

Continuous Production of Biodiesel in Supercritical Ethanol: A Comparative Study between Refined and Used Palm Olein Oils as Feedstocks

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A produção de biodiesel a partir de óleos de oleína de palma refinada (RPO) e oleína de palma usada (UPO) em etanol supercrítico foi comparativamente investigada num reator contínuo. Após o uso de RPO para fritar frango, os níveis de ácidos graxos insaturados (UFAs) e ácido graxo livre (FFA) aumentaram 10 e 5%, respectivamente. As condições ótimas para ambos os óleos foram 300 °C, 30 MPa, razão molar etanol:óleo 30:1 e 60 min de tempo de residência. Embora os UFAs sejam inativos e sensíveis à degradação térmica, o FFA em UPO catalisou ao mesmo tempo as reações em etanol supercrítico. Devido ao efeito antagonístico de UFAs e FFA, o conteúdo de éster máximo do biodiesel de UPO (73%) foi um pouco menor que aquele do biodiesel de RPO (80%). Os demais componentes do biodiesel resultante eram glicerídeos não-reagidos, principalmente mono e diglicerídeos. Além do mais, a reação com UPO atingiu o equilíbrio mais rapidamente que aquela com RPO, devido ao efeito catalítico de FFA.

Biodiesel production from refined palm olein (RPO) and used palm olein (UPO) oils in supercritical ethanol was comparatively investigated in a continuous reactor. After use of RPO for chicken frying, levels of unsaturated fatty acids (UFAs) and free fatty acid (FFA) increased by 10 and 5%, respectively. The optimal conditions for both oils were 300 °C, 30 MPa and 30:1 ethanol:oil molar ratio at 60 min of residence time. Although the UFAs are inactive and sensitive to thermal degradation, the FFA in UPO catalyzed the reactions in supercritical ethanol at the same time. Due to the antagonistic effect of UFAs and FFA, the maximum ester content of UPO biodiesel (73%) was slightly lower than for RPO biodiesel (80%). The other compounds in resultant biodiesel were unreacted glycerides, mainly mono- and di-glycerides. Furthermore, UPO reaction reached equilibrium faster than RPO reaction due to the catalytic effect of FFA.

Keywords: biodiesel, fuel properties, hydrated ethanol, supercritical transesterification

Introduction

Biodiesel is an alternative fuel for use in compression-ignition engines, and can be produced from lipid-based biomass and various alcohols. Current biodiesel production processes face a number of constraints, especially in terms of prices, flexibility and renewability of feedstocks. Because the feedstock price was reported as accounting for approximately 70% of the total production cost of biodiesel,¹ the feasibility of commercialized biofuel is

strongly dependent on feedstock price. Feedstock flexibility refers to the ability to process multiple feedstocks without either major modification of the process or pretreatment. Even though many types of lipid-based biomass have been promoted as alternative feedstocks for biodiesel production, the conventional alkaline-catalytic process is not capable of handling them efficiently.² Finally, for feedstock renewability, methanol, which is widely employed as the reacting alcohol due to its low price and high reactivity, is commercially synthesized from natural gas, which is a non-renewable resource.

With regard to feedstock price, used cooking oil offers an interesting alternative feedstock, especially for

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developing countries, due to its low price. According to average price (www.alibaba.com) used cooking oil is approximately half the price of refined palm oil. With regard to feedstock flexibility, pretreatment of used cooking oil is required when the conventional alkaline-catalytic process is employed, in order to maximize the ester content.³ Otherwise, assistive methods such as acid-catalytic and enzyme-catalytic methods are required. With regard to feedstock renewability, ethanol, which is normally produced by fermentation of agricultural biomass, is a renewable alcohol that could be used as biodiesel feedstock. In addition, bioethanol is commercialized as a fuel in many countries, such as USA, Brazil, China and Thailand. However, hydrated ethanol cannot be used in the conventional alkaline-catalytic process due to soap formation. Whilst absolute or anhydrous ethanol has been successfully used experimentally as the reacting alcohol for biodiesel production using the alkaline-catalytic process,⁴ its price is higher compared with methanol and hydrated ethanol. Thus, used cooking oil and hydrated ethanol are attractive feedstocks to simultaneously produce low-price and entirely green biodiesel.

The supercritical ethanol (SCE) process is a catalyst-free technology invented to produce biodiesel and reported widely in the literature.⁵⁻⁸ Hydrated ethanol can be used without further purification or modification of the process. However, there has so far been no comparative study between the use of refined and used oils as feedstocks. This work selected refined palm olein oil (RPO) and used palm olein oil (UPO) as feedstock due to their wide use for cooking in South East Asia and South America. This work investigated the effects of oil type on the ester content in the resultant biodiesel produced by the SCE process in a continuous reactor. Furthermore, the effects of operating parameters such as temperature, pressure and ethanol:oil molar ratio were also examined. It was hypothesized that the impurities in UPO have some influence on biodiesel production with SCE.

