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Comparison of biodiesel yield from seed oils extracted by ultrasound-assisted chemical solvent and supercritical CO_2 methods

Maria Cristina Macawile[1,2*], Joseph Auresenia[1]

[1] *Gokongwei College of Engineering, De LaSalle University 2401 Taft Avenue, Malate, Manila, 1004 Philippines*
[2] *College of Engineering, Architecture, and Technology, De LaSalle University - Dasmariñas DBB-B, 4115 West Ave, Dasmariñas, Cavite, 4114, Philippines*

ABSTRACT

The seeds from *Hibiscus cannabinus* and *Gliricidia sepium*, also known as kenaf and kakawate seeds respectively, were used as sources of oil in the production of biodiesel. The oil was extracted using two methods: ultrasound-assisted chemical solvent (UACS) and supercritical fluid. The performances of two methods were compared based on their oil and biodiesel yields. Using supercritical CO_2 ($SCCO_2$), the highest oil yield recorded was 13.19% from kenaf at operating conditions of CO_2 flow rate=2.5ml/min, T=70°C, P=30MPa, and 11.79% from kakawate at operating conditions of CO_2 flow rate = 2.5ml/min, T=60°C, P=30 MPa. Using multi-walled carbon nanotubes and concentrated sulfuric acid under thermal decomposition, a sulfonic catalyst was produced and used in simultaneous esterification-transesterification reactions. The individual chemical compositions of kakawate and kenaf methyl esters were analyzed using gas chromatography–flame ionization detector. Higher biodiesel yields were observed for oil samples extracted using $SCCO_2$.

Keywords: Biodiesel, Extraction, Kakawate, Kenaf, Supercritical carbon dioxide.

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Corresponding Author:
Maria Cristina Macawile
mamacawile@dlsud.edu.ph

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1. INTRODUCTION

Biodiesel is one of the promising alternative resources for diesel engines. It is defined as mono-alkyl, usually methyl esters of vegetable oils, animal fats, waste cooking oils, or potentially other triacylglycerol containing feedstock. It is renewable, biodegradable, environment-friendly, non-toxic, and readily available (Atabani et al., 2013).

The use of vegetable oil has been a significant concern in biodiesel production because it competes with the said oil's use for food materials and consumption. Issues on food security and other environmental problems caused by utilizing the land for fuel rather than food in developing countries were seen as matters that needed to be addressed immediately. Consequently, a need for an alternative to vegetable oil has risen, and the use of second-generation feedstock has shown potential to be one. Non-edible oils from kakawate and kenaf seeds are promising alternatives to the first-generation feedstock to ensure sustainable biodiesel production.

A number of studies have already been conducted to evaluate the performance of kakawate and kenaf seed oil in the production of methyl esters. In one study, oil from kakawate seed was obtained using a Soxhlet extractor, and sodium methoxide catalyst was added to generate kakawate methyl esters (Knothe et al., 2015). In a similar study, Soxhlet extracted oil from kenaf seeds underwent transesterification using a 1% sodium methoxide catalyst (Knothe et al., 2013). Soxhlet extraction is a well-established and widely used analytical method for removing oil from solid samples using various organic solvents. However, this method requires a longer reaction time, a larger amount of toxic

solvents and typically results in low yield or low-quality of extracts (Pawliszyn, 2012).

Supercritical fluid extraction is a new separation method established in recent years. It is regarded for its selectivity for operating with solvent at slightly elevated pressure and temperature. Among the supercritical fluids, $SCCO_2$ is a non-toxic, non-flammable, inexpensive, naturally abundant, relatively inert, and environmentally friendly solvent. Over the years, it has earned significant attention as an alternative to organic solvent to extract oils. Several studies have found that $SCCO_2$ extraction is more effective than Soxhlet extraction. Among these are the $SCCO_2$ extraction studies conducted by Aladic et al. (2015) on obtaining the highest tocopherol content and lowest pigment concentration from hemp seeds, as well as the $SCCO_2$ extraction studies conducted by Przygoda and Wejnerowska (2015) on acquiring high tocopherol concentration from quinoa seeds. Moreover, $SCCO_2$ has proven its efficacy in extracting oil from different seeds of Moringa oleifera (Porto et al., 2016), Silybum marianum (Celik et al., 2015), Dipteryx alata (dos Santos et al., 2016), Passiflora edulis (Barrales et al., 2015), Punica granatum (Liu et al., 2009), Juniperus communis L. (Larkeche et al., 2015), Helianthus annuus (Rai et al., 2016), and Dracocephalum kotschyi (Sodeifian et al., 2017).

