

Article

Comparison of Biodiesel Obtained from Virgin Cooking Oil and Waste Cooking Oil Using Supercritical and Catalytic Transesterification

Jeeban Poudel ¹, Sujeeta Karki ², Nawaraj Sanjel ³, Malesh Shah ⁴ and Sea Cheon Oh ^{2,*}

¹ Waste & Biomass Energy Technology Center, Kongju National University, 1223-24 Cheonan-Daero, Seobuk-gu, Cheonan-si, Chungnam 31080, Korea; jeeban1985@gmail.com

² Department of Environmental Engineering, Kongju National University, 1223-24 Cheonan-Daero, Seobuk-gu, Cheonan-si, Chungnam 31080, Korea; sujeetakarki@gmail.com

³ Energize Nepal Project, Kathmandu University, 45200 Dhulikhel, Nepal; sanjelnawaraj@gmail.com

⁴ Department of Mechanical Engineering, Kathmandu University, 45200 Dhulikhel, Nepal; maleshji@gmail.com

* Correspondence: ohsec@kongju.ac.kr; Tel.: +82-41-521-9423

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Abstract: Comparative analysis of transesterification of virgin cooking oil (VCO) and waste cooking oil (WCO) in catalyzed and supercritical transesterification process using methanol and ethanol as solvents has been conducted in this study. The luminous point of this research was the direct comparison of catalytic and supercritical process using the ester composition obtained from virgin cooking oil and waste cooking oil transesterification. Oil to alcohol molar ratio of 1:6 and reaction condition of 65 °C and 1 bar pressure were considered for the catalytic process, while 260 °C and high pressure (65 and 75 bar for methanol and ethanol, respectively) were accounted for the supercritical process. Distinct layer separation was observed for both processes. Ester, fatty acid and glycerol composition was studied for both the upper and lower layers separately, from which 100% ester composition in the upper layer and a mixture of ester and other composition in the lower layer was obtained for the catalytic process owing to succeeding filtration and washing. However, mixture of ester (>75%) and other composition was obtained in both layers for the supercritical process where purification process was not implemented. The similarity in the result obtained demonstrates the superiority of waste cooking oil compared to virgin cooking oil, taking cost into consideration.

Keywords: biodiesel; supercritical transesterification; catalytic transesterification; virgin cooking oil; waste cooking oil; alcohols

1. Introduction

Biodiesel is a soaring alternative to reinstate petroleum-based fuels obtained from renewable sources such as vegetable oil, animal fat and waste cooking oil, due to the fact that the petroleum oil, coal and natural gas are narrowing down and will eventually be exhausted in the near future [1]. Combustion of the non-renewable fossil fuels emits excessive toxic gases like CO, CO₂, NO, NO₂ and SO₂, which are known as greenhouse gases (GHG), and are responsible for the greenhouse effect [2–4]. The use of biodiesel as an alternative fuel is becoming imperative due to the depletion of fossil fuels, and can significantly reduce CO and particulate matter (PM) emissions as they contain oxygen. Additionally, they have energy security, nontoxicity, local availability and recyclability [5–7]. Furthermore, other advantages for the use of biodiesel are not limited to its lower Sulphur content, improved combustion efficiency, higher biodegradability, domestic origin, and enhanced lubrication properties [6]. Likewise, it can be used in diesel engines in a blended form with conventional diesel

without modifications of the engine [8–10], although use of only biodiesel poses problems due to its high density, high viscosity, high iodine content, and low volatility [11].

The American Society for Testing and Materials (ASTM) defines biodiesel as mono-alkyl esters of long chain fatty acids (FA) derived from a renewable feedstock, such as vegetable oils, animal fats and used cooking oils [12], via reaction with alcohol such as methanol and ethanol [13]. The acknowledged process used to produce biodiesel is transesterification, which converts feedstock into fatty acid ester with allied properties to that of diesel fuel oil [14,15]. Stoichiometrically, transesterification of 1 mole of triglyceride in the presence of 3 moles of alcohol produces 3 moles of fatty acid esters and 1 mole of glycerol, where diglycerides and monoglycerides are the intermediate products. There are four basic approaches for biodiesel production from oils and fats: base-catalyzed transesterification; direct acid-catalyzed transesterification; enzyme catalytic conversion [16–20] of the oil into its FA and then to biodiesel, and non-catalytic transesterification using supercritical alcohols [21,22].