Experimental

Materials

Commercial grade ethanol, 96.5% m/m, obtained from a local distributor, and RPO (with a major fatty acid composition of 37% palmitic, 46% oleic and 11% linoleic acids) from Morakot Industries Co., Ltd., were used with no further purification. The UPO was collected from a traditional fried chicken restaurant, in Bangkok, Thailand. The virgin RPO was also supplied from Morakot Industries Co., Ltd. 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 water content (EN 14214), iodine value (ASTM D5554) and acid value (ASTM D664). The distribution of fatty acids in both RPO and UPO samples was measured by conversion to fatty acid methyl esters (FAME) by the AOCS Ce 2-66 method. Then, the FAME samples were analyzed for the composition percentage by the AOCS Ce 1h-05 testing method. The analytical grade methyl heptadecanoate (99.5%) and *n*-heptane (99.5%), used in the measurement of the ester content of the biodiesel, were supplied by Fluka and Fisher, respectively.

Transesterification apparatus and procedure

The schematic diagram of the tubular reactor used in this work is shown in Figure 1. The reactor consisted of a coiled tubular reactor (SUS316 tubing of 3.18×10^{-3} m outside diameter, 7.11×10^{-4} m thickness and 80 m length) which was heated by a nitrate-based molten salt bath. The temperature of the molten salt bath was controlled by a proportional-integral-derivative (PID) controller (Sigma model SF48).

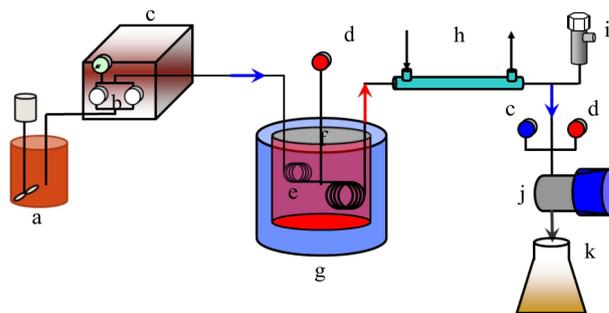


Figure 1. Schematic diagram of lab-scale tubular reactor showing the (a) reactants mixer; (b) high pressure pump; (c) pressure gauge; (d) thermocouple; (e) preheater; (f) reactor; (g) molten salt bath; (h) double pipe heat exchanger; (i) relief valve; (j) back-pressure regulator; and (k) sampling flask.

The RPO or UPO and ethanol were mixed at the desired molar ratio and agitated during the experiment. The mixture was pumped through the preheater into the reactor by a high-pressure pump (Thar Technology Co. Ltd., model P50).

The residence time was calculated from total flow rate of the reactants. The thermocouples were set at the reactor inlet, outlet and molten salt bath. After the outlet flow was steady, the back-pressure regulator (Swagelok Co. Ltd., model Z85943001) was closed to increase the pressure of the system. The pressure at the high-pressure pumps and back-pressure inlet were monitored by two pressure gauges (Swagelok Co. Ltd., model EN 837-1). In addition, the

0.5 μm inline filter (Swagelok Co. Ltd., model SS-2F-0.5) was attached to the back-pressure inlet to prevent damage from solid particles. The relief valve (Swagelok Co. Ltd., model SS-4R3A) was installed at the heat exchanger outlet. Once the system pressure was constant, which took approximately 3 hours until the system reached its steady state, the biodiesel products were sampled in triplicate at 15 min intervals and analyzed for ester content following the EN14103 standard method.

In this work, we calculated the residence time (τ , min) using equation 1:

$$\tau = \frac{V}{\frac{\dot{m}_e}{\rho'_e} + \frac{\dot{m}_o}{\rho'_o}} \quad (1)$$

where V is the reactor volume (cm^3), \dot{m} is the mass flow rate (g min^{-1}) at ambient conditions and ρ' is the density (g cm^{-3}) of the pure substance at the reaction conditions. The subscripts e and o indicate that parameter for ethanol and palm oil, respectively. The density of hydrated ethanol (95.5%) at elevated temperatures and pressures was taken from the literature.⁹ Since palm oil has a high boiling point (approximately 500 °C), the effect of pressure on its density is very small.¹⁰ Thus, the density of RPO and UPO was assumed to be a linear function of temperature only.¹¹