The high free fatty acid (FFA) content of second-generation feedstocks, such as non-edible seed oils, can be addressed by utilizing an acid catalyst that can simultaneously perform esterification and transesterification reactions (Macawile et al., 2020). Acid catalysts are categorized as homogenous and heterogeneous, with the latter having various advantages such as ease of separation, reusability, and lower energy consumption (Shu et al., 2009). The catalyst support used in the synthesis of heterogeneous acid catalysts varies from commercially available material like mesoporous silica to substances that are still being studied like agricultural wastes and industrial byproducts (Istadi et al., 2015, Melero et al., 2010, Devi et al., 2014 and Suryaputra et al., 2013). One of the emerging carbon-based catalyst supports is multiwalled carbon nanotubes (MWCNT), which can withstand high reaction temperatures and longer reaction time due to their excellent thermal and mechanical properties (Kish et al., 2010).

Presently, much research is conducted to see how different types of feedstock are used to increase biodiesel yield. This study examines not only different types of high FFA feedstock but also the effect of two extraction methods. The effectiveness of UACS and $SCCO_2$ as extraction methods was investigated with an assessment based on the quality of kakawate and kenaf seed oils as well as the amount of biodiesel yield.

2. MATERIALS AND METHODS

2.1 Preparation of Materials

The kenaf seeds were procured from Kenaf Green Industries in Tel Aviv, Israel, while kakawate seeds were collected locally from Laguna, Philippines. The seeds were cleaned from impurities and were oven-dried at 105ºC to a constant mass. The two types of seed were ground into powder by a fast rotating mill (Thomas Wiley Mill Model 4) at 800 rpm. The solvents such as n-hexane (RCI Labscan Inc.), methanol (RCI Labscan Inc.), carbon dioxide (99.97 %, Linde Philippines Inc.) were used without further purification. The pristine multi-walled carbon nanotube (p-MWCNT) with a purity of > 98%, 20-30 nm diameter, 10-30 μm length, and 110 m^2/g specific area, was purchased from Times Nano, Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, China.

2.2 Ultrasound-assisted Chemical Solvent Extraction of Oil

The ultrasound-assisted chemical solvent (UACS) extraction of oil from kenaf and kakawate seeds was performed with the aid of an ultrasonic cleaning bath (Elmasonic E120H, 11.8" x 9.4" x 7.9"). Three different weight ratios of ground seed to n-hexane (10:1, 20:1, and 30:1) were prepared and placed in a 500 ml flask. The mixture was ultrasonicated for 90 minutes at various temperatures of 50ºC, 60ºC, and 70ºC. It was further centrifuged at 5000 rpm for 60 minutes, and the n-hexane solvent was recovered using a rotary vacuum evaporator (Heidolph USA). All experiments were carried out in triplicate, and the % oil yield was expressed using Equation (1).

% oil yield = (amount of extracted seed oil, g / amount of seed, g) x 100 (1)

2.3 Supercritical CO2 Extraction of Oil

The supercritical carbon dioxide ($SCCO_2$) extraction of oil from seeds was performed at different working conditions of pressure (20 MPa, 30 MPa, and 40 MPa), temperature (50ºC, 60ºC, and 70ºC), and constant flow rate of 3 ml/min of CO_2. As shown in Fig. 1, the $SCCO_2$ extraction set-up is composed of (a) CO_2 source, (b) cooling jacket, (c) chiller (Eyela Model no: CA115), (d) intelligent, high-performance liquid chromatography (HPLC) pump (PU-2080 Plus, Jasco International Co., Ltd, Japan), (e) laboratory oven (Memmert GmbH + Co. kG, Germany) (f) 10 mL reactor cell, (g) back pressure regulator (BPR) (BP-2080 Plus, Jasco International Co. Ltd, Japan) and (h) oil collector. The experiments were carried out in triplicate, with a constant weight of 3 g of ground seeds and a reaction time of 90 minutes.

2.4 Preparation of Acid Catalyst

The p-MWCNT was oxidized prior to its use in the functionalization process. A mixture of 1 g p-MWCNT and 100 ml of 1:1 ratio of HNO_3:HCl was subjected to 1 hour of ultrasonication treatment and 3 hours of mixing and heating at 80ºC. The treated p-MWCNT was filtered and washed with deionized distilled water several times until the filtrate's pH remain unchanged. The samples were dried at