In the catalyzed method, pretreatment is necessary for the oil in which free fatty acid (FFA) exceeds 4%. For the pretreatment, an acid process using sulfuric acid solution can be used in order to reduce the FFA to less than 2%, after which transesterification is effective [23–26]. The purification procedure of the soapy product due to application of catalyst is another complication in the catalyzed method. Meher et al. [27] published an excellent review of biodiesel production by transesterification, which canvasses several successful transesterifications using several low molecular weight alcohols, homogenous acid and base catalysts. Basic homogeneous catalysts have surpassed the acid catalysts because of the faster reaction time. However, for oils with a high concentration of free fatty acids (acid value higher than 2 mg KOH/g), a pre-treatment step is recommended [28]. Heterogeneous catalytic transesterification is also one of the promising technologies for production of biodiesel as the catalyst can be recycled; there is no or very little amount of waste water produced during the process; and, separation of biodiesel from glycerol is much easier [29]. Also, a study by Di Serio et al. suggests the reaction condition to be less drastic compared to the supercritical process [30]. Hernandez et al. [31] introduced a new heterogeneous catalyst by modifying a commercial hydrotalcite for oil transesterification with methanol. Also, the paper advocates about the use of different heterogeneous catalysts by incorporating various references. However, homogeneous and heterogeneous catalytic reactions have several limitations, including sensitivity to high water and FFA content, complicated separation and purification of biodiesel, an enormous amount of reaction time and an exorbitant cost of catalysts which make the process uneconomical. Owing to the limitations of homogeneous and heterogeneous catalytic reactions for biodiesel production, a sustainable and environmentally friendly technology using supercritical alcohols (SCA) has been receiving substantial attention [32]. This supercritical transesterification technology evades many shortcomings posed by the catalytic process. In addition, compared to the catalyzed method, supercritical fluid reaction is expeditious, i.e., long hours of reaction time is considered in the catalyzed method, whereas the supercritical fluid method is completed in a few minutes [33,34]. On the other hand, the supercritical fluid method requires high temperature and pressure, which makes the system economically less viable and also raises issues concerning safety [32]. Moreover, this technology has some limitations related to the harsh operating environment and their effect on the materials. Corrosion and salt deposition are the two main challenges for most of the industrial applications, especially for supercritical water [35]. However, before moving on to the economic analysis, confirming and comparison of the product obtained is indispensable as catalytic transesterification is a well-established commercial process followed all over the world. Therefore, comparison of biodiesel obtained from the catalyzed and supercritical fluid methods was studied. Methanol and ethanol were used as solvents in supercritical fluid method, whereas only methanol was used as reactant for transesterification reaction in the catalytic process. Virgin cooking oil (VCO) and waste cooking oil (WCO) were used as raw materials for biodiesel production. Various research has been accomplished using VCO and WCO so far [36–39]. Demirbas [40] studied biodiesel conversion of waste cooking oil via base-catalytic and supercritical methanol transesterification. However, the comparative study of the catalytic and supercritical

transesterification process using VCO and WCO has not yet been studied. Furthermore, this study attempts the comparison using two different alcohols—ethanol and methanol.

WCO, which is economical compared to edible vegetable oil, is an insured substitute to VCO. A study on the production cost of biodiesel using animal fat and waste cooking oil as feedstock shows reduction in cost by more than half compared to fresh vegetable oil [41]. Considering the cost factor, waste cooking oil is the raw material for this study although the comparison has been made using the VCO and WCO.

2. Experimental Section

WCO and VCO were used as raw materials in this work. The experiments were conducted using the catalyzed and supercritical fluid methods. Table 1 illustrates the experimental conditions used in this study. The catalyzed transesterification reaction was carried out in a round-bottom flask with heating mantle. The oil was maintained at 60 °C and a known amount of catalyst (KOH), well stirred with methanol, was introduced in the flask gradually. Generally, in catalyzed transesterification reaction, depending on the percentage of FFA content, less than 2–4% of the catalyst has proven to be of suitable quantity [34] and, accordingly in our research, we have considered the catalyst amount to be 0.86% and 1.25% in VCO and WCO, respectively. The mixture was then allowed to settle down for more than 24 h, which resulted in the formation of two predominant layers in separating funnel. The product mixture of each experiment were primarily stratified, decanted, filtered, washed and finally dried. Water washing of each set was carried out three times with warm distilled water at a temperature of approximately 55 °C, whereas drying was done at 110 °C and was held at this temperature for 60 min. To shift the equilibrium towards the product side, use of excess alcohol was practiced (oil: alcohol of 1:6 molar ratios) as transesterification reactions are normally reversible.

Table 1. Experimental conditions used in this study.

Components	Reaction Method	
	Catalyzed Method	Supercritical Fluid Method
Molar Ratio (Oil: Alcohol)	1:6	1:6
Reaction temperature	65 °C	260 °C
Reaction pressure	1 bar	65 bar for methanol 75 bar for ethanol
Reaction holding time	60 min	0 min
Catalyst	KOH	Not used

Figure 1 demonstrates the schematic diagram of the batch-type reactor manufactured by Parr Instrument Co. (USA) with a volume of 25 mL. The permissible reactor conditions are 500 °C and 55 MPa. Methanol and ethanol were used as solvents in the supercritical fluid method. As solvents, methanol (99.5% purity) manufactured by Ducksan Chemical Co. (Seoul, Korea) and ethanol (99.9% purity) produced by OCI Company Ltd. (Seoul, Korea) were used. The reaction was carried out at a temperature of 260 °C for the same molar ratio, i.e., oil and alcohol of 1:6, which ensures the supercritical condition with rigorous stirring at a rate of 500 rpm. Instead of varying the individual conditions, the optimum conditions were taken from a previous study [26]. After the preset temperature was reached, the reactor was rapidly cooled in chilled water to stop the reaction immediately. The reaction pressures were 65 and 75 bar while using methanol and ethanol, respectively. The critical temperatures and pressures of alcohols are $T_c = 512.6$ K, 513.9 K; $P_c = 80.9$ bar, 61.4 bar for methanol and ethanol, respectively. Therefore, the supercritical fluid reaction in this work was near critical methanol (NCM) and supercritical ethanol (SCE). The products obtained from the catalyzed and supercritical fluid methods were further analyzed by GC-MS (Agilent GC with MSD detector, Agilent technologies, Santa Clara, CA, USA). Table 2 shows the GC analysis conditions for this study.