Biodiesel sample analysis

The fatty acid ethyl ester (FAEE) content in biodiesel samples was measured by gas chromatography (GC) on a Shimadzu GC model GC-14B SPL equipped with a capillary column (30 m \times 0.25 mm o.d. \times 0.25 μm film thickness, DB-WAX, J&W Scientific) and a flame ionization detector. A known amount of the biodiesel sample and an internal standard, methyl heptadecanoate, were diluted with *n*-heptane before injection and standardized following the EN 14103 method. The %FAEE content (wt.%) was defined as the ratio of the weight of FAEE obtained from GC to the total weight of the biodiesel sample. The biodiesel sample that was obtained from the optimal conditions was further analyzed for its fuel properties by the American Standard of Testing Materials (ASTM) testing methods, including the kinematic viscosity (D445), density (D1298), higher heating value (D240), flash point (D93), distillation characteristic (D2887) and cetane index (D967).

Due to the biodiesel samples that were obtained from optimal condition having approximately 80% (m/m) FAEE content, the samples were additionally analyzed using a high-temperature GC, Varian Technology model CP3800, equipped with a capillary column

(30 m \times 0.250 mm \times 0.1 μm , Rtx®-65TG, Restek) and a flame ionization detector to identify the other components. The temperatures of the injector and detector were kept isothermally at 360 °C during analysis time. The column temperature was set at 150 °C, holding for 3 min and increased to 370 °C at a heating rate of 15 °C min^{-1} . Furthermore, gas chromatography coupled with mass spectrometry (GC-MS), a Shimadzu model QP2010 equipped with a capillary column (30 m \times 0.25 mm \times 0.25 μm , DB-5ms, J&W Scientific), was employed to qualitatively analyze the degradation products observed at temperatures over 300 °C. The injection port, ion source and interface temperature were 250, 200 and 230 °C, respectively. The column was held at 50 °C for 5 min, increased to 200 °C at 15 °C min^{-1} and was then held constant at 200 °C for 35 min.

Results and Discussion

RPO and UPO characterization

The RPO and UPO samples were analyzed by the standard methods as described in the experimental section. The analytical results are shown in Table 1. Used oil is mostly sold to local biodiesel producers including private and public companies for approximately 0.42-0.58 USD *per* kilogram.

The fatty acid profile and molecular weight of UPO differs slightly from RPO due to chicken fat contamination. Chicken fat dissolved into RPO beyond the frying process, increases the levels of oleic and linoleic acids in UPO. Consequently, the UPO has a higher degree of unsaturation than RPO, which corresponds to a higher iodine value (Table 1). Because of the higher levels of UFAs, the molecular weight of UPO is slightly lower than that of RPO.

The acid value of UPO is commonly higher than the RPO because hydrolysis commonly occurs during the cooking process.¹³ The excess amount of FFA shows catalytic activity in supercritical methanol as reported elsewhere.¹⁴ The ester content in the biodiesel samples obtained from RPO and UPO should be the result of increased levels of FFA.

The water content in both RPO and UPO samples was very low because the samples were settled several days before sampling the top layer. The viscous bottom layer is likely to contain a higher water content, although the small amounts (less than 1% by weight) precluded analysis. Thus, because of the small amount of water and the supercritical reaction conditions, the effects of water content can be ignored in this study.

Kinematic viscosity and density of UPO are slightly higher than those of RPO as a result of hydrolytic and

Table 1. The physical and chemical properties of RPO, UPO and chicken fat

Fatty acid	Carbon number	Degree of unsaturation	MW / (g mol ⁻¹)	RPO / wt.%	UPO / wt.%	Chicken fat / wt.% ¹²
Lauric acid	12	0	200	0.46	0.83	n.r.
Myristic acid	14	0	228	1.22	1.24	n.r.
Palmitic acid	16	0	256	47.94	42.41	21.0
Stearic acid	18	0	284	4.23	2.34	5.5
Total saturated fatty acids				237	227	31
Palmitoleic acid	16	1	254	n.d.	n.d.	7.7
Oleic acid	18	1	282	37.00	41.46	48.5
Linoleic acid	18	2	280	9.15	14.16	17.3
Total unsaturated fatty acids (UFAs)				61	117	149
Molecular weight / (g mol ⁻¹)				928	914	n.r.
Iodine value / (g per 100 g)				53.5 ± 5	68.5 ± 5	n.r.
Acid value / (mg KOH g ⁻¹)				0.2	11.1	n.r.
Water content / (g per 100 g)				0.0	0.1	n.r.
Kinematic viscosity / (mm s ²)				31.8	45.0	n.r.
Density / (g cm ⁻³)				0.904	0.916	n.r.

n.d.: not detected; n.r.: not reported.

polymerization reactions.¹⁵ It should be noticed that the polymerized glycerides could not be converted to FAEE through the transesterification reaction due to the change in the chemical structure. Therefore, the lowered %FAEE content in biodiesel obtained from UPO could be expected due to higher viscosity and density.