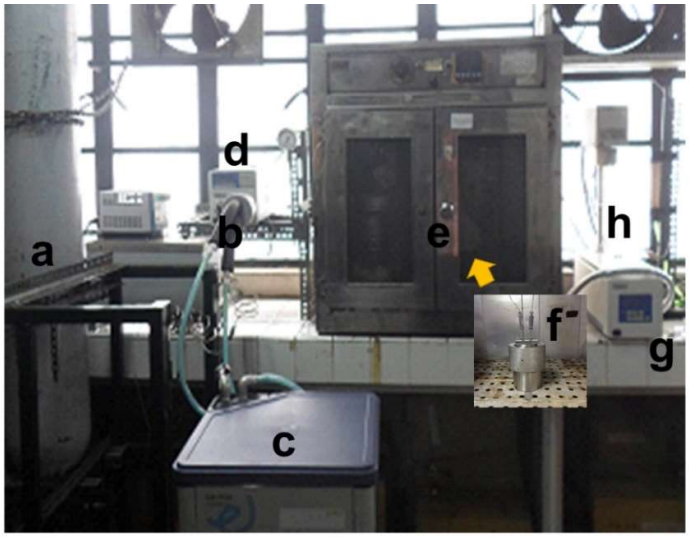

Fig. 1. Actual photo of the supercritical CO_2 system

120°C for 12 hours to obtain an oxidized MWCNT (o-MWCNT).

Sulfonation was performed under thermal treatment with concentrated H_2SO_4 (Yu et al., 2008). A 100 mg of o-MWCNT and 50 ml of acid were mixed in a 250 ml flask. It was ultrasonicated for 30 minutes and continuously mixed at 250-300 °C in an electrothermal heater for 10 hours. The mixture was diluted with water and filtered using Whatman filter paper No.1. Continuous washing and filtering of solids were carried out until the pH of the washing remains constant. The solids were dried at 120°C for at least 4 hours to obtain the sulfonated multi-walled carbon nanotube (SO_3H-MWCNT).

2.5 Characterization of Catalyst

The presence of functional groups caused by oxidation and sulfonation processes was confirmed using Fourier Transform Infrared spectrometer (Thermoscientific Nicolet 6700). The surface morphology of the catalyst was analyzed using Scanning Electron Microscope (JSM 5310, JEOL USA Inc.).

2.6 Transesterification of Seed Oil

Transesterification of oil was performed using an ultrasound-assisted process with methanol and catalyst. A mixture of 1:30 oil to methanol ratio and 10 wt.% SO_3H–MWCNT catalyst was placed in a 20 ml screw-cap glass vial. The ultrasonic bath was set at a temperature of 80°C for 1 hour. The vials were placed in a water bath shaker (Memmert Waterbath Model WNB 14) for another 8 hours at the same temperature, and mixture was allowed to settle overnight. It was centrifuged at 5000 rpm for 30 minutes until layers were formed. The top layer is composed of biodiesel and excess methanol, while the lower layer is made up of unreacted oil, catalyst, and glycerol. The top layer was collected, and excess methanol was removed by evaporation under a fume hood. The FAME content was analyzed by gas chromatography (GC)-flame ionization detector (Perkin Elmer Clarus 500) using an Elite 5 capillary column (30 m length, 0.32 mm ID, 0.25 µm thickness). The yield of biodiesel was calculated using Equation (2).

% biodiesel yield = (weight of biodiesel, g / weight of oil, g) x 100 (2)

A 1 µl of the sample was injected into the GC injection port. The injector and detector temperature were set at 250°C and 280°C, respectively. Moreover, the GC oven was initially programmed at 60°C for 3 minutes, increased to 140°C with a rate of 15°C/min, and finally ramped to 220°C with 4°C /min for 15 minutes. The internal standard used was tridecanoic acid.

3. RESULTS AND DISCUSSION

3.1 Surface functionalities of SO3H-MWCNT

Fig. 2 shows the Fourier Transform Infrared spectrometer (FTIR) spectra of MWCNT samples. The o-MWCNT and SO_3H-MWCNT were found to have a broad -OH stretch at 3672.65 cm^{-1} and 3415.96 cm^{-1}, respectively. It also shows peaks at 1383.09 cm^{-1} (o-MWCNT) and 1369.89 cm^{-1} (SO_3H-MWCNT), attributed to the stretching of COO^- in carboxylic acid salts. The occurrence of -OH and COO^- groups in o-MWCNT and SO_3H-MWCNT is an indication of successful oxidation. Oxidation creates defects on the end termini of the MWCNT walls, which becomes the primary target location for further functionalization processes (Guldi and Martin 2010). The absorption at 2851.40 cm^{-1} and 2919.25 cm^{-1} are associated with anti-symmetric and symmetric stretching of aliphatic compounds. Moreover, the presence of $–CH_2$ and $–CH_3$ aliphatic in o–MWCNT disappeared after thermal decomposition and resulted in the existence of carbonyl groups (C=O). The presence of carbonyl functional groups is a characteristic peak of

incompletely carbonized material (Akinfalabi et al., 2017). A strong symmetric stretch of sulfonic acids was detected at 1076.55 cm^{-1}, confirming the successful sulfonation process of MWCNT.

