

Production, Analysis, and Evaluation of Biodiesel from mixed Castor SEED oil, Bitter Almond oil, and Waste Fish Oil

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Abstract: Utilization of priceless raw materials for biodiesel (BD) production is an essential target to reduce its production cost. Therefore, this work inspects the exploitation of a non-conventional feedstock, namely a mixture of non-edible oils (40% castor bean oil+ 30% bitter almond oil, and 30% waste fish oil w/w) in the production of ethylic biodiesel (EBD) and methylic/ethylic biodiesel (MEBD) through KOH-catalyzed transesterification reaction with ethanol and mixed methanol/ethanol, respectively. Effect of alcoholysis variables, such as alcohol/oil molar ratio, reaction period, reaction temperature and KOH amount, were examined. The alcoholysis outcomes revealed that the kind of implemented alcohol affected the optimum conversion of the oils mixture to BD. The maximum yield of FAMEE ($96.33 \pm 1.0\%$) was attained at 0.75 wt.% KOH, 6/1 alcohol/oils blend molar ratio, 45 minutes, and 55°C reaction temperature, while the best FAEE yield ($95.11\% \pm 2.50\%$) was obtained at 1.0 %wt.KOH, 7/1 ethanol/oils blend molar ratio, 65°C, and a reaction time of 60 minutes. The fuel properties of the prepared fuels were assessed and discussed following ASTM D 6751 specifications. The results also exhibited that properties of FAMEE and FAEE were much better than those of BD from castor bean oil, suggesting their suitability as realistic alternative fuels to diesel fuel. ¹H NMR and FTIR techniques affirmed the transformation of the oils blend to BD. Pseudo-first-order kinetics was obeyed on the alcoholysis of the said mixed oils.

Keywords: Mixed non-eatable oils, Biodiesel, Fuel properties assessment, Identification of biodiesels, Kinetics

Introduction

The liquid biofuel that is obtained by the chemical processes of different vegetable oils or animal fats with alcohol is named biodiesel (BD). It is utilized separately or as a blend with petrodiesel (PD) in diesel engines. The most common method employed for BD synthesis is the TE reaction. It involves the reaction of triglycerides with an alcohol in the existence of a base catalyst (KOH or NaOH), an acid catalyst (H_2SO_4 or HCl) or an enzyme catalyst (lipase) (Verma et al., 2016; Kudre et al., 2017). First-generation biodiesels (BDs) have generated from edible oils, which their utilization in BD synthesis was associated with many drawbacks, including energy versus food dispute. Besides, it was reported that about 80% of the final price of BD production relates to the production cost of the parent oil employed in its preparation. Additionally, utilization of food crops for energy production might also increase acreage, which in turn causes deforestation. As such, production of the second-generation BDs has been accomplished relying on the exploitation of non-edible oils (NEO) to avoid issues generated during exploiting eatable oils for BD production (Ong et al., 2019).

Many NEO, such as *Hevea brasiliensis* (Karnjanakom et al., 2016), *Ceiba Pentandra* (Silitonga et al., 2014), *Cerbera manghas*, *Calophyllum inophyllum* (Silitonga et al., 2014), *Jatropha curcas* (Silitonga et al., 2014), *Madhuca indica* (Lamba et al., 2019), *Sterculia foetida* (Silitonga et al., 2013) *Silybum marianum* L. (Fadhil et al., 2016), Wild (*Brassica juncea* L.) (Aldobouni et al., 2016), Bitter almond (*Prunus dulcis* var. amara) (Al-

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Tikrity et al.,2107), waste fish oils (Fadhil et al.,2015; Al-Tikrity et al.,2016), and waste cooking oils (Vanessa et al.,2015) were explored as feedstocks for producing different BDs.