The effects of temperature

The changes of FAEE with reaction temperature for biodiesel production obtained from RPO and UPO are shown in Figures 2a and b, respectively.

For both oil samples, the total FAEE content steadily increases with temperature and levels off at temperatures over 315 °C. The constant of total FAEE content appears because the degradation of ethyl linoleate (C18:2) reduces total FAEE content. It was reported that the UFAs begin to degrade at 300 °C and reaction times exceeding 30 minutes.¹⁶ The slightly higher total FAEE content in UPO biodiesel was due to higher linoleic acid content in the UPO sample. To prevent the degradation of ethyl linoleate (C18:2), the effects of other operating parameters were accordingly investigated at 300 °C.¹⁷ According to GC-MS results, it was found that the degradations products are varied such as ethyl esters, including ethyl undecanoate (C11:0), ethyl nonanoate (C9:0), alkane and alkene hydrocarbons (C6-C9). The GC-MS results conformed to our previous work.¹⁸

A slow reaction rate of UFAs with supercritical alcohols has been reported in the literature.^{19,20} Since UPO has higher levels of UFAs than RPO, lower reactivity of UPO was to be

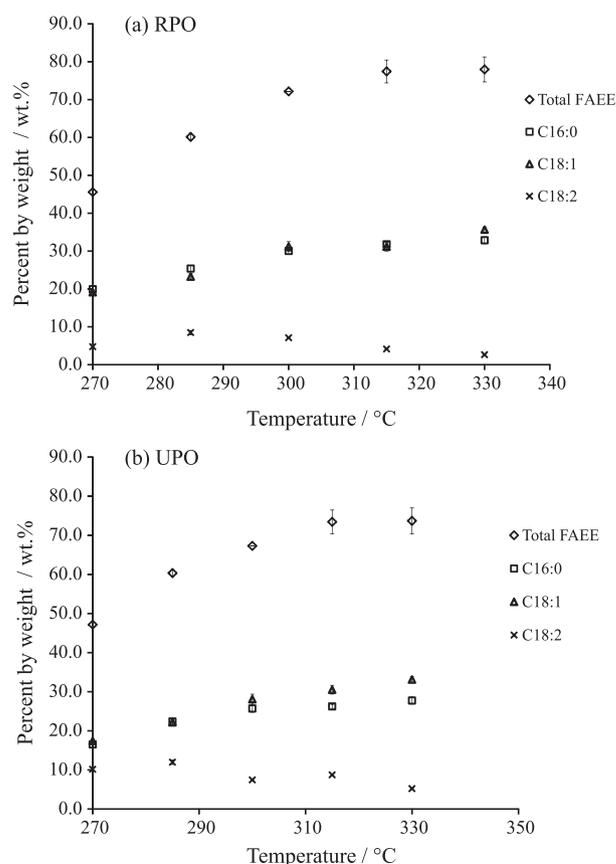


Figure 2. FAEE content as a function of reaction temperature at total flow rate of 3.5 mL min⁻¹, ethanol:oil molar ratio of 30:1 and pressure of 20 MPa.

expected. The effect of UFAs on rate of reaction is reduced by the catalytic effect of FFA in UPO as mentioned in the RPO and UPO characterization section.¹⁴ Therefore, the

Table 2. The optimal condition of this work comparing to the other works on continuous production of biodiesel in SCE

Vegetable oil	T / °C	P / MPa	Molar ratio	%FAEE content	Reference
Soybean	300	20.0	1:30	70.0	Vieitez <i>et al.</i> ²¹
Soybean	325	20.0	1:20	ca. 70	da Silva <i>et al.</i> ²²
Castor	300	20.0	1:30	75.0	Vieitez <i>et al.</i> ²³
Sunflower	345	16.0	1:40	91.0	Velez <i>et al.</i> ⁸
Sunflower ^a	200	20.0	1:25	ca. 80	Santana <i>et al.</i> ²⁴
Waste soybean oil ^b	300	20.0	1:20	82.2	Gonzalez <i>et al.</i> ²⁵
Used soybean oil ^c	325	20.0	ca. 1:18	ca. 73	Abdala <i>et al.</i> ²⁶
Palm olein	300	30.0	1:30	80.1	This work
Used palm olein	300	30.0	1:30	73.4	This work

^a1:3 molar ratio of ethanol: CO₂ was added as co-solvent; ^b10% (m/m) of water was added to enhance the reaction; ^c20% (m/m) of *n*-hexane was added as co-solvent.

reaction rate of UPO is slightly slower than that of RPO due to the antagonistic effect of UFAs and FFA.