3.2 Surface Morphology of Ground Seeds

Samples of ground seeds were analyzed using Scanning Electron Microscope (SEM) to determine any changes in its surface morphology after oil extraction. The SEM micrographs of kakawate (Fig. 3a) and kenaf (Fig. 4a) seeds were compared to those that underwent UACS extraction. The extraction process caused the removal of a film layer, recognized as oil, from the seeds. Also, the dryness and roughness of the seed surface are much more visible in Figs. 3(b) and 4(b). All these observations indicate that the oil was successfully extracted from kenaf and kakawate seeds.

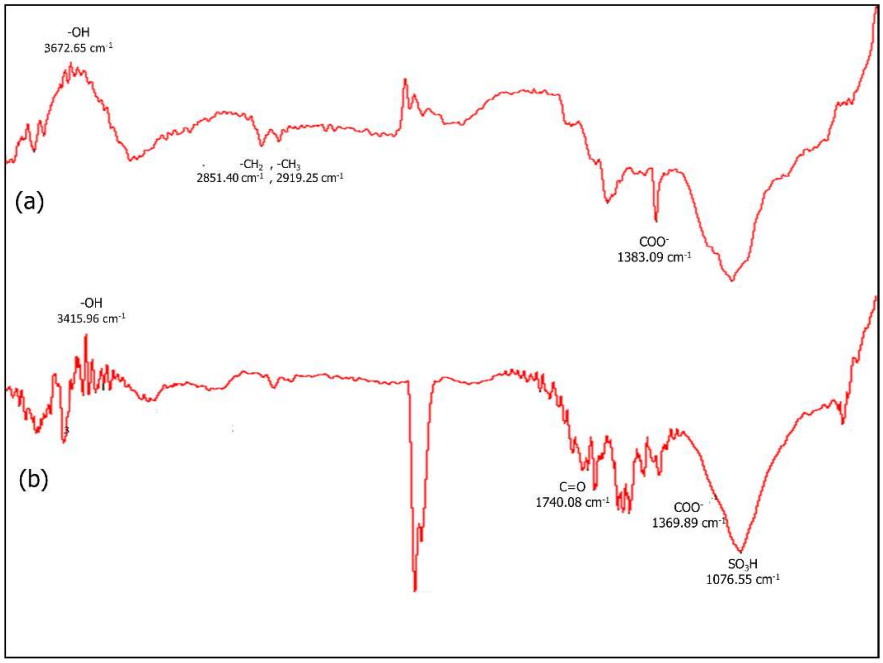

Fig. 2. FTIR Spectra of (a) o-MWCNT and (b) SO_3H- MWCNT

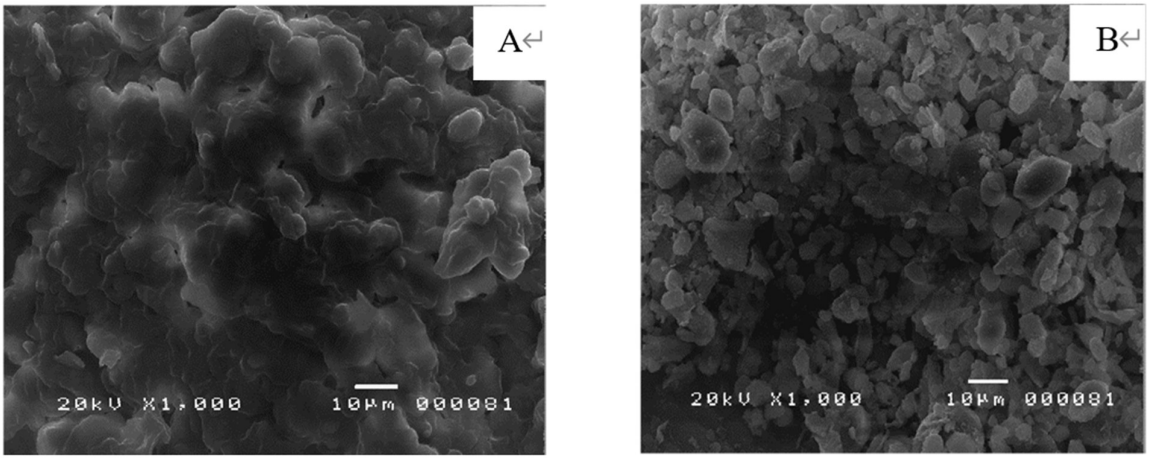

Fig. 3. Scanning electron micrographs of kakawate ground seed (a) before extraction and (b) after extraction