The castor (*Ricinus communis* L.) which is a non-eatable plant has a high commercial value besides its industrial applications as an outcome of its oil which could be employed in the synthesis of various products, like high profitable value polymers, pharmaceuticals and BD fuel. The high oil level of castor beans which ranges between 40-55% makes it a valuable raw oil for BD synthesis. However, the density, polarity and viscosity of castor bean oil (CBO) are higher than other oils, as a consequence of its chemical composition which is mainly composed of ricinoleic acid (R-12-hydroxy-9-cis-octadecenoic acid) as a superlative fatty acid ($\pm 89\%$). Hence, BD from CBO possesses high density and viscosity as well. Accordingly, BD from CBO is blended with PD or other low density and viscosity BDs to become a useful fuel for diesel engines (Barbosa et al.,2010; Saez-Bastante et al.,2015; Keera et al.,2018).

Almonds (*Prunus amygdalus*) is one of the Rosacea's family. Based on its taste, two kinds of almonds were distinguished: sweet almond and bitter almond. Sweet almond is widely utilized as the main component in the manufacture of food products, while bitter almond supplies the main source of bitter almond oil (BAO) which acts as an ingredient in cosmetics. The presence of cyanogenic glucosides, like amygdalin and prunasin added the bitter flavor in bitter almonds (Borras et al.,2014;Cortes et al.,2018). The BAO has considered as a non-eatable oil as a consequence of its content of Hydrocyanide, Benzaldehyde, and glycoside amygdaline. The occurrence of Hydrocyanide made the crude bitter almond oil (BAO) poisonous so that a dosage of 7.7 mL may cause death. As such, it was exploited as a useful precursor for BD creation (Fadhil and Mohammed,2018).

The occurrence of different water sources, like Tigris, Euphrates Rivers and Marshes made Iraq a fish producing country. Besides, certain species of fish were bred in ponds to meet the increasing need for white meats due to their health and nutritional importance. Production of fish leaves behind various solid waste, such as viscera, frame, head and skin scales(Fu et al.,2017). These parts are rich with fat and could be a significant threat to the environment. As an actual solution to eliminate the accumulation of such fatty wastes is the reclamation of oil from those wastes to be utilized for producing BD fuel(Fadhil et al.,2015; Al-Tikrity et al.,2016). The transesterification (TE) of mixed NEO with methanol to produce BD with favorable physical and chemical properties was established in the literature. The synthesis of BD from mixed *Jatropha curcas* and *Ceiba pentandra* oils has resulted in the production of BD with higher oxidation stability than that produced from *Ceiba pentandra* oil separately (Damanik et al.,2017). The TE of mixed CBO and WCO with methanol improved the Cetane number to 100 (Hadiyanto et al.,2018). Methanolysis of a mixture of CBO and waste fish oil (WFO) (50:50 w/w)(Fadhil et al.,2017) and mixed CBO and waste chicken oil (50:50 w/w)(Fadhil and Ahmed, 2016) produced BDs with kinematic viscosities much lower than that produced from CBO individually, and also within the safe limits prescribed by ASTM standard. The preparation of BD from CBO mixed with NEO or edible oils has also reported in the literature (Barbosa et al.,2010). Nonetheless, TE reaction of a mixture of NEO, namely CBO, BAO and WFO with ethanol and mixed methanol/ethanol, to yield ethylic biodiesel (EBD) and mixed methylic/ethylic biodiesel (MEBD) has not been yet declared in the literature to the best of our knowledge.

The present context reports the synthesis of EBD and MEBD from a blend of NEO viz. CBO, BAO and WFO via alcoholysis reaction. The oils blend has assessed for its chemical and physical features, and then transesterified with various alcohols to yield varied alkyl esters via the optimized procedure was inspected. The resulting BDs were identified by ^1H NMR and FTIR spectroscopy in addition to the assessment of their fuel properties.

Methods

Materials and chemicals

The castor beans and bitter almond kernels were collected from trees planted in Mosul and Dohuk cities, respectively in July 2018, while the fish wastes have obtained from the fish Slaughterhouse in the city of Mosul. Analytical grade solvents and chemicals implemented were purchased from different origins (Merck, Germany and Scharlau, Spain) and utilized without any pre-treatment.