Because the UFAs have low reactivity, the high operating temperature requires enhancing the rate of reaction in the catalytic-free process. However, the UFAs tend to degrade at temperatures over 300 °C and then lowered %FAEE content would be obtained.¹⁶ This contradiction is a great barrier for the catalytic-free SCE process to achieve the 96.5% (m/m) FAEE content to comply with the international standard for biodiesel (EN14214). According to the literature as summarized in Table 2, the reported %FAEE content were below the 96.5% (m/m) at their optimal conditions.

The assistive techniques that keep the catalyst-free concept, such as the addition of co-solvents, the two-step or the Saka-Dadan process¹⁴ and the dual-reactor process,²⁷ could be employed to enhance the FAEE content. On the other hand, addition of heterogeneous catalysts such as CaO and MgO has also been reported as techniques to maximize FAEE content using the SCE process.^{28,29} However, it was reported that the FFA in feedstock somewhat poisons those heterogeneous catalysts.^{30,31}

Effects of pressure

According to Figure 3, it is clear that the change of the total FAEE content for both RPO and UPO samples is similar. As a result of a higher reactivity of RPO (see The Effects of Temperature section), total FAEE content in biodiesel obtained from RPO is higher than that in UPO biodiesel for all conditions. The comparison of the results with da Silva *et al.*,²² who investigated effects of pressure at temperature of 300 °C and ethanol:oil molar ratio of 20:1 is illustrated in Figure 3. It was found that the total FAEE content observed in this work is higher than that reported

by da Silva *et al.*²² due to a small level of UFA and high ethanol:oil molar ratio.

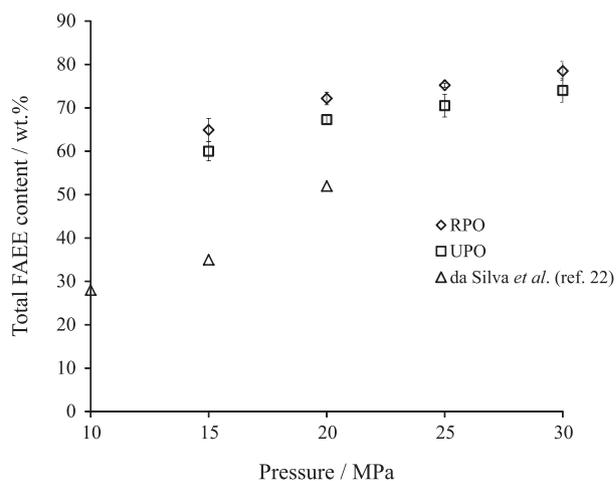


Figure 3. Effect of pressure on total FAEE content (wt.%) for biodiesel production in SCE at total flow rate of 3.5 mL min⁻¹, ethanol:oil molar ratio of 30:1 and temperature of 300 °C.

The operating pressure insignificantly affects the tendency of both RPO and UPO curves in Figure 3 because it influences reactivity of SCE less than temperature does, since the reactivity of SCE is dominated by its acidity, which reversely depends on the degree of hydrogen bonding. The study of the proton nuclear magnetic resonance (NMR) chemical shift of ethanol demonstrated that, below the critical pressure, hydrogen bonding of ethanol suddenly drops when temperature reaches the critical temperature. Above the critical pressure of ethanol, hydrogen bonding gradually decreases with temperature, but rises sharply when pressure exceeds the critical pressure. However, hydrogen bonding remains virtually constant with increasing pressure, especially above 300 °C.³²

Effects of ethanol:oil molar ratio

The change of total FAEE content with ethanol:oil molar ratio is illustrated in Figure 4. Because the critical point of vegetable oil and ethanol mixture is reduced when the ethanol:oil molar ratio increased, the FAEE content is enhanced at constant temperature and pressure.³³ On the other hand, an excessive ethanol:oil molar ratio also lowers the density of reaction mixture. Consequently, in the continuous flow system, the lowered density requires a large reactor volume for a sufficient residence time to achieve complete conversion. Since the total FAEE in biodiesel sample obtained from both RPO and UPO at ethanol:oil molar ratios of 30:1 and 40:1 are similar, the optimal ethanol:oil molar ratio is 30:1 to avoid excess alcohol used in the SCE process.