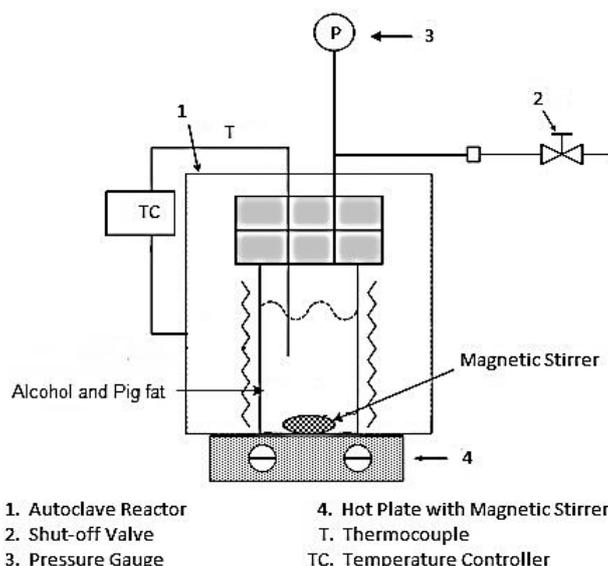


Figure 1. Schematic diagram of the experimental apparatus.

Table 2. Operation conditions of GC/MS (Agilent GC with MSD detector) analysis used in this study.

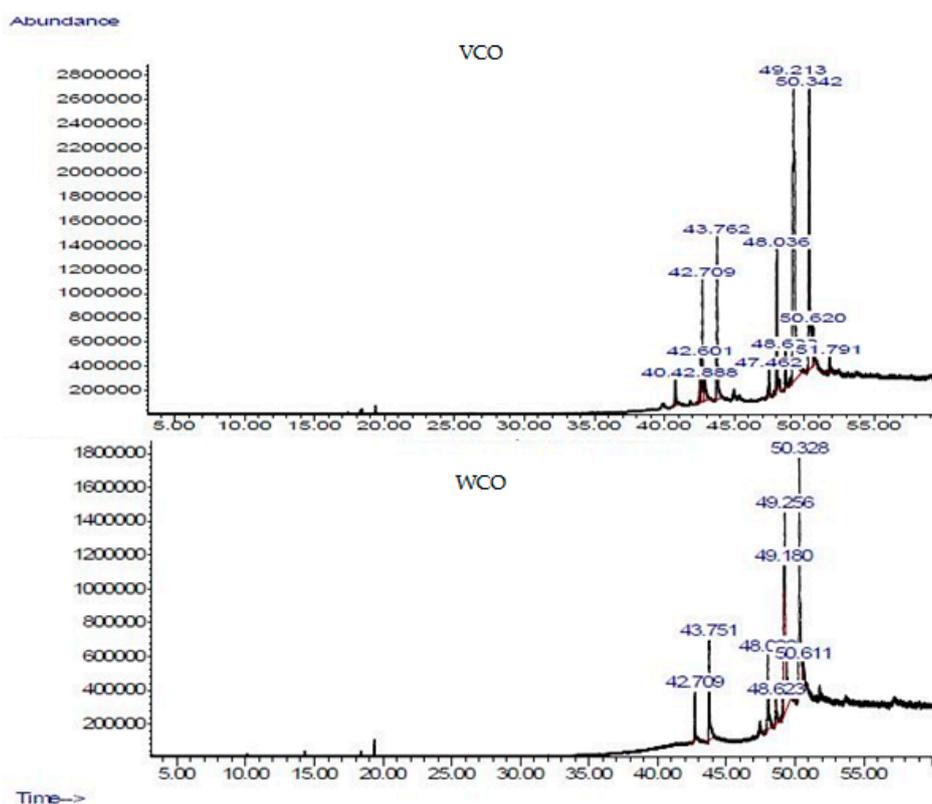
Instrument	Condition
GC	6890 GC, Agilent
MSD	5975, Agilent
Methods	
Column	DB-WAX (30 mm × 250 μm, 0.25 μm thickness)
Oven temperature	250 °C at 5 °C/min
Carrier gas	He, 1 mL/min
Injection volume	1 μL
Detector temperature	250 °C
Mass scan range	29–800 amu

3. Results and Discussion

The FA and FFA composition obtained for VCO and WCO is depicted in Table 3. FFA content of the reactant triglyceride was determined by titration against 0.1M KOH solution using phenolphthalein as the indicator. From Table 3, it can be observed that FFA content in WCO increased after cooking. The FA content of 18:2 in WCO is significantly higher than in VCO, whereas the FA content of 18:3 is lower for WCO due to the oxidative cleavage of double bonds during cooking [42]. The term defined by “others” include ester components other than the abovementioned esters. The virgin oil may even include some insoluble solids such as meal and metal oxides from the processing units along with significant amounts of phospholipids in the form of impurities [43,44]. The GC analysis of the VCO and WCO is shown in Figure 2. The horizontal component in the GC curve is the retention time, while the vertical component denotes the abundance of the particular component. From the figure, it can be inferred that all the FA composition is detected after retention time of 40 min for the GC condition. The components obtained after retention time of 40 min was considered as the raw material composition.

Table 3. Fatty acid compositions of virgin cooking oil (VCO) and waste cooking oil (WCO) used in this study.

Sample	Fatty Acid (FA) (wt %)						Free Fatty Acid (FFA) (wt %)
	13:2	16:1	18:1	18:2	18:3	Others	
VCO	6.49	9.86	2.41	13.58	58.48	9.19	0.28
WCO	3.38	9.89	2.41	36.70	43.21	4.42	3.15