Extraction and analysis of oils

The extraction of oils from castor and bitter almond kernels was accomplished in a Soxhlet extractor with hexane as a solvent. After stripping the solvent from the oils via vacuum distillation by the aid of a rotary

evaporator, the yields of the got oils were calculated on a weight basis. Extraction of WFO from the fish waste was carried out following the procedure presented in our previous work (Fadhil and Ahmed,2018). The oils were well-mixed at the following ratios: 40% CBO, 30% BAO and 30% WFO w/w. Properties of the oils and their blend including the density at 15.6°C, kinematic viscosity at 40°C, flash point, acid value, refractive index, pour point and the saponification number have specified as per the ASTM standard methods.

Biodiesel production and analysis

The oils blend was fed to a 500 mL round-bottomed flask joined with a mechanical stirrer, condenser and thermostat to prepare MBD and MEBD. KOH was completely dissolved in alcohol under stirring. The alcoholic solution of KOH was added to the oil. The mixture was refluxed with stirring at 600 rpm using a magnetic stirrer for given reaction time. At the end of the operation, the attained mixture was transferred to a separator to yield two layers, while the alkyl ester layer was washed with distilled water to remove water-soluble impurities, such as soaps and alcohol. Lastly, it was dried over Na₂SO₄. The following formula was applied in the calculation of BD yield(Fadhil and Ahmed,2018):

$$\text{BD yield (\%)} = \frac{\text{Weight of the purified alkyl ester (g)}}{\text{Weight of oils blend used (g)}} \times 100$$

Adsorption chromatography method was applied to specify the purity of the as-produced fuels (Bindhu et al.,2012). Proton nuclear magnetic resonance (¹H NMR) was also employed to affirm the conversion of the oils blend to its alkyl esters on 1H NMR spectrophotometer, GmbH 400.22 Mhz. The MEBD was identified using Fourier transform infrared (FTIR) spectrometer (Model: A Bruker EQUINOX 55, USA) equipped with a detector having a spectral range 4,000-400 cm⁻¹. Assessment of the properties of the obtained fuels achieved as per ASTM standard test methods. Content of soaps in the biodiesels was specified based on AOCS Cc 17-95, while the total glycerin content was determined as suggested by Pisarello et al.(2010). Various blends of BD and PD have prepared and then evaluated for their properties following the ASTM standard test methods.

Results and Discussion

Oils yield and properties

The content of oils in the castor beans, bitter almond kernels and fish waste, were 51.55, 42.0 and 76.0 % w/w, respectively. The oils contents in these precursors are higher than those published for *Sterculia striata* seed (40.0% %)(Ong et al.,2013) and pork waste (Dias et al.,2009). As a result, BD synthesis from such NEO or their blends is reliable. It is obvious from Table 1 which displays physicochemical properties of the CBO, BAO, WFO and their blend that the density, kinematic viscosity and refractive index of the CBO, have been markedly reduced as a consequence of blending with the other NEO. This result attributes to the lower density, kinematic viscosity and refractive index values of the other NEO compared to CBO. As fixed in **Table 1**, the properties of the oils blend were comparable to those of conventional NEO utilized for the synthesis of BD in literature (Reshad et al.,2015; Ong et al.,2019).

Table 1. Properties of the oils and their blend compared to other non-edible oils

Property	CBO	BAO	WFO	Oils blend	CCIO ^a	CI60CP40 ^b	Rubber seed oil ^c
Density @ 15.6 g/mL	0.9730	0.9200	0.9188	0.9376	0.9640	906.2	0.9100
Kinematic Viscosity@ 40°Cmm ² /s	261.33	41.39	35.99	57.47	56.74	29.57	30.0
Flash Point °C	185	200	272	193	-	-	-
Acid Value mg KOH / g oil	0.10	1.11	1.31	1.15	36.26	15.82	24
Refractive index@20°C	1.4780	1.4682	1.4680	1.4674	-	-	1.4700
Pour Point °C	<-15	-7	0.0	-10	-	-	3.0
Saponification Value mg KOH / g oil	188.47	216.12	211.60	196.70	-	-	235.28