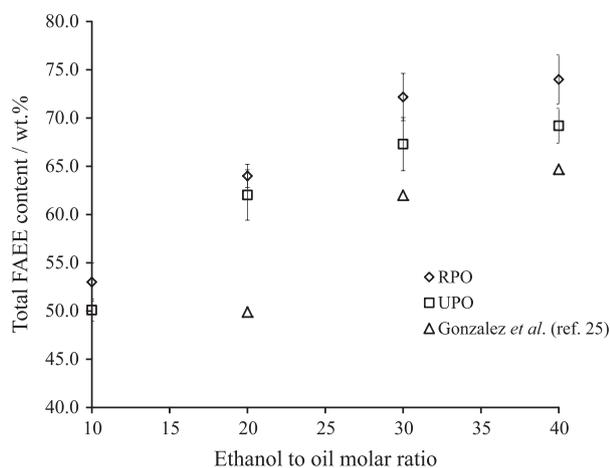


Figure 4. Total FAEE content as a function of ethanol:oil molar ratio at flow rate of 3.5 mL min^{-1} , temperature of $300 \text{ }^\circ\text{C}$ and pressure of 30 MPa .

When the ethanol:oil molar ratio is more than 30:1, the FAEE content in UPO biodiesel increases slower than that in RPO biodiesel because the FFA concentration in UPO was diluted by ethanol. Because the FFA in UPO performs as an acid catalyst as mentioned in the effect of temperature section, the rate of reaction is reduced following addition of excess ethanol. Furthermore, the high level of UFAs also reveals the lower reactivity of UPO. The results found in this work are higher than that reported by Gonzalez *et al.*²⁵ because UPO has a high FFA concentration and a low level of UFAs. Therefore, the FAEE content in the resultant biodiesel is approximately 5% lower when using UPO instead of RPO as feedstock.

Effects of residence time

The effects of residence time are illustrated in Figures 5a and b, respectively. The total FAEE content in

RPO biodiesel steadily increases until 60 min of residence time (Figure 5a), while the total FAEE content in UPO reaches the maximum value at 30 min of residence time (Figure 5b). This behavior reveals that the catalytic effect of FFAs in UPO is reduced because the FFAs are consumed by the esterification in the SCE process. Although the by-product of esterification is water, the hydrolysis reaction also takes place and generates fresh FFA molecules; however, the hydrolysis reaction rate is much slower than the rate of esterification and transesterification reactions at $300 \text{ }^\circ\text{C}$ and 30.0 MPa .¹⁴

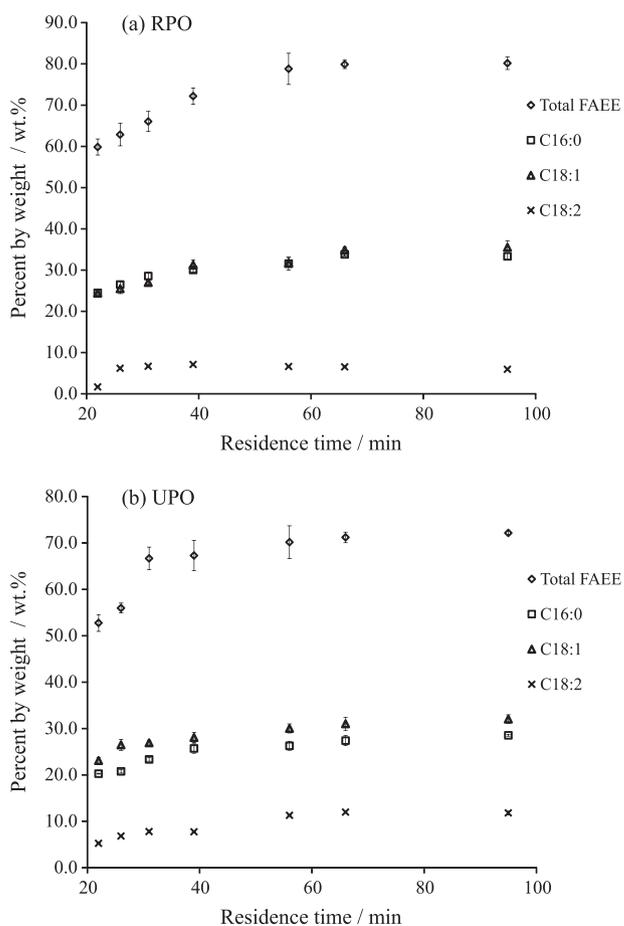


Figure 5. FAEE content as a function of residence time at ethanol:oil molar ratio of 30:1, temperature of $300 \text{ }^\circ\text{C}$ and pressure of 30 MPa .

Fuel properties of biodiesel samples

The fuel properties of samples obtained from the optimal conditions ($300 \text{ }^\circ\text{C}$, 30.0 MPa and 30:1 ethanol:oil molar ratio) were analyzed. The analytical results and the European biodiesel specification are shown in Table 3.