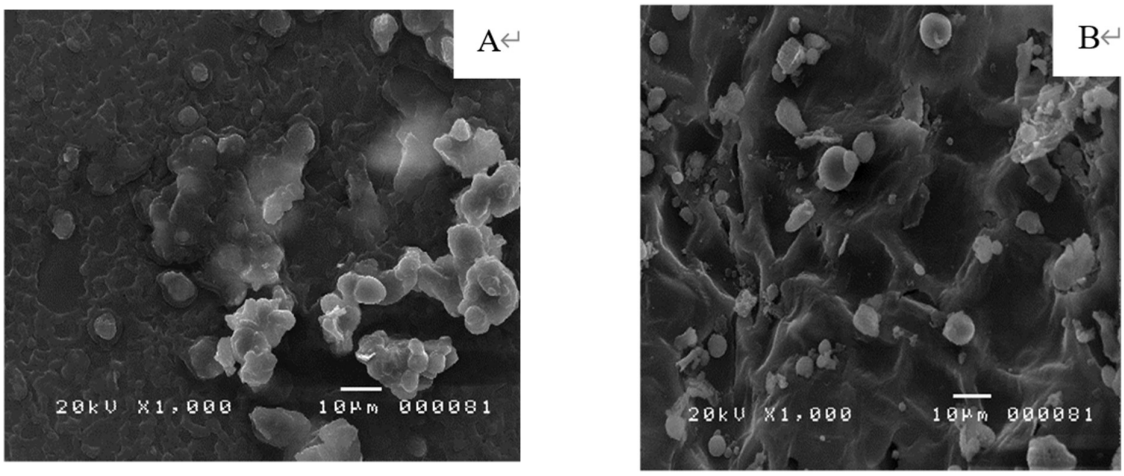

Fig. 4. Scanning electron micrographs of kenaf ground seed (a) before extraction and (b) after extraction

3.3 Extraction of Oil

A total of 24 experimental runs were conducted using UACS and $SCCO_2$ extraction methods. The highest oil yields of kakawate (20.08%) and kenaf (29.46%) seeds were observed from samples extracted using UACS. Aside from the high ability of n-hexane to extract oil, ultrasound improves oil extraction by propagating pressure waves through the mass of seeds. It causes the compression and shearing of solvent molecules that produce localized pressure, rupture of seed tissues and intracellular substances, and release into the solvent (Goula, 2013). As shown in Figs. 5(a)-5(b) and 6(a)-6(b), reaction temperature and solvent to seed ratio were the two factors that were varied during UACS extraction. Increasing the temperature from 50°C to 70°C increased the oil yield by 1.52 % for kakawate seeds and 13.22 % for kenaf seeds. The kinetic energy of the reactant molecules had increased as the temperature approached the boiling point of the n-hexane producing higher oil yield. Moreover, increasing the solvent to seed ratio from 10:1 to 30:1 increased the oil yield by 5.27% for kakawate seeds and 4.65% for kenaf seeds. The use and addition of n-hexane enhanced the mixing quality, allowing for far more contact between the reactants.

In general, experimental runs using UACS extraction resulted in a higher oil yield than those using $SCCO_2$. As shown in Figs. 5(c)-5(d) and 6(c)-6(d), reaction temperature and pressure were the two factors that were varied during $SCCO_2$ extraction. The highest oil yield from kakawate seed and kenaf seed was 11.88% and 11.90%, respectively. The oil yield increased when the operating temperature was raised from 50°C to 70°C, similar to the results obtained using the UACS method. In general, when the temperature of the $SCCO_2$ increased, its diffusivity and density also increase, allowing a higher degree of selectivity and faster mass transfer of reactants. Moreover, an increase in pressure from 20 MPa to 30 MPa, at a constant temperature of 60°C, led to a higher extraction yield. However, there is a slight decrease in the oil yield after an additional 10 MPa of pressure was placed in the system. The change in density of $SCCO_2$ is caused by the combined effect of pressure and temperature (Cheung, 1999).

3.4 Biodiesel Yield

The extracted oils from kakawate and kenaf seeds underwent simultaneous esterification and transesterification process using 10 wt% SO_3H–MWCNT, 1:30 oil to methanol molar ratio at 80°C for 8 hours. High methanol to oil ratio was used to drive the reaction at the product side, and a higher reaction temperature was employed as a suggested condition for non-edible seed oil feedstock. The selected operating conditions were almost in the same range as reported in a single step production of biodiesel from the study of Devi et al. (2014) using high FFA containing *Pongamia glabra* (>99% yield, 1:45 methanol to oil ratio, 20 wt. % catalyst, 4 h, 160°C), from the reports of Melero et al. (2010) employing crude palm oil (95% yield, 20:1 methanol-to-oil ratio, 6 wt.% catalyst, 4 h, 140°C) and from the findings of Morales et al. (2011) on using lipidic waste and low-grade oils on simultaneous esterification – transesterification reaction (80% yield, 30:1 methanol-to-oil ratio, 8 wt.% catalyst, 2 h, 160°C).

