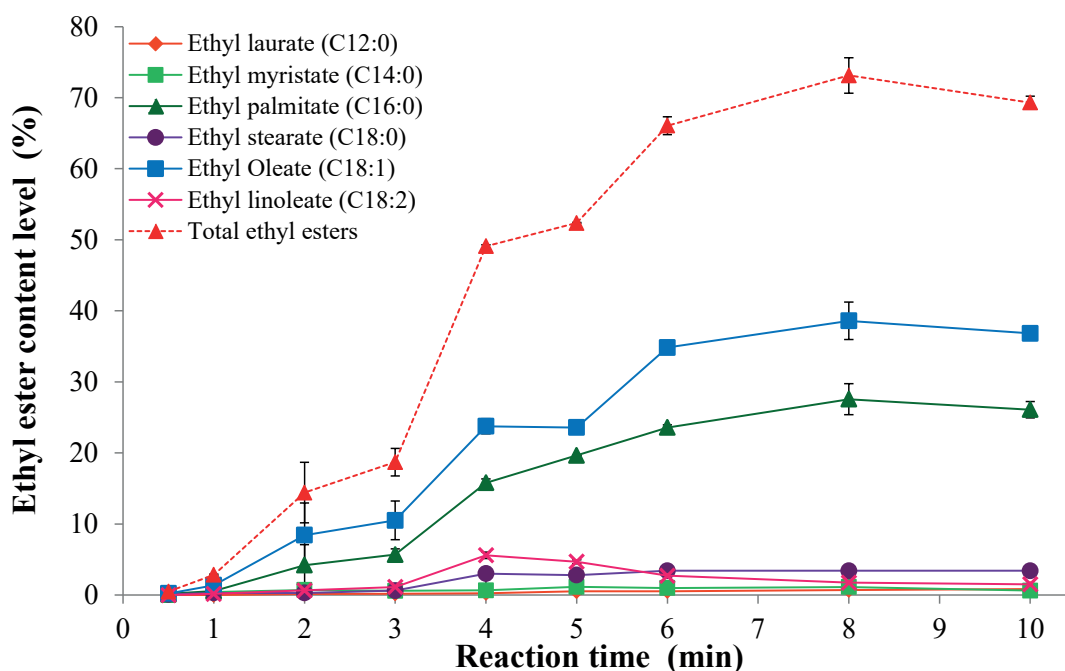

Figure 2. Ester contents of biofuel samples from UPO as a function of reaction time (reaction conditions: 400 °C, 15 MPa at 18:1 of ethanol to oil molar ratio).
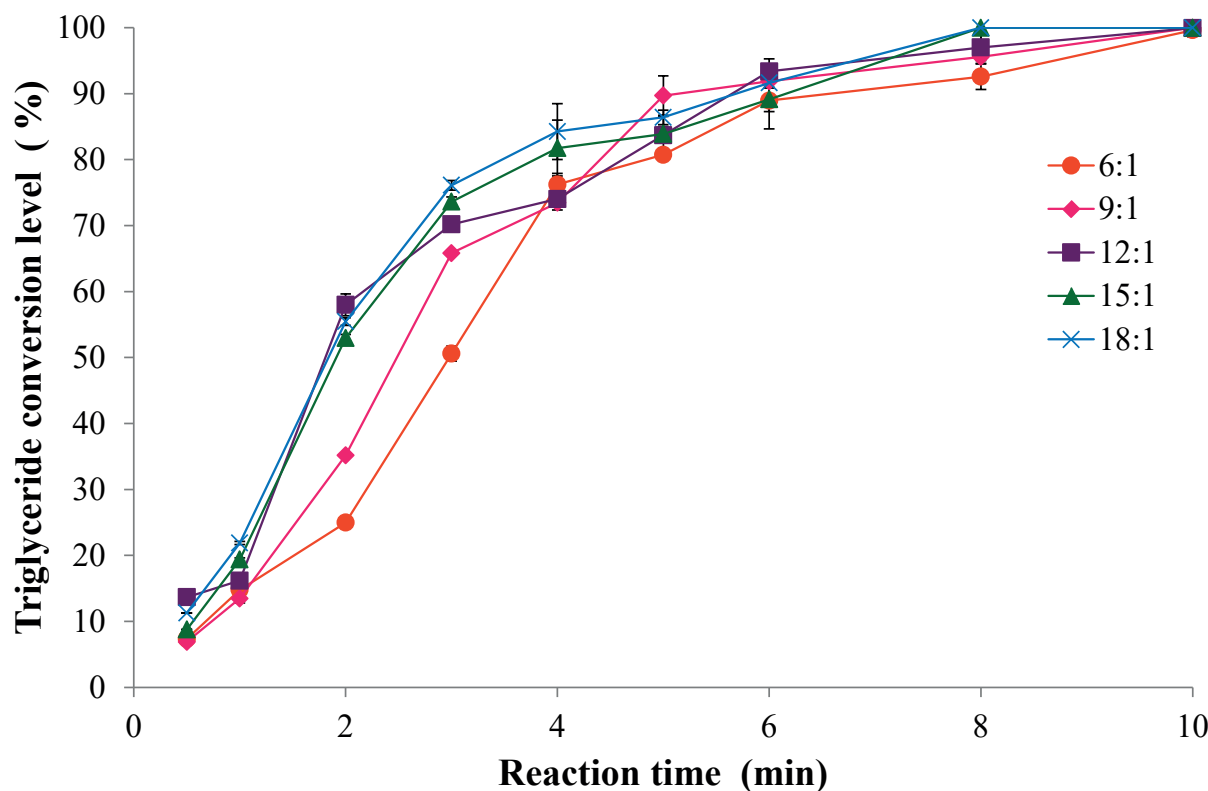
Figure 3. Triglyceride conversion level (%X_{TG}) of biofuel samples from UPO as a function of reaction time at 400 °C and 15 MPa.