It is clear that the ester content of both samples lies outside the limits of the European specification. Although the ester content of 96.5% is required in many biodiesel specifications, including the European (EN 14213 and

Table 3. Selected fuel properties of biodiesel samples and the European biodiesel specification values (EN14214)

Properties	Biodiesel sample		Limits	
	RPO	UPO	Min	Max
Ester content / wt.%	80.1	73.4	96.5	–
Kinematics viscosity at 40 °C / (mm s ⁻²)	5.5	4.5	3.5	5.0
Density at 15 °C / (kg m ⁻³)	870	871	860	900
Cetane index	53	52	51	–
Flash point / °C	175	176	120	–
Heating value / (MJ kg ⁻¹)	36	33	–	–

EN 14214), US (ASTM D6751), Japanese (JASO M360), Thai (TIS 2313-2549) and South African (SANA 1935) biodiesel standards, this is not specified in some countries, such as India and Brazil.³⁴ India and Brazil are interested in blending biodiesel with petrol-diesel fuel to use in automobiles,³⁵ while the other countries expect to use pure biodiesel (B100) in the vehicles. According to the high-temperature GC results, the other components in RPO and UPO biodiesel obtained from optimal conditions were the unreacted glycerides, mainly diglycerides and monoglycerides.

The viscosity of RPO biodiesel is also out of the range for the European specification, whilst the viscosity of UPO biodiesel lies within the specification range. A viscosity range of 3.5-5.0 mm s⁻² is mostly specified in biodiesel standards, such as the European, Japanese, Thai, Austrian and South African standards. However, ranges of viscosity in the US and Indian specifications are between 1.9-6.0 and 2.5-6.0 mm s⁻², respectively. In addition, the limit of viscosity range is not specified in the Brazilian specification, but it needs to be reported.³⁴ Thus, the viscosity of RPO biodiesel lies within the ranges of those specifications. The viscosity of blended fuel can be adjusted by the proportion of biodiesel and petro-diesel, as demonstrated in the literature.^{36,37} For example, 20% (v/v) of the RPO and UPO biodiesels obtained in this work could be blended with 80% (v/v) of common petrol-diesel, which has a viscosity of 3.0 mm s⁻², to give B20 fuel that has an approximate viscosity of 4.0 mm s⁻².

The density, the cetane index and the flash point of both biodiesel samples are within the limited values of EN14214 specification. The heating value is not specified in the standard of biodiesel for vehicles, but its minimum limit is 35.0 MJ kg⁻¹ for biodiesel as heating oil in the European standard (EN 14213). Thus, the UPO biodiesel is not appropriate for use as a heating oil due to its relatively low heating value.

Conclusions

The comparative study of biodiesel feedstocks, RPO and UPO, was successfully conducted. The ester content of the resultant biodiesel decreased due to higher UFAs in UPO. Biodiesel samples derived from both RPO and UPO could be used as an alternative fuel after slight improvement in their viscosity characteristics. Not only the FFA content in used cooking oil is important, but also the amount of UFAs in considering the operating conditions, especially temperature, for biodiesel production under the SCE process. Due to differences in degree of unsaturation, biodiesel production under the SCE process reached equilibrium at 30 and 60 min of reaction time for UPO and RPO, respectively. Thermal degradation of UFAs was not observed at 300 °C and 90 min of reaction time. According to the fuel properties of biodiesels, both RPO and UPO biodiesels obtained from the SCE process should be blended with petro-diesel fuel before use in vehicles.

Acknowledgments

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References

- Chhetri, A.; Watts, K.; Islam, M.; *Energies* **2008**, *1*, 3.
- Sawangkeaw, R.; Ngamprasertsith, S.; *Renewable Sustainable Energy Rev.* **2013**, *25*, 97.
- Banerjee, A.; Chakraborty, R.; *Resour. Conserv. Recycl.* **2009**, *53*, 490.
- Alamu, O. J.; Waheed, M. A.; Jekayinfa, S. O.; *Fuel* **2008**, *87*, 1529.
- Balat, M.; *Energy Sources* **2008**, *30*, 429.
- Gui, M. M.; Lee, K. T.; Bhatia, S.; *J. Supercrit. Fluids* **2009**, *49*, 286.
- da Silva, C.; de Lima, A. P.; de Castilhos, F.; Cardozo Filho, L.; Oliveira, J. V.; *Biomass Bioenergy* **2011**, *35*, 526.
- Velez, A.; Soto, G.; Hegel, P.; Mabe, G.; Pereda, S.; *Fuel* **2012**, *97*, 703.
- Abdurashidova, A.; Bazaev, A.; Bazaev, E.; Abdulagatov, I.; *High Temp.* **2007**, *45*, 178.