**Figure 2.** GC chromatogram of VCO and WCO used as raw material.

The pictures of the samples obtained after catalytic and supercritical transesterification are exhibited in Figures 3 and 4, respectively. Clear separation of the ester composition and glycerol layers is visible in all the cases. Figure 5 shows the GC diagram of the lower and upper layers obtained from the catalytic transesterification of VCO and WCO. Figures 6 and 7 illustrate the GC diagram of the lower and upper layers obtained from the supercritical transesterification of VCO and WCO, respectively. The details of GC analysis obtained for catalyzed and supercritical transesterification in terms of fatty acid methyl esters (FAMES), fatty acid ethyl esters (FAEEs), FA, glycerol and others are arranged in Table 4. Comparing Figures 2 and 5, Figures 6 and 7, all the products obtained before 40 min were considered as the transesterified products, i.e., FAMES or FAEEs. The specific composition obtained for all the conditions of Table 4 are included in Tables 5 and 6, where all components are aliphatic compounds. In general, the physical and chemical properties and the performance of methyl esters are comparable to those of the ethyl esters. Methyl and ethyl esters have almost the same heat content. The viscosities of ethyl esters are slightly higher, whereas the cloud and pour points are slightly lower than those of methyl esters [45]. From Table 4 it can be inferred that the upper layer is the biodiesel for catalytic transesterification as 100% composition is FAMES attributing to the filtration act succeeding the reactions, whereas the lower layer of WCO and VCO also contains 55.03% and 44.04% of esters, respectively. The lower layer comprises the

mixtures of FAME along with glycerol, FA and other unidentified components. The higher percentage of glycerol in WCO product can be attributed to higher FFA content in the WCO. Contrarily, the supercritical transesterification does not show clear distinction on FAME or FAEE composition although Figure 4 depicts two distinct layers. In NCM condition, VCO and WCO contain significant amounts of FAMES in both upper and lower layers with considerably higher amounts present in the lower layers, i.e., 96.23% and 93.67% for VCO and WCO, respectively. Similarly for SCE, both VCO and WCO have higher FAEEs in the lower layer of the product, i.e., 96.19% and 94.93% for VCO and WCO, respectively. For both NCM and SCE, the upper layer contains a significant amount (>70% in all cases) of ester composition. The difference in ester composition is significant for NCM transesterification. This trend in supercritical transesterification is due to the severe experimental conditions where decomposition and regeneration occur simultaneously. Multiple processes of condensation, cyclization and polymerization occur during supercritical reaction [46] in a small reactor, resulting in indistinctive upper and lower layers. Longer residence time and higher volume of the reactor will somehow mitigate these drawbacks. However, longer residence time will have trade-off relations due to multiple processes causing a decrease in FAME or FAEE composition in the product. He et al. [47] evaluated the results obtained for the transesterification of soybean by varying the content of supercritical methanol (SCM) and justified that the decrease in reaction yield is the decrease in the content of unsaturated esters caused by isomerization, hydrogenation and thermal decomposition that consume such esters, especially C18:2 (linoleic) and C18:3 (linolenate), which are more susceptible to thermal decomposition in contrast to mono-unsaturated and saturated esters [48]. So, optimum reaction condition is necessary to countenance the advantage of the supercritical transesterification process over catalytic transesterification. For instance, Kusdiana and Saka [33] obtained a conversion in methyl esters as high as 95 wt % in about 240 s in a batch reactor, while Minami and Saka [49] reported conversions of around 90 wt % in 30 min reaction for methyl esterification of oleic acid in continuous mode. Conversion of 99.8% was obtained for SCM and SCE at holding time of 60 min by Jeeban et al. [22] for transesterification of pig fat. Analogous conversion can be obtained at lower holding time by increasing the transesterification temperature or by increasing the voltage of the electrical heater. However, no work yet is able to portray the optimum working condition for supercritical transesterification, as most are still in the elemental phases.

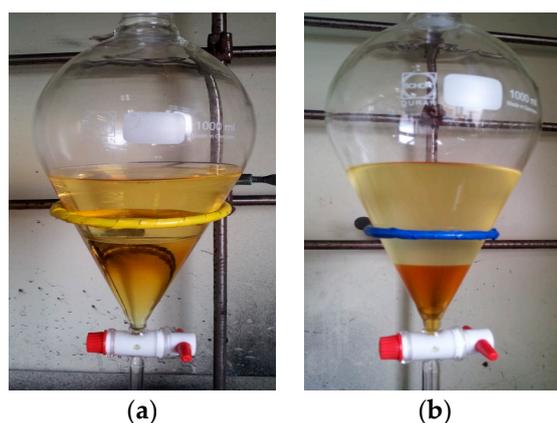


Figure 3. The upper and lower layer obtained from catalyzed transesterification (a) VCO, and (b) WCO.

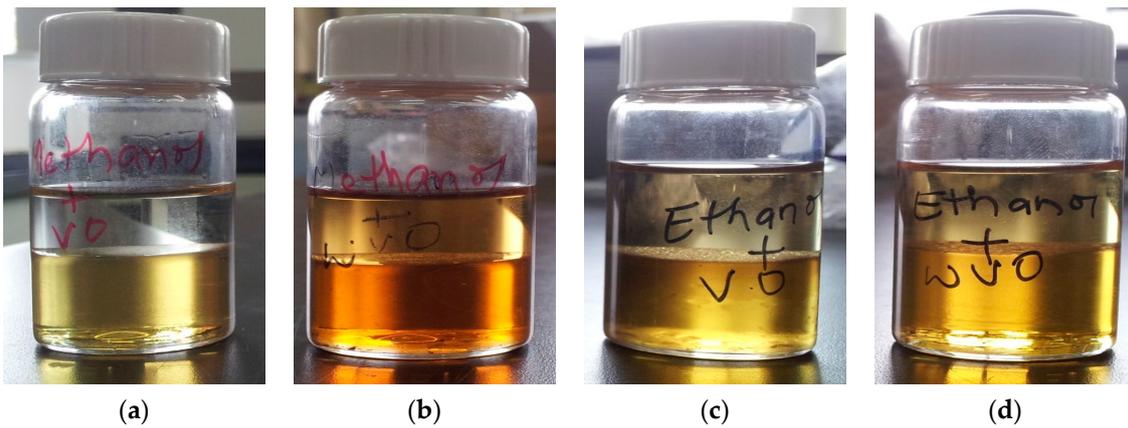


Figure 4. The upper and lower layer obtained from supercritical transesterification (a) VCO + methanol (b) WCO + methanol (c) VCO + ethanol, and (d) WCO + ethanol.