^a Crude *Calophyllum inophyllum* oil from Ong et al.,2019;^b *Calophyllum inophyllum*-*Ceiba pentandra* oil mixture (60:40 wt%) from Ong et al.,2019;^c from Ong et al.,2019

Alcoholysis reaction of the oils blend

The main characteristic that influences the conversion of oil to its alkyl esters, as well as the selection of the optimum base catalyst for the alcoholysis process, is free fatty acid (FFA) content of it (Armendáriz et al.,2015). The oils blend used for BD synthesis in this work has an FFA content of 0.575%, which is much below that announced for other NEO, like *Nigella sativa* (15.17 %)[33] and *Ceiba pentandra* (10.11%) (Khan et al.,2015). Thus, BD production from the said oils blend is reasonable. Moreover, utilization of low FFA content oils for the synthesis of BD reduces its production cost comparing to those with high FFA contents, which their conversion to BD required a dual-step process, namely acid-base TE process, leading to a higher cost of production.

Different amounts of KOH ranged from 0.25-1.50 wt.% were tried on the alcoholysis reaction of mixed NEO to MBD and MEBD. The experiments were performed using 6/1 alcohol/ NEO molar ratio, 60 °C, 600 rpm rate of stirring, and 60 minutes reaction time as fixed in **Fig.1a**. With increasing KOH amount from 0.25 wt.% to 1.50 wt.%, growth in the BD yield was noticed. This outcome suggested that increasing the KOH amount will provide more active sites for the reaction, leading to a better conversion of the oil to BD (Syazwani et al.,2107). Nonetheless, ethanolysis of NEO mixture required a higher amount of KOH (1.0 wt.%) to reach the highest conversion than that required to get the maximum yield of MEBD (0.75 wt.%). When the KOH % exceeded the optimal amount, the BD yield declined as a result of the reaction of more triglycerides with KOH, leading to a more formation of soaps. So, the BD yield diminished (Syazwani et al.,2107).

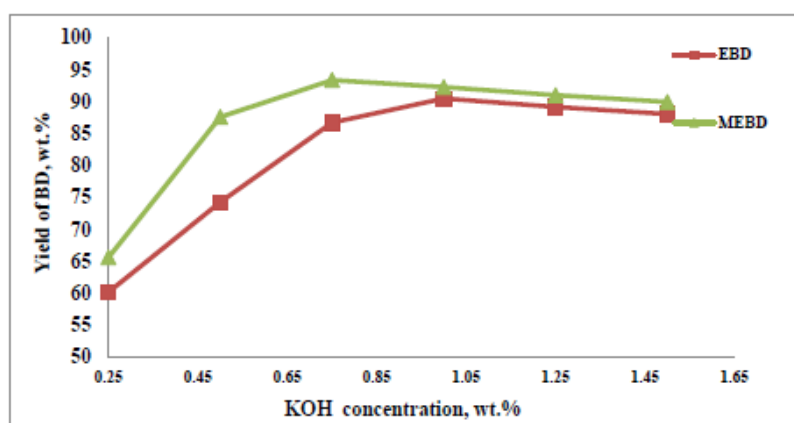


Figure 1. Effect of KOH concentration on FAEE and FAMEE yield

As alcoholysis reaction is greatly affected by varying alcohol/oil molar ratio, transesterification of the NEO mixture with the said alcohols was accomplished using different molar ratios of alcohol/NEO as given in **Fig.1b**. The experiments were accomplished at 65°C using the optimal amounts of KOH obtained earlier for 60 minutes with a stirring speed of 600 rpm. It is evident from **Fig.1b** that the conversion of NEO mixture to EBD and MEBD raised as the molar ratio of alcohol/NEO increased. The TE with mixed alcohols gave the highest yield of MEBD at a molar ratio of 6:1, while a molar ratio of 7:1 ethanol/NEO blend has given the best conversion. Nonetheless, the molar ratio of alcohol/NEO might increase the polarity of the reaction mixture, giving rise to a higher solubility of glycerin in the ester phase. As a result, it drives the equilibrium back to the reactants side. Hence, the BD yield declined (Gaurav et al.,2014).