10. Goodrum, J. W.; Geller, D. P.; *Bioresour. Technol.* **2002**, *84*, 75.
11. Anand, K.; Ranjan, A.; Mehta, P. S.; *Energy Fuels* **2010**, *24*, 3262.
12. Marulanda, V. F.; Anitescu, G.; Tavlarides, L. L.; *J. Supercrit. Fluids* **2010**, *54*, 53.
13. Lam, M. K.; Lee, K. T.; Mohamed, A. R.; *Biotechnol. Adv.* **2010**, *28*, 500.
14. Minami, E.; Saka, S.; *Fuel* **2006**, *85*, 2479.
15. Kulkarni, M. G.; Dalai, A. K.; *Ind. Eng. Chem. Res.* **2006**, *45*, 2901.
16. Imahara, H.; Minami, E.; Hari, S.; Saka, S.; *Fuel* **2008**, *87*, 1.
17. Vieitez, I.; da Silva, C.; Alckmin, I.; de Castilhos, F.; Oliveira, J. V.; Grompone, M. A.; Jachmanian, I.; *J. Supercrit. Fluids* **2011**, *56*, 265.
18. Sawangkeaw, R.; Teeravitud, S.; Bunyakiat, K.; Ngamprasertsith, S.; *Bioresour. Technol.* **2011**, *102*, 10704.
19. Choi, C.-S.; Kim, J.-W.; Jeong, C.-J.; Kim, H.; Yoo, K.-P.; *J. Supercrit. Fluids* **2011**, *58*, 365.
20. Rathore, V.; Madras, G.; *Fuel* **2007**, *86*, 2650.
21. Vieitez, I.; Pardo, M. J.; da Silva, C.; Bertoldi, C.; de Castilhos, F.; Oliveira, J. V.; Grompone, M. A.; Jachmanián, I.; *Energy Fuels* **2009**, *23*, 558.
22. da Silva, C.; de Castilhos, F.; Oliveira, J. V.; Filho, L. C.; *Fuel Process. Technol.* **2010**, *91*, 1274.
23. Vieitez, I.; Pardo, M. J.; da Silva, C.; Bertoldi, C.; de Castilhos, F.; Oliveira, J. V.; Grompone, M. A.; Jachmanián, I.; *J. Supercrit. Fluids* **2011**, *56*, 271.
24. Santana, A.; Macaira, J.; Larrayoz, M. A.; *Fuel Process. Technol.* **2012**, *102*, 110.
25. Gonzalez, S. L.; Sychoski, M. M.; Navarro-Diaz, H. J.; Callejas, N.; Saibene, M.; Vieitez, I.; Jachmanian, I.; da Silva, C.; Hense, H.; Oliveira, J. V.; *Energy Fuels* **2013**, *27*, 5253.
26. Abdala, A. C. A.; Colonelli, T. A. S.; Trentini, C. P.; Oliveira, J. V.; Cardozo-Filho, L.; Silva, E. A.; Silva, C.; *Energy Fuels* **2014**, *28*, 3122.
27. D'Ippolito, S. A.; Yori, J. C.; Iturria, M. E.; Pieck, C. L.; Vera, C. R.; *Energy Fuels* **2006**, *21*, 339.
28. Umdu, E. S.; Tuncer, M.; Seker, E.; *Bioresour. Technol.* **2009**, *100*, 2828.
29. Sawangkeaw, R.; Tejvirat, P.; Ngamcharassrivichai, C.; Ngamprasertsith, S.; *Energies* **2012**, *5*, 1062.
30. Kouzu, M.; Hidaka, J.-s.; *Fuel* **2012**, *93*, 1.
31. Lukić, I.; Kesić, Ž.; Maksimović, S.; Zdujić, M.; Liu, H.; Krstić, J.; Skala, D.; *Fuel* **2013**, *113*, 367.
32. Hoffmann, M. M.; Conradi, M. S.; *J. Phys. Chem. B* **1998**, *102*, 263.
33. Anitescu, G.; Deshpande, A.; Tavlarides, L. L.; *Energy Fuels* **2008**, *22*, 1391.
34. Hoekman, S. K.; Broch, A.; Robbins, C.; Ceniceros, E.; Natarajan, M.; *Renewable Sustainable Energy Rev.* **2012**, *16*, 143.
35. Abdelnur, P. V.; Saraiva, S. A.; Catharino, R. R.; Coelho, M.; Schwab, N.; Garcia, C. M.; Schuchardt, U.; Souza, V.; Eberlin, M. N.; *J. Braz. Chem. Soc.* **2013**, *24*, 946.
36. Mesquita, F. M. R.; Feitosa, F. X.; Carmo, F. R. d.; Santiago-Aguiar, R. S.; Sant'Ana, H. B.; *Braz. J. Chem. Eng.* **2012**, *29*, 653.
37. Verduzco, L. F. R.; *Renewable Sustainable Energy Rev.* **2013**, *19*, 652.

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