all the ethanol to oil molar ratios (Figure 3). With the triglyceride conversion close to 100%, it can be concluded that a reaction time of 10 min is optimal to ensure the complete transesterification reaction for biofuel production with SCE at 400 °C.

Effect of molar ratio

The molar ratio of alcohol to oil has been reported to be one of the most important variables affecting the yield of fatty acid alkyl ester (He *et al.*, 2007). In this study, an ethanol to oil molar ratio 2–6 fold higher than the stoichiometric requirement (3:1) was considered because ethanol is consumed by multiple reactions such as the transesterification of triglycerides, esterification of FFA, and etherification reaction of glycerol, as observed in the mass balance analysis (see Section Mass balance). Figure 4 shows the change of the total FAEEs and triglyceride conversion with variation of the ethanol to oil molar ratio at a fixed reaction time of 10 min. The FAEEs content was observed to increase with increasing ethanol to oil molar ratio, and is consistent with the literature (Song *et al.*, 2008; Varma and Madras, 2007). This finding is explained by the lowering of the critical point of the UPO-ethanol mixture with increasing alcohol content (Anitescu *et al.*, 2008; Sakdasri *et al.*, 2015). However, the FAEEs yield was observed in the highest values only of 71.76% at the molar ratio of 12:1. This is not only due to the thermal

decomposition, but also the contaminant of several compounds in UPO that cannot be converted to ethyl ester. As reported in the literature (Gonzalez *et al.*, 2013; Abdala *et al.*, 2014), the maximum ester content reachable from the waste feedstock can be determined by the novel parameter, called convertibility. The convertibility of soybean fried oil and used frying oil was found to be 92.1% and 93.1%, respectively.

The presence of mono-, di-, and triglycerides in the biofuel is a key indicator of the biodiesel quality (Dias *et al.*, 2014); the levels of remaining glycerides in the samples produced in this study are presented in Figure 5. The EN 14214 requires levels of mono-, di-, and triglycerides below 0.80, 0.20, and 0.20 mass%, respectively. Thus, the glyceride levels in biofuel samples produced using ethanol to oil molar ratios from 9:1 were within the requirements of this specification.

Table 2 shows the distillation (volatility) characteristic of biofuel samples obtained from varied ethanol to oil molar ratios. Because a small amount of sample is available, this characteristic was analyzed using the simulated distillation gas chromatograph (ASTM D2887-14).This characteristic has an important effect on the safety and performance of the fuels and is directly related to the boiling point of the fuel composition. The results indicate that all of the biofuel samples had lower initial boiling points (IBPs) than the standard biodiesel (120 °C) because of the decomposition of FAEEs into the low-molecular-weight compounds, as

Table 2. Distillation characteristics of biofuel samples from UPO as a function of ethanol to oil molar ratio (reaction conditions: 400 °C at 15 MPa, and 10 min reaction time).