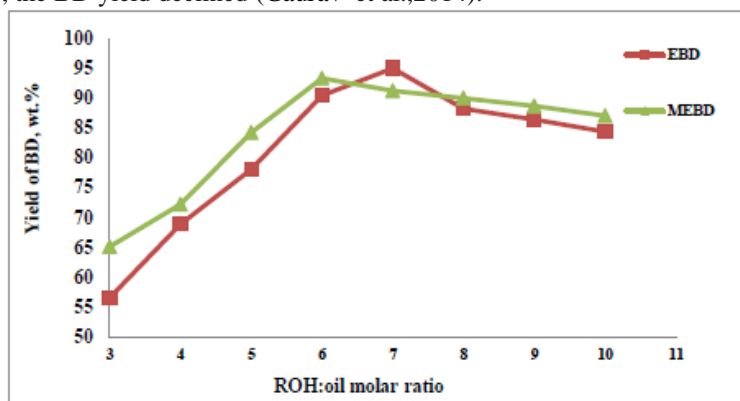


Figure 2. Effect of alcohol/NEO molar ratio on FAEE and FAMEE yield

The BD yield and alcoholysis reaction rate are greatly influenced by altering the reaction temperature. Raising the reaction temperature decreases the oil viscosity, and also lessens the reaction time. So, the impact of the reaction temperature on the EBD and MEBD yields has studied through conducting the alcoholysis reaction at different temperatures, namely 30 °C, 40 °C, 50, 55 °C, 60 °C, 65 °C and 70 °C. The experiments were carried out by employing the optimal amounts of KOH and the optimal alcohol/NEO molar ratios obtained previously for 60 minutes at 600 rpm rate of stirring. Fig.1c showed that the BD yield raised with the rise of the reaction temperature.

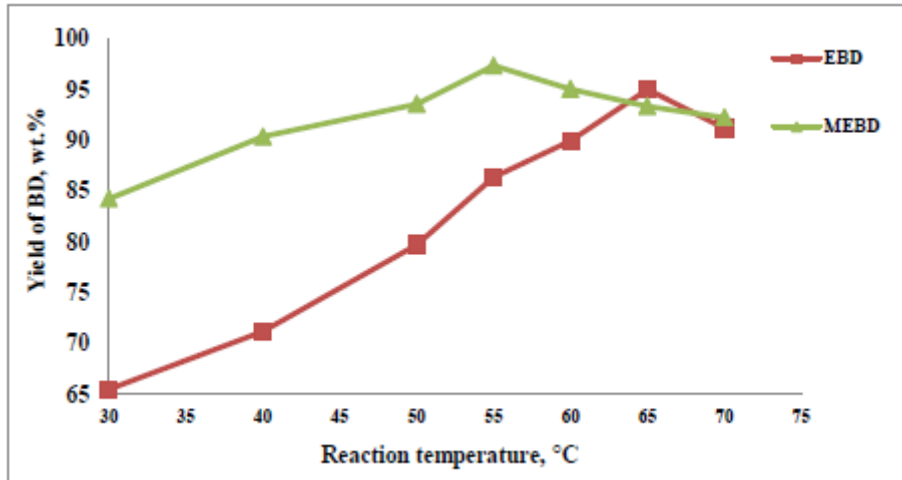


Figure 3. Effect of reaction temperature on FAEE and FAMEE yield.

The optimal temperature for alcoholysis of NEO with mixed alcohols was 55 °C. On the other hand, ethanolysis of NEO blend produced the maximum EBD yield at 65 °C. Both temperatures are below the boiling points of the utilized alcohols. Thus, such an outcome may lessen the cost of BD production. Soap formation was noticed when the reaction temperatures exceeded the optimal temperature (Hassen et al., 2014).