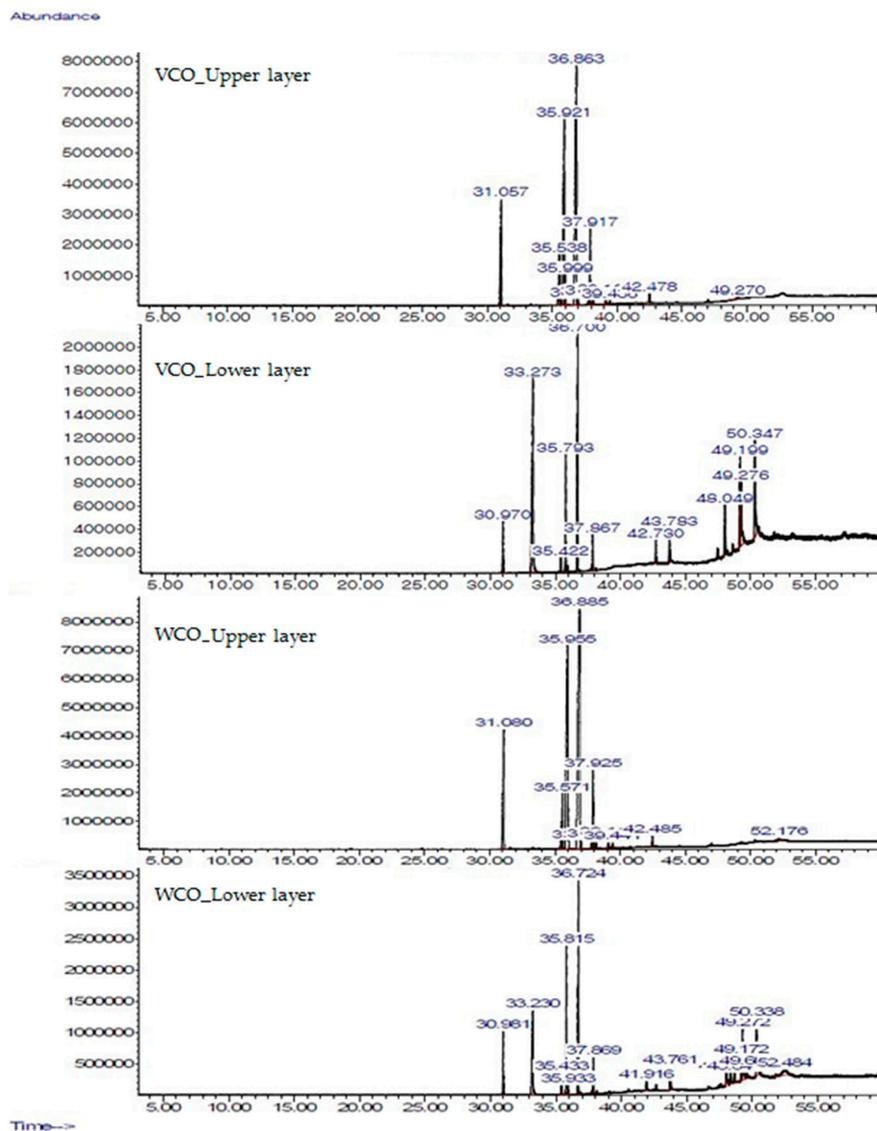


Figure 5. GC chromatogram of products by the catalyzed method.