Distillation characteristics °C	Ethanol to oil molar ratio					Diesel/biodiesel standard specification EN ISO 3405
	6:1	9:1	12:1	15:1	18:1	
IBP	98.0	98.0	98.0	98.0	98.0	Take note
50%	304.2	303.0	305.0	306.2	298.6	245 °C–310 °C
90%	360.6	361.4	367.0	386.0	361.0	360 °C (max)
FBP	526.0	530.0	532.4	530.0	530.8	Take note
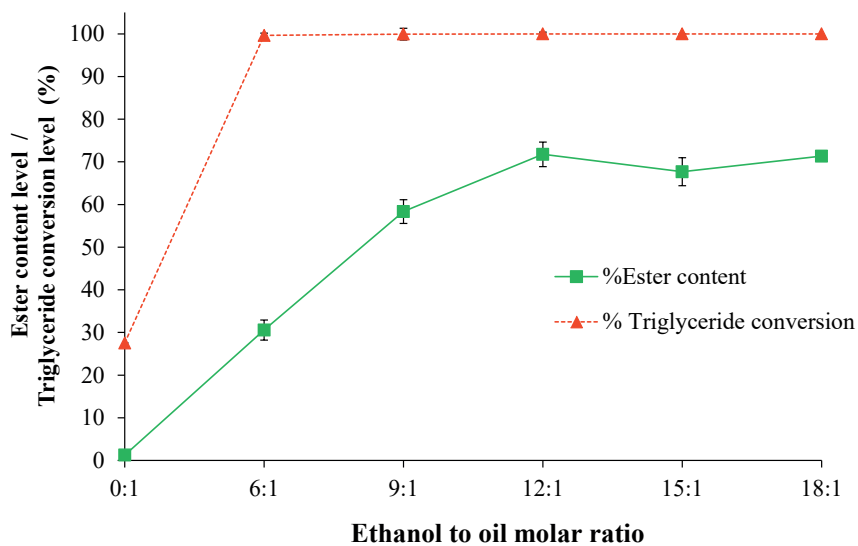
Figure 4. Ester content and triglyceride conversion, and glyceride levels of biofuel samples from UPO as a function of ethanol to oil molar ratio (reaction conditions: 400 °C at 15 MPa, and 10 min reaction time).
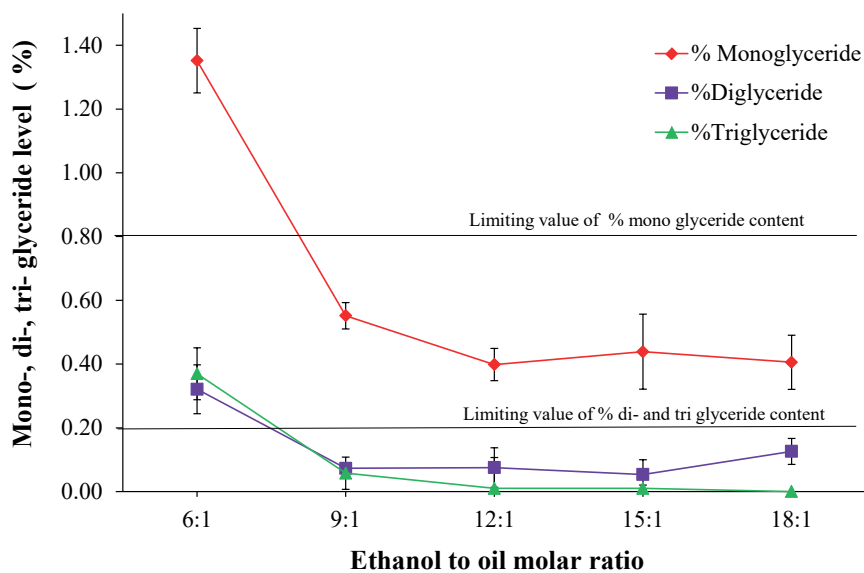
Figure 5. Glycerides levels in biofuel samples from UPO as a function of ethanol to oil molar ratio (reaction conditions: 400 °C at 15 MPa, and 10 min reaction time).

proposed in previous studies (Sawangkeaw *et al.*, 2011). Note that the low-molecular-weight could solve the cold start problem of biofuel. The temperatures corresponding to 50% distillation ranged from approximately 298.6 °C to 306.2 °C. These values align within the temperature range specified by EN ISO 3405 (245 °C–310 °C). However, the temperature of 90% distillation recovery (360.6 °C–386.0 °C) was observed to be slightly above the maximum limit of EN ISO 3405.