As shown in Table 1, the highest recorded % biodiesel yield from kakawate and kenaf seed oils is 33.4% and 97.9%, respectively. These data show that the operating conditions employed in the conversion of oil to biodiesel are far better suited to kenaf oil. On the other hand, the low yield achieved in the conversion of kakawate seed oil to biodiesel could be addressed through process optimization.

A higher biodiesel yield was also observed for oil samples extracted using $SCCO_2$. When comparing the average %biodiesel yield from two types of seeds, it appears that the seeds' high pigment concentration interfered with transesterification, resulting in poor methyl ester production. This can be observed from Fig. 7 where the oils extracted using the UACS method are darker in color. The oils extracted using $SCCO_2$ exhibited a golden-yellow shade,

while oils produced using the UACS method showed brown and green shades. The seed's pigment was removed along with the oil and considered as impurities of the product. These findings indicate that n-hexane is a less selective solvent for oil extraction than $SCCO_2$ and that the oil produced using UACS method may contain some undesirable compounds in biodiesel production (Gomez and de la Ossa et al., 2001).

Moreover, the higher acid values of oils produced from UACS method are possibly the cause for its lower % biodiesel yield. The kakawate and kenaf methyl esters produced from $SCCO_2$-extracted oils have a higher biodiesel yield by 5.05% and 37.09%, respectively. The quality of oil extracted using $SCCO_2$ was also observed in the study of Gomez and de la Ossa et al. (2001), where more free fatty acids (9.2%) were extracted from borage seeds using n-hexane solvent. Friedrich and List (1982) first reported that oil obtained from $SCCO_2$ extraction is substantially equivalent to a degummed, hexane extracted crude oil. The method of extraction and type of solvent affect the quality of oil and its fatty acid composition (Abdolshahi et al., 2015).