The influence of the reaction time on the yield of alcoholysis products was studied through changing the time from 15 to 90 minutes with 15 minutes increments. All experiments were done by fixing KOH, alcohol: NEO and the reaction temperatures at their optimal values obtained earlier, while a stirring rate of 600 rpm was employed. It can be seen from Fig.1d that increasing the reaction period improved the BD yield. A reaction time of 45 minutes was the optimal period, as it yielded the highest conversion of the mixed NEO to MEB, while 60 minutes were enough to give the highest yield of the EBD. The loss of BD in the form of soaps as a consequence of the hydrolysis of the formed alkyl esters has noticed as the reaction periods exceeded the optimal values (Silitonga et al., 2015).

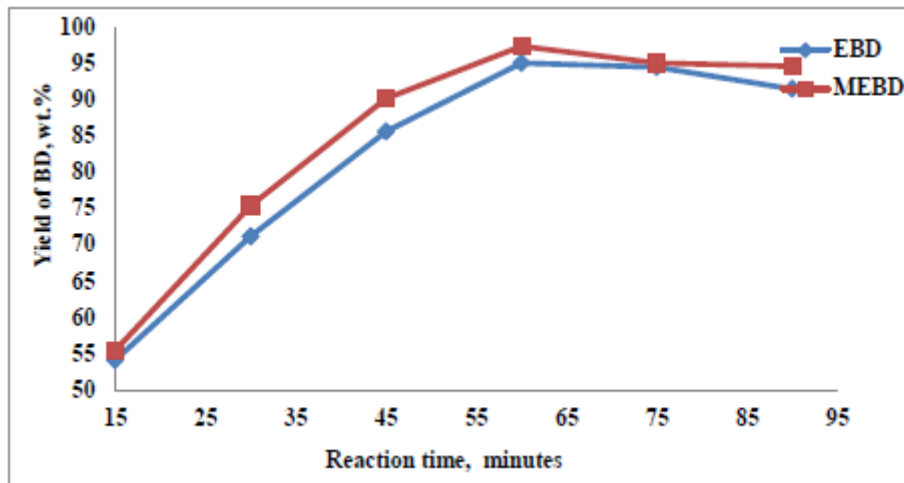


Figure 4. Effect of reaction time on FAEE and FAMEE yield

Above results disclosed that the transesterification reaction of NEO blend with ethanol and mixed alcohols produced the highest yield of MEBD at conditions lower than those required for the ethanolysis reaction. These outcomes might ascribe to the solubility of the oil in the implemented alcohol, which expected to be better in mixed methanol/ethanol than ethanol, resulting in a better mass transition between the oil and alcohol phases.

Analysis of BDs from NEO mixture

The EBD and MEBD prepared from mixed CBO, BAO and WFO have analyzed by ¹H NMR spectroscopy. The conversion of oil mixture to its EBD was confirmed through the appearance of a quartet peak at 4.09-4.14 ppm, which attributes to the methylenic protons (-OCH₂-) of the ester group as depicted in Fig.5. Conversion of the mixed oils to EBD was quantified making use of the equation suggested by Hincapié et al.(2011).

$$CEE (\%) = 100 \times [I_{TGA+EE} - I_{TGA}] / [I_{\alpha CH_2}]$$

where I_{TGA+EE} represents the integration of peak assigned to the glyceryl methylenic and (-OCH₂-) of the ethoxy protons appeared at 4.07-4.14 ppm, I_{αCH₂} is the integration of peak corresponding to the α-methylene protons (2.3 ppm), and I_{TGA} is the integration of peak corresponding to the glyceryl methylenic protons (4.27-4.33 ppm) in the ¹H NMR spectra of EBD.