The effect of the ethanol to oil molar ratio on the boiling point distribution of the biofuel samples is illustrated in Figure 6. The biofuel samples obtained from 6:1 to 15:1 ethanol to oil molar ratios had diesel as the main fraction, approximately 70%. The diesel fraction slightly decreased to 60% when the reaction was performed at an 18:1 ethanol to oil molar ratio because of the increasing light fractions (gasoline and kerosene). The light fractions correspond to the low molecular weight compounds, generated from the thermal decomposition of polyunsaturated fatty acid and etherification of glycerol. However, it has been reported that the gasoline and kerosene fractions considerably improve the cold flow properties and viscosity but decrease the flash point (Sawangkeaw *et al.*, 2011). With the existence of the high amount of diesel fraction (up to 75%), that resultant biofuel is very promising as diesel fuel. In addition, the percentage of the residual fraction decreased with an increasing ethanol to oil molar ratio and remained

nearly constant at alcohol to oil molar ratios above 12:1. Therefore, it could be concluded that the ethanol to oil molar ratio of 12:1 is the optimal ratio to avoid surplus alcohol use in the SCE process.

Mass balance

As previously mentioned, this novel process can increase the fuel yield; thus, the mass balance should be consideredto compare the obtained experimental with theoreticalvalues. In this study, the mass balance of the overall theoretical reactions was calculated based on the simple reactions involved in the process, following Marulanda *et al.*(2010). The transesterification reaction of a stoichiometric mixture of triglyceride (TG) and ethanol produces FAEEs and glycerol, as shown in Equation 2.

$$TG + 3EtOH = 3FAEEs + glycerol \qquad (2)$$

With the addition of FFA in UPO feedstocks, esterification reactions of FFA with ethanol will also occur:

$$FFA + EtOH = FAEE + H_2O \qquad (3)$$

The complete mass balance of biofuel production under the optimal molar ratio (12:1) is shown in Figure 7. In accordance with the acid value of 9.62 mg KOH/g oil, the FFA content is estimated to be 4.50 wt. %, and the
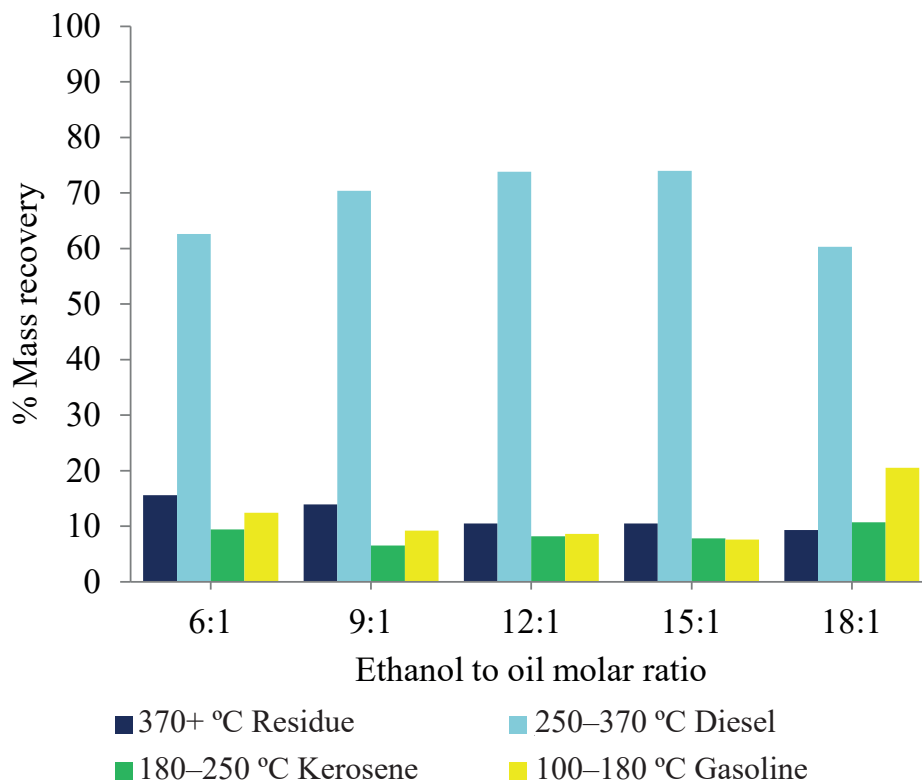

Figure 6. The boiling point distribution of biofuel samples from UPO as a function of the ethanol to oil molar ratio (reaction conditions: 400 °C at 15 MPa, and 10 min reaction time).

triglyceride content is 95.50 wt. % on the basis of 100.00 kg UPO feedstock. It is evident that 100.00 kg of UPO will theoretically react with 16.14 kg of ethanol, which was divided into 15.38 kg and 0.76 kg for the consumption of the transesterification and esterification reactions, respectively. Therefore, the outlet products will be obtained after evaporation and separation processes, consisting of 48.42 kg of excess ethanol, 99.86 kg of FAEEs (fuel phase), and 16.28 kg of glycerol and water phase.