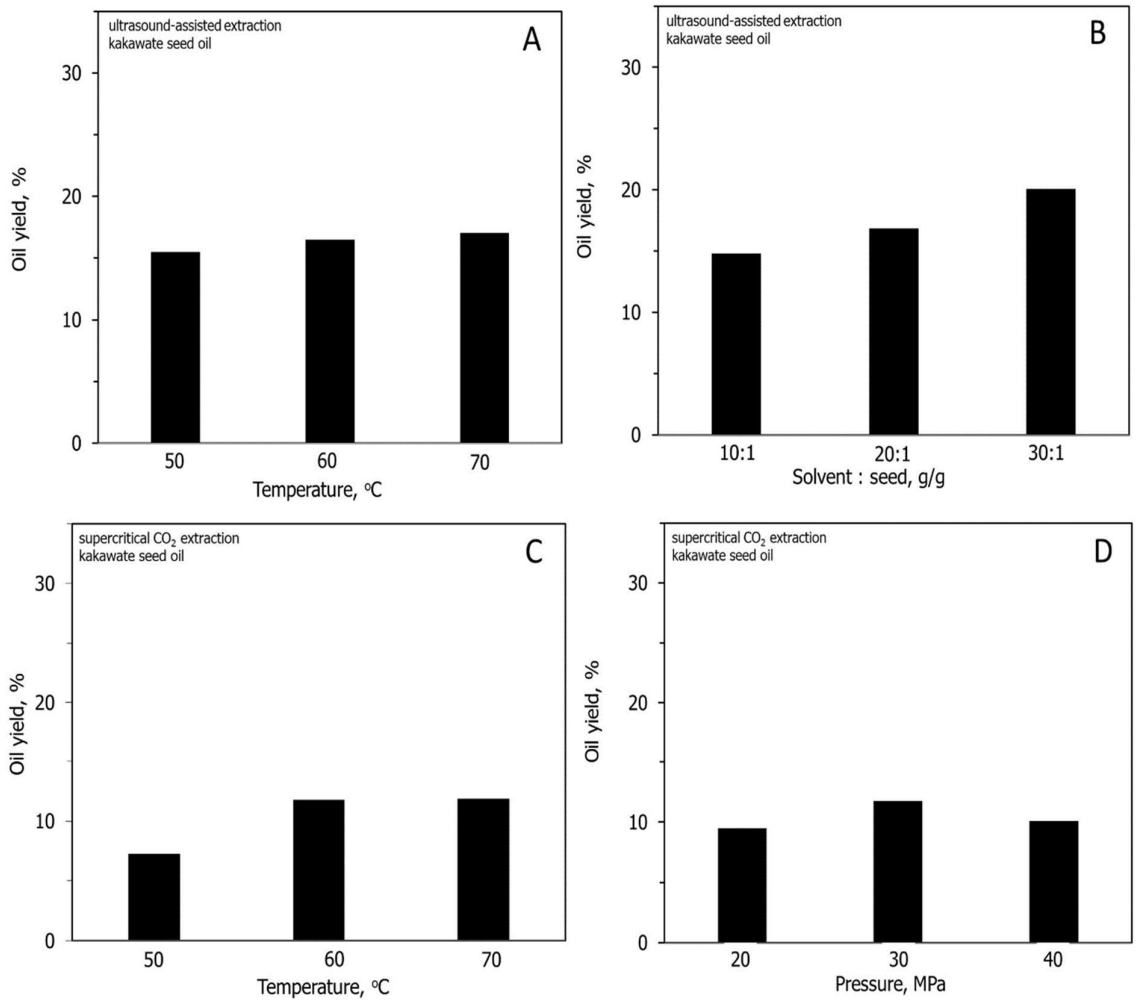

Fig. 5. Extraction of kakawate seed oil using (a) ultrasound-assisted chemical solvent extraction at 20:1 solvent : seed ratio, (b) ultrasound-assisted chemical solvent extraction at 60 °C, (c) supercritical CO2 extraction at 30 MPa, and (d) supercritical CO2 extraction at 60 °C

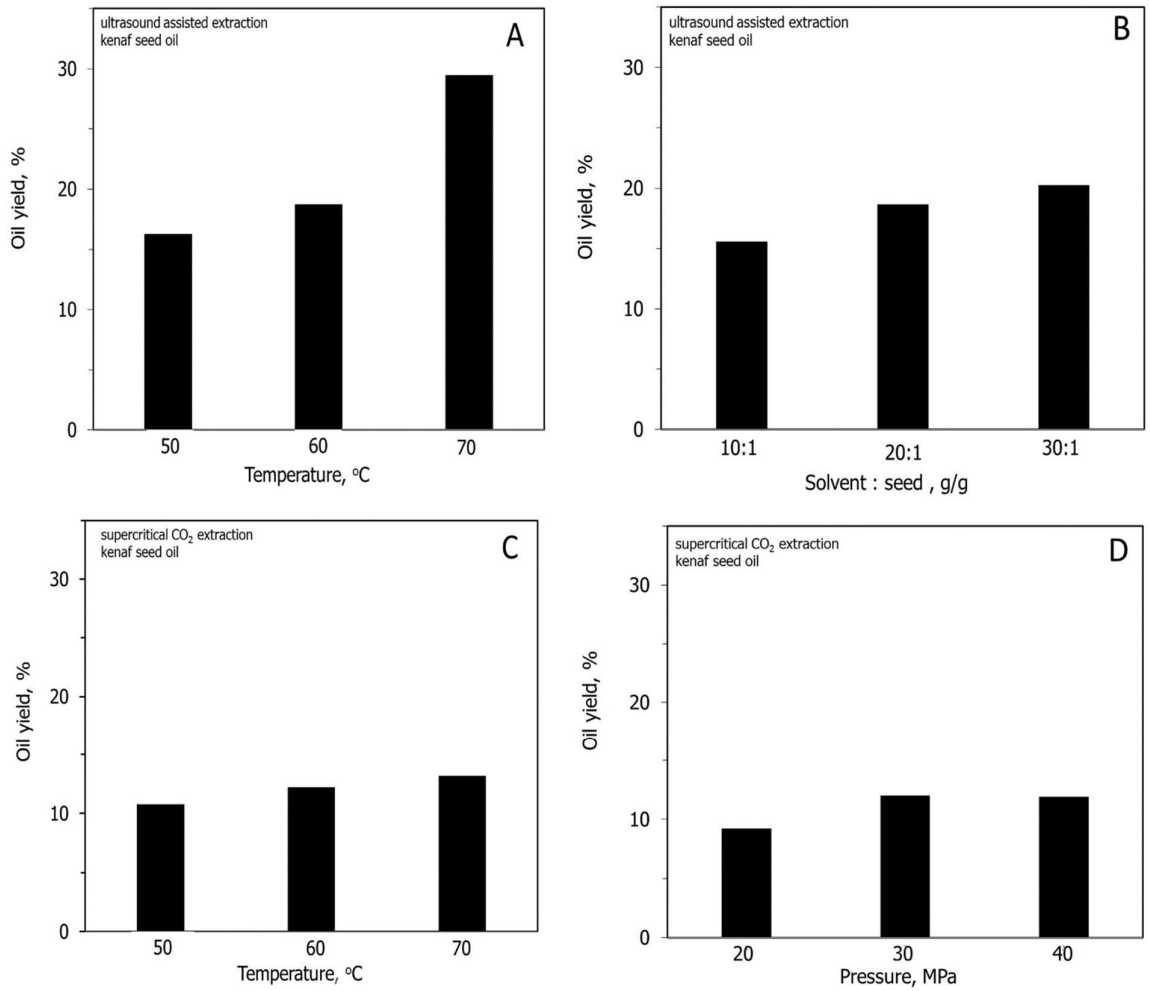

Fig. 6. Extraction of kenaf seed oil using (a) ultrasound-assisted chemical solvent extraction at 20:1 solvent:seed ratio, (b) ultrasound-assisted chemical solvent extraction at 60°C, (c) supercritical CO2 extraction at 30 MPa, and (d) supercritical CO2 extraction at 60°C.