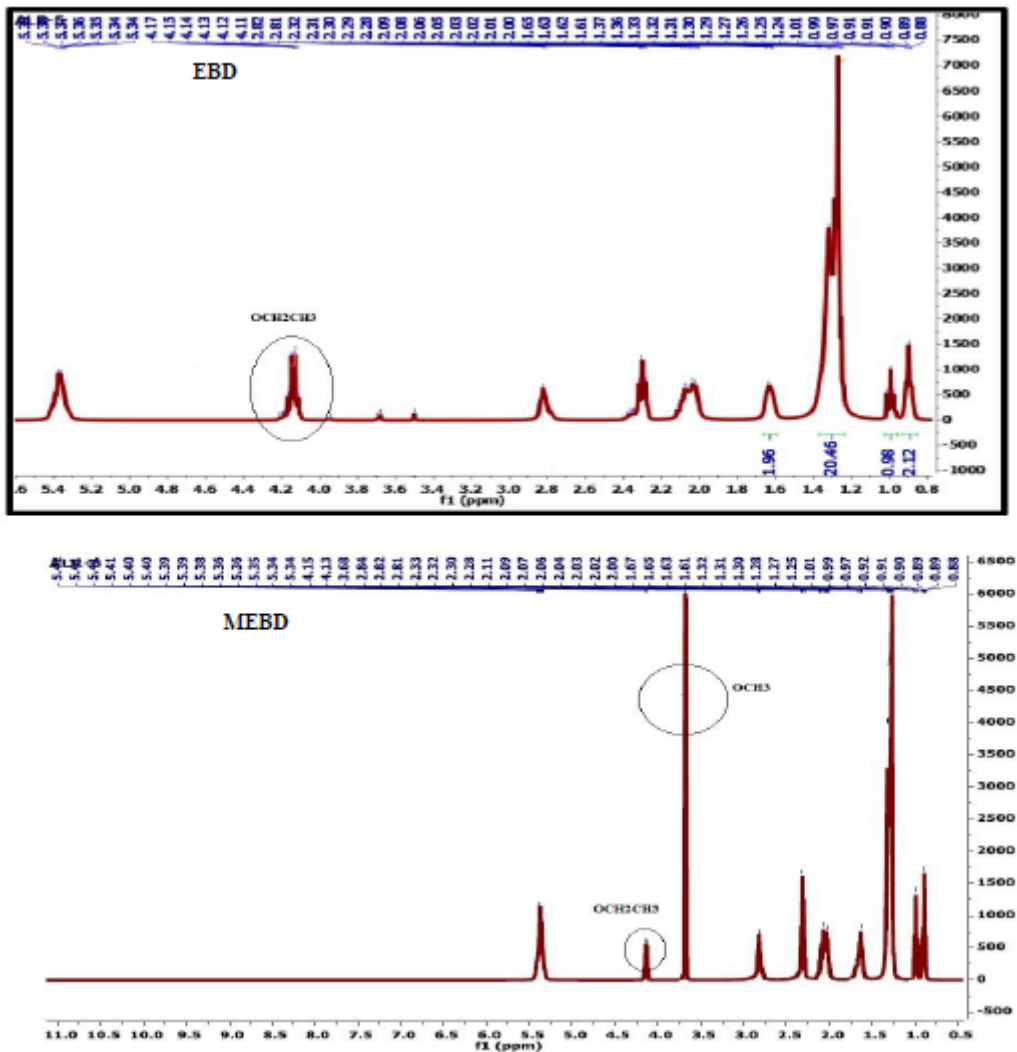


Fig.5. ¹H NMR spectra of EBD and MEBD.

Following the above equation, conversion of the NEO blend to EBD was 92.64 %, which is close to that obtained practically (95.11 % ± 2.50). The presence of both methylic and ethylic esters in the MEBD was affirmed through the appearance of a strong singlet at 3.7 ppm which relates to the methoxy ester protons (-O-CH₃), a triplet of α-methylene protons (α-CH₂) at 2.01–2.75 ppm, and a quartet at 4.07– 4.14 ppm, which attributes to the methylenic protons from the ethoxylated group (-O-CH₂-CH₃) as depicted in Fig.5.

The NEO mixture and its MEBD have also characterized by the FTIR technique, and the spectrums are presented in Fig.6.