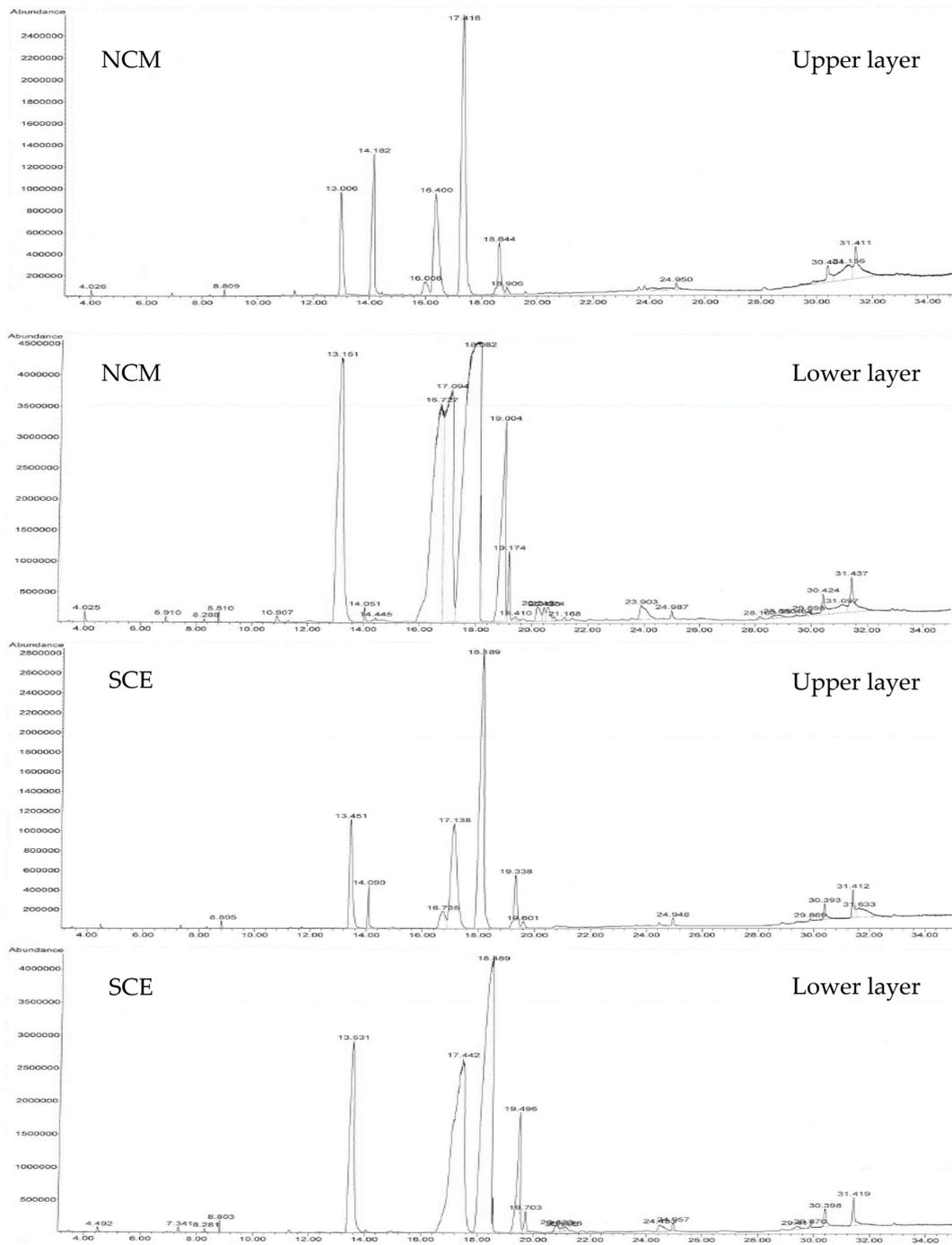


Figure 6. GC chromatogram of products from VCO by the supercritical method.

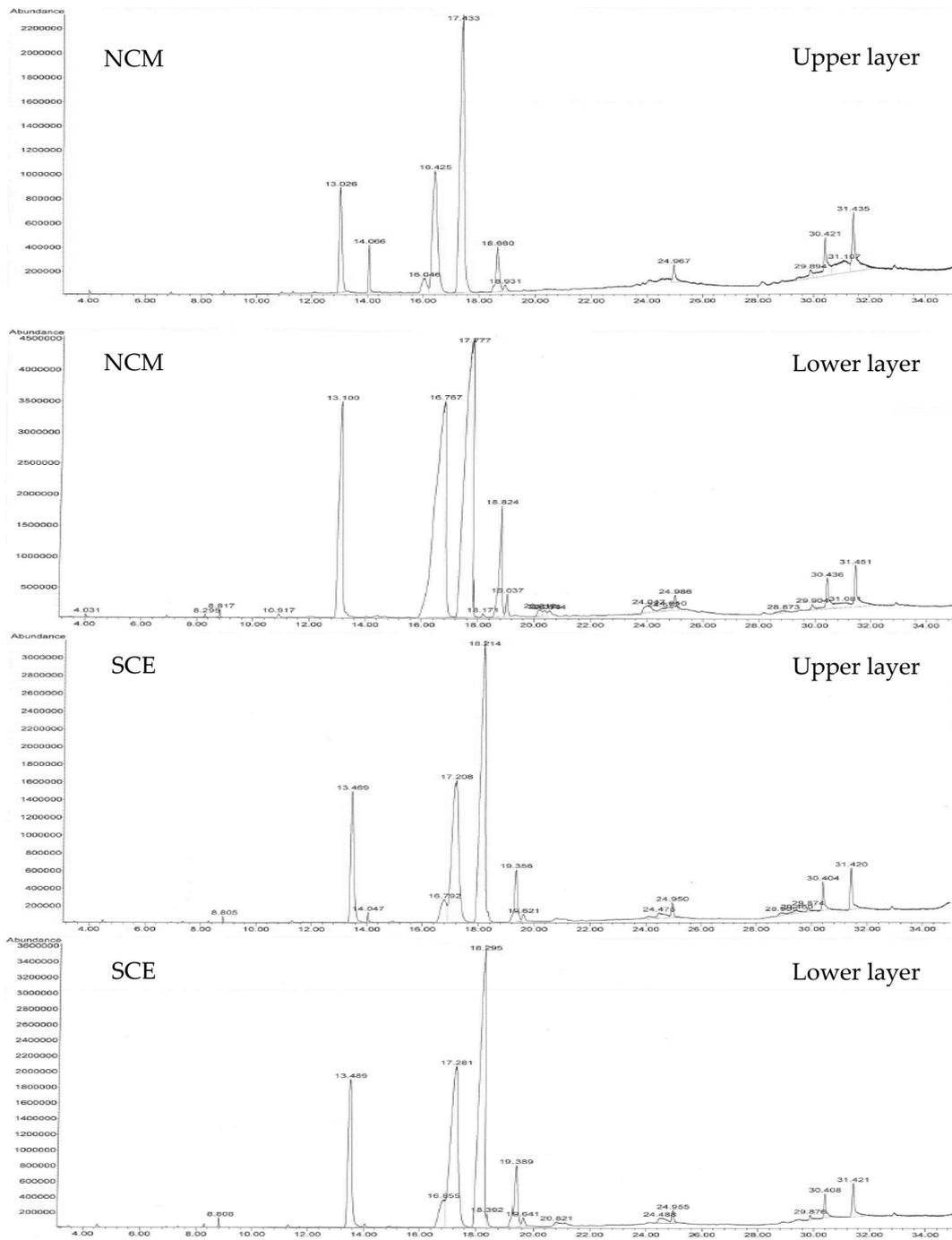


Figure 7. GC chromatogram of products from WCO by the supercritical method.