Table 1. Result on esterification-transesterification.

Type of seed oil	Mode of oil extraction	Acid value, mg KOH/g	Esterification – transesterification operating conditions				% Biodiesel yield
			Oil: methanol	Catalyst, wt%	Time, h	Temperature, °C	
kakawate	UACS	26.7	1:30	10	8	80	28.35
kakawate	$SCCO_2$	22.8	1:30	10	8	80	33.40
kenaf	UACS	116.2	1:30	10	8	80	60.81
kenaf	$SCCO_2$	104.1	1:30	10	8	80	97.90

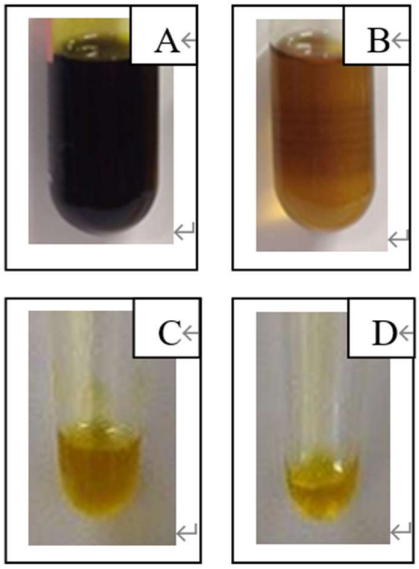

Fig. 7. Extracted oil samples: (a) kakawate seed oil using ultrasound-assisted chemical solvent, (b) kenaf seed oil using ultrasound-assisted chemical solvent, (c) kakawate seed oil using supercritical carbon dioxide, and (d) kenaf seed oil using supercritical carbon dioxide

3.5 Fatty Acid Methyl Ester Identification

The most frequent fatty acids in oils are palmitic, stearic, lauric, linoleic, and linolenic (Romano and Sorichetti, 2011). Based on the GC-FID result, these fatty acids were also present in kakawate and kenaf seed oils. Table 2 summarizes the composition of kakawate and kenaf methyl esters. The highest methyl ester composition in kakawate is linoleic acid methyl ester (35%), a di-unsaturated fatty acid. On the other hand, kenaf exhibited high concentrations of oleic acid methyl ester (39.81%) and palmitic acid methyl ester (37.16%), a mono-unsaturated methyl ester and a saturated methyl ester, respectively. According to the U.S. Department of Energy, perfect biodiesel should comprise mono-unsaturated fatty acids (U.S. Department of Energy, 2004). A high percentage of saturated fatty acid methyl esters causes problems on low-temperature properties of biodiesel (Knothe et al., 2015). In this case, kakawate methyl esters and kenaf methyl esters have 50.83% and 53.81% of unsaturated fatty acid methyl esters, respectively.

4. CONCLUSION

The heterogeneous acid catalyst, synthesized using thermal decomposition of H_2SO_4, showed high catalytic performance for simultaneous esterification-transesterification of $SCCO_2$-extracted kenaf seed oil. A maximum yield of 97.9 % was achieved at 1:30 oil to methanol ratio, 10 wt.% catalyst loading, 8 hours of reaction time, and temperature of 80ºC. An oil extracted using $SCCO_2$ resulted in a significant biodiesel yield, indicating that a higher–quality feedstock was used in the process. On the other hand, to increase biodiesel yield when using kakawate seed oil as a feedstock, process parameters such as methanol to oil molar ratio, temperature, and reaction time during the esterification-transesterification process should be optimized.

Table 2. Methyl esters composition of kakawate and kenaf

Lipid Number	Kakawate		Kenaf	
	Methyl Ester Composition	%	Methyl Ester Composition	%
C6:0	Caproic acid methyl ester	4.37	Caproic acid methyl ester	1.12
C11:0	Undecanoic acid methyl ester	3.23	Undecanoic acid methyl ester	0.80
C14:0	-	-	Tetradecanoic acid methyl ester	0.99
C16:0	Palmitic acid methyl ester	22.71	Palmitic acid methyl ester	37.16
C17:0	Heptadecanoic acid methyl ester	2.15	Heptadecanoic acid methyl ester	1.37
C18:0	Stearic acid methyl ester	16.72	Stearic acid methyl ester	4.75
C18:1	Oleic acid methyl ester	15.83	Oleic acid methyl ester	39.81
C18:2	Linoleic acid methyl ester	35.0	Linoleic acid methyl ester	14.00

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