Table 3 presents the experimentally observed values in a 4-mL batch reactor, which were simplified to the basis of 100.00 kg UPO as feedstock, compared with the theoretically obtained value from Figure 7. The fuel yield was increased by approximately 8.15%, as indicated by the mass of the fuel phase (108.15 kg) divided by the mass of UPO (100.00 kg). However, the increased fuel yield from UPO was less compared with that obtained using RPO as the feedstock (Sawangkeaw et al., 2011). This finding was most likely because of the lower triglyceride content in UPO compared with RPO, as mentioned in the Section "Properties of RPO and UPO".

The observed weight of the glycerol phase (2.32 kg) was lower than the theoretical value (16.28 kg) because of the etherification of glycerol and ethanol at 400 °C. The presence of the etherification reaction is indicated by the slightly higher weight of ethanol consumed in the experiment (64.56−42.88 = 21.68 kg) compared with the theoretical value (16.14 kg). The etherification products are identified in the Section "Reaction between glycerol and supercritical ethanol". It has been reported that the products of the etherification reaction are completely miscible with biofuel and even help to improve some of its properties (Marulanda et al., 2010).

A gas phase of approximately 11.21% was observed, as determined by the weight loss method; however, no further analysis of this phase was possible because of the small volume of gaseous products obtained from the 4-mL reactor. These gaseous products may include methane, ethane, and carbon dioxide, as reported for biofuel production from palm oil, as a product of high-temperature thermal cracking (Sawangkeaw et al., 2011).

Reaction between glycerol and supercritical ethanol

As mentioned above, the disappearance of ethanol and glycerol results from the etherification reaction. Thus, the ethanol–glycerol mixture was placed in a constant volume batch reactor at 400 °C and 15 MPa with a reaction time of 10 min to confirm the occurrence of the etherification reaction. The ethanol to glycerol molar ratio was set at 9:1 because it is the molar ratio after 100% of the triglycerides conversion is achieved. Table 4 lists the products obtained from the ethanol-glycerol reaction and biofuel samples identified by GC–MS. The observation of 2-ethoxy-1,3-propanediol and 1,2,3-triethoxypropane in both samples confirmed that the etherification reaction occurred in the supercritical condition. Moreover, the 2-ethoxy-1,3-propanediol in the biofuel sample implied that the product from the ethanol–glycerol reactions can dissolve in the fuel phase and can increase the fuel yield by approximately 8.15%. As proposed in the previous study, the reaction products of glycerol, mainly ether isomers of glycerol, could be directly used as part of the biofuel and improve some fuel properties (Marulanda et
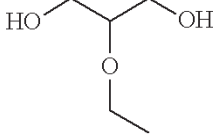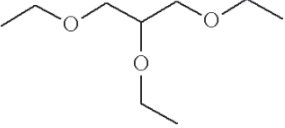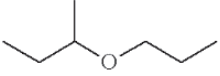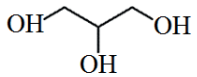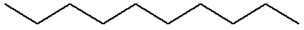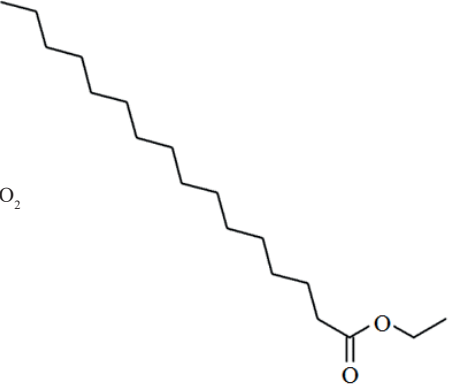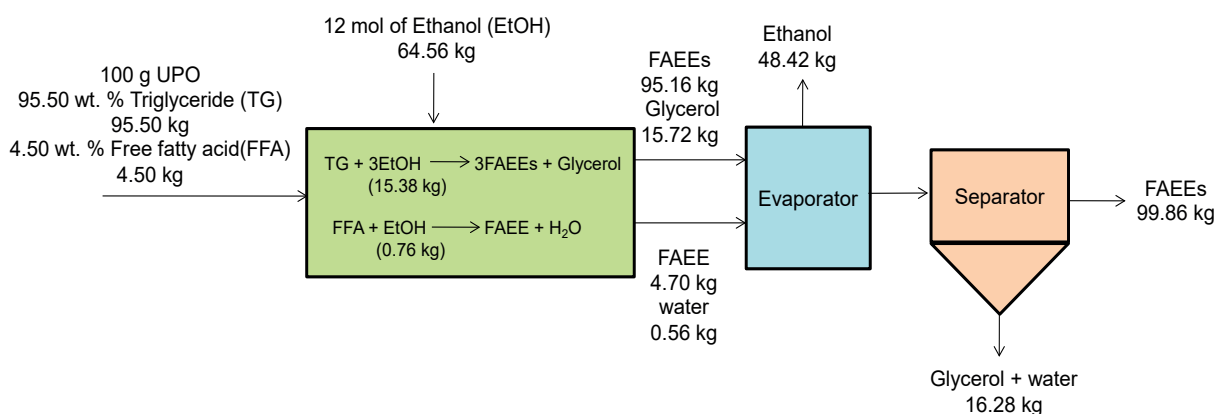