Table 4. Compositions of product obtained from catalyzed and supercritical fluid method.

Raw Material	Method	Product	Composition (wt %)				
			FAMEs	FAEEs	FA	Glycerol	Others
VCO	Catalyst	Upper layer	100	0	0	0	0
		Lower layer	44.04	0	21.99	28.90	8.67
	NCM	Upper layer	70.50	0	17.29	12.02	0.18
		Lower layer	96.23	0	2.35	0.16	1.26
	SCE	Upper layer	0	89.40	4.10	2.11	4.39
		Lower layer	0	96.19	2.13	0	1.68
WCO	Catalyst	Upper layer	100	0	0	0	0
		Lower layer	55.03	0	24.98	14.57	5.43
	NCM	Upper layer	75.91	0	14.32	2.08	7.70
		Lower layer	93.67	0	4.54	0.28	1.51
	SCE	Upper layer	0	90.27	5.95	0.38	3.40
		Lower layer	0	94.93	4.59	0	0.49

NCM = near critical methanol; SCE = supercritical ethanol; FAME = fatty acid methyl esters; FAEE = fatty acid ethyl esters.

Table 5. Components obtained from the catalyzed and supercritical processes of VCO in terms of area % as obtained from GC analysis.

Compound Name	Total Amount (area %)					
	Upper Layer			Lower Layer		
	Catalyzed	NCM	SCE	Catalyzed	NCM	SCE
Octanoic Acid, Methyl/Ethyl Ester	-	0.107	0.102	-	0.248	-
4-Decenoic Acid, Methyl/Ethyl Ester	-	0.061	-	-	0.182	0.209
3-(Allyloxy)-2-cyclohexen-1-one	-	-	0.093	-	-	-
2,4-Decadienal, [(E,E)-]	-	0.117	0.241	-	0.182	0.209
Tetradecanoic Acid, Methyl/Ethyl Ester	-	0.114	-	-	-	-
Hexadecanoic Acid, Methyl/Ethyl Ester	11.952	13.183	13.665	3.734	8.416	12.079
Glycerin	-	0.164	-	28.896	12.024	2.112
Heptadecanoic Acid, Methyl/Ethyl Ester	-	0.076	0.422	-	-	-
Octadecanoic Acid, Methyl/Ethyl Ester	5.412	-	-	1.01	2.115	3.44
7-Octadecenoic Acid, Methyl/Ethyl Ester	28.314	-	-	-	-	-
CIS-Linoleic Acid Methyl/Ethyl Ester	45.507	-	-	-	-	-
8-Octadecenoic Acid (Z)-, Methyl/Ethyl Ester	-	-	-	-	16.53	-
9-Octadecenoic Acid (Z)-, Methyl/Ethyl Ester	-	35.381	-	7.858	-	-
Methyl/Ethyl Oleate (Oleic Acid Methyl/Ethyl Ester)	-	-	33.986	-	-	23.457
Methyl/Ethyl Linoleate (Linoleic Acid Methyl/Ethyl Ester)	-	-	41.162	-	-	43.885
9,12-Octadecadienoic Acid, Methyl/Ethyl Ester	-	-	-	-	37.155	-
9,12-Octadecadienoic Acid (Z,Z)-, Methyl/Ethyl Ester	0.348	36.908	-	18.489	-	-
11,14,17-Eicosatrienoic Acid, Methyl/Ethyl Ester	-	-	0.246	-	-	-
9,12,15-Octadecatrienoic Acid, Methyl/Ethyl Ester	-	-	0.68	-	-	-
9,12,15-Octadecatrienoic Acid, Methyl/Ethyl Ester, (Z,Z,Z)	-	0.156	0.276	2.455	6.04	6.538
9,11-Octadecadienoic Acid, Methyl/Ethyl Ester, (E,E)-	-	-	0.317	-	-	-
Eicosanoic Acid, Methyl/Ethyl Ester	-	0.177	0.104	-	-	-
11-Eicosenoic Acid, Methyl/Ethyl Ester	-	0.64	-	-	-	-
Docosanoic Acid, Methyl Ester	-	-	0.768	-	-	-
1,2-Epoxy-1-vinylcyclohexene	-	2.191	1.081	-	-	-
Methyl/Ethyl 2,3,4,6 -Tetra-O-Methyl/Ethyl-.Alpha.-D-Glucoside	-	-	0.246	-	-	-
Hexadecanoic Acid; Palmitic Acid	-	-	0.68	3.087	1.957	0.517
15-Crown-5	-	0.156	0.276	-	-	-
1,4,7,10,13,16-Hexaoxacyclooctadecane	-	0	0.317	-	-	0.398
6-Octadecenoic Acid, (Z)-; Petroselinic acid	-	0.177	0.104	-	-	-
9-Octadecenoic Acid (Z)-; Oleic Acid	-	0.64	-	7.8	3.401	1.505
9,12-Octadecadienoic Acid (Z,Z)-; Linoleic Acid	-	-	0.768	11.107	11.932	2.08
Tetradecanedioic Acid Dimethyl/Diethyl Ester	-	-	-	1.885	-	-
Methyl Pentadecyl Ether	-	-	-	5.007	-	-
Bicyclo[10.1.0]tridec-1-ene	-	-	-	8.673	-	-
21-Krone-7	-	-	-	-	-	3.78

Table 6. Components obtained from the catalyzed and supercritical processes of WCO in terms of area % as obtained from GC analysis.