Figure 7. Flow sheet of the process with mass balance of biofuel production under the optimal molar ratio (12:1).

Table 3. Simplified mass balance of biofuel production from UPO with SCE at 400 °C, 12:1 ethanol to oil molar ratio, and 15 MPa as observed in the experiment.

Process	Feed (kg)		Outlet (kg)			
	UPO	Ethanol	Fuel phase	Ethanol	Glycerol + water phase	Gas phase
SCE	100	64.56	108.15	42.88	2.32	11.21

Table 4. Identified compounds in the product of the ethanol–glycerol reaction and product of biofuel based on GC–MS.

Name	Formula	Structure	Fractional group
2-Ethoxy-1,3-propanediol[a, b]	$C_5H_{12}O_3$		Ether
1,2,3-Triethoxypropane[a]	$C_9H_{20}O_3$		Ether
2-Propoxybutane[a]	$C_7H_{16}O$		Ether
Glycerol[a]	$C_3H_8O_3$		Hydroxyl
Nonane[b]	C_9H_{20}		Alkane
Decane[b]	$C_{10}H_{22}$		Alkane
Ethyl hexadecanoate[b]	$C_{18}H_{36}O_2$		Ester

[a]Appearance in the product of the ethanol–glycerol reaction.
[b]Appearance in the biofuel sample.

al., 2009; Anitescu et al., 2008; Aimaretti et al., 2009). Aimaretti et al. (2009) reported that approximately 10 % of glycerol reaction products has a marginal influence on the kinematic viscosity. However, the compatibility of those compounds with diesel fuels, and their influence on engine performance, should be investigated in further research.

In the past decade, the prices of glycerol have plummeted because of the rapid increase in global biodiesel production, especially conventional acid and base catalysis processes (Rahmat et al., 2010). Therefore, the purification of crude glycerol to prepare a commercial product, which is a mixture of glycerol, remaining catalyst, soap, unreacted alcohol, and unreacted triglycerides, does not occur to be economically feasible. Although some alternative uses for glycerol have been suggested, the oversupply has led to an environmental problem (Gholami et al., 2014).

Accordingly, this novel process with SCA at 400 °C can be considered an environmentally friendly process because of the reduced release of glycerol.

CONCLUSION

Biofuel production from UPO with SCE with a low ethanol to oil molar ratio was successfully investigated at 400 °C. The high temperature and long reaction time resulted in degradation of unsaturated fatty acids, resulting in a reduction in the total FAEE levels. The optimal reaction conditions were an ethanol to oil molar ratio of 12:1 and a reaction time of 10 min. Under these conditions, almost 99% triglycerides conversion was attained. In addition, the levels of glycerides (mono-, di-, and tri-glycerides) were observed to be within the maximum limits set by the European Standard (EN 14214) for biodiesel fuel. The 50% distillation recovery was within the range of EN ISO 3405, whereas the 90% distillation recovery was slightly outside of that range. The side reaction between glycerol and SCE was also examined in this study. The reaction products from glycerol, mostly 2-ethoxy-1,3-propanediol, can positively contribute to improve the cold flow properties and increase the fuel yield by approximately 8%.

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