Compound Name	Total Amount (area %)					
	Upper Layer			Lower Layer		
	Catalyzed	NCM	SCE	Catalyzed	NCM	SCE
2,4-Decadienal, [(E,E)-]	-	-	0.152	-	-	0.152
Hexadecanoic Acid, Methyl/Ethyl Ester	6.301	9.315	12.846	6.301	9.315	12.846
Glycerin	13.942	2.075	0.382	13.942	2.075	0.382
Octadecanoic Acid, Methyl/Ethyl Ester	1.938	2.478	3.87	1.938	2.478	3.87
9-Octadecenoic Acid (Z), Methyl/Ethyl Ester	14.311	21.051	-	14.311	21.051	-
10-Octadecenoic Acid, Methyl/Ethyl Ester	0.786	-	-	0.786	-	-
Methyl/Ethyl Oleate (Oleic Acid Methyl/Ethyl Ester)	-	-	28.822	-	-	28.822
Methyl/Ethyl Linoleate (Linoleic Acid Methyl/Ethyl Ester)	-	-	39.298	-	-	39.298
9,12-Octadecadienoic Acid, Methyl/Ethyl Ester	26.334	-	-	26.334	-	-
9,12-Octadecadienoic Acid (Z,Z)-, Methyl/Ethyl Ester	-	37.439	-	-	37.439	-
9,12,15-Octadecatrienoic Acid, Methyl/Ethyl Ester	-	4.982	-	-	4.982	-
9,12,15-Octadecatrienoic Acid, Methyl/Ethyl Ester, (Z,Z,Z)-	2.996	0.643	5.437	2.996	0.643	5.437
Hexadecanoic Acid; Palmitic Acid	4.366	1.586	1.056	4.366	1.586	1.056
1,4,7,10,13,16-Hexaoxacyclooctadecane	0.778	7.7	2.902	0.778	7.7	2.902
2-(bromomethyl)-2-octyl-15-crown-5	-	-	0.345	-	-	0.345
Octadecanoic Acid	1.473	-	-	1.473	-	-
cis-7,cis-11-Hexadecadien-1-yl Acetate	2.72	-	-	2.72	-	-
9-Octadecenoic Acid (E)-; trans-Oleic Acid	-	-	2.001	-	-	2.001
9-Octadecenoic Acid (Z)-; Oleic Acid	10.103	5.343	-	10.103	5.343	-
Octaethylene Glycol Monododecyl Ether	1.695	-	-	1.695	-	-
9,12-Octadecadienoic Acid (Z,Z)-; Linoleic Acid	7.96	7.389	2.891	7.96	7.389	2.891

Further, there are no traces of FA concentration in the upper layer of the catalyzed method considering the lower layer which contains high amounts of FA that is even higher compared to supercritical transesterification product. The NCM method for both VCO and WCO produces comparatively higher amounts of FA in the upper layer than in the lower layer. However, for the SCE method, both layers contain comparable amounts of FA. The higher amount of FA present in the catalyzed product is the result of lower conversion efficiency of catalyzed transesterification than supercritical transesterification. The absence of FA in the upper layer for the catalyzed process and availability of FA in both layers of the supercritical process is solely due to the filtration and washing succeeding the reactions. The accommodation of proper and efficient purification along with transesterification will elevate the yield of biodiesel using the supercritical method, which is further aided with shorter reaction and processing time [33,34]. Higher amounts of glycerol, i.e., 28.90% and 14.57%, are obtained from the catalyzed method in the lower layer of the products in VCO and WCO, respectively. Excluding the upper layer obtained while using the NCM method for VCO, which gives 12.02% of glycerol, other product layers obtained from the supercritical method provides very little amounts of glycerol, ranging from 0 to 2.11%. If closely observed, higher FA and glycerol quantity in Table 4 results in lower composition of esters and vice versa. Higher percentage of FA and glycerol in the NCM compared to the SCE method must be due to the near critical condition of methanol where the solvent did not attain complete supercritical condition, making it partially incapable of taking advantage of superiority of supercritical conditions. It is also evident that at the subcritical state of alcohol, the reaction rate is very low and gradually increases as either temperature or pressure rises [50].

The requirement of high temperature and pressure in supercritical transesterification raises issues concerning safety. However, the absence of a pre-treatment step, soap removal, and catalyst removal can significantly reduce the capital cost of a biodiesel plant while using supercritical transesterification, while the expected high operating cost due to high temperature and pressure can be a major impediment for this technology. Considering the purity of esters and the economic sustainability, continuous production of biodiesel using supercritical transesterification of WCO can compete with the existing alkali- and acid-catalyzed processes. The sensitive key factors for the economic feasibility of the plant are raw material price, plant capacity, glycerol price and capital cost [51].

4. Conclusions

Two representative transesterification methods used for the production of biodiesel fuel, namely, catalytic and supercritical transesterification were studied in this research. VCO and WCO are emerging concerns in the research for biodiesel production, which are used as raw material in this study. However, the cheap cost factor associated with WCO makes it a propitious substitute to fresh vegetable oil. Since WCO demonstrates similar properties in terms of product, the associated cost and its impact on reducing environmental pollution makes it much more superior than VCO.

The ester composition obtained from the supercritical process is proportionate with catalytic transesterification owing to the fact that the catalytic process has to undergo consecutive filtering and washing, while the product obtained via the supercritical process does not undergo filtering and purification. The shorter reaction time if associated with purification and process optimization, supercritical transesterification will greatly change the course of biodiesel production, which even has a great potential to be established commercially, although economic analysis is imperative.

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