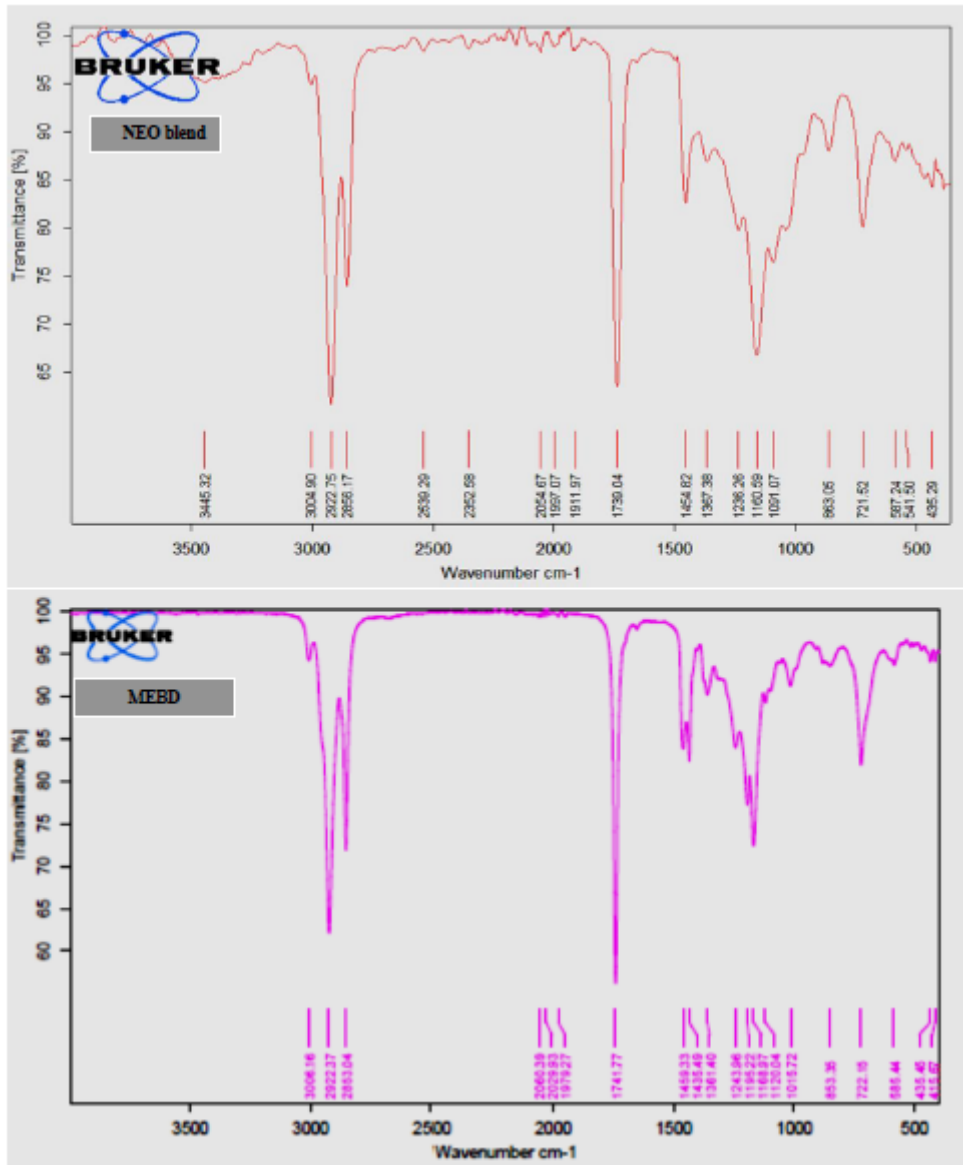


Fig. 6. The FTIR spectra of the NEO mixture and its MEBD

The symmetric and asymmetric stretching vibrations of the methyl group (\square CH₃), which appeared between 3006-2853 cm⁻¹ are characteristic bands of the alkyl esters. The absorption bands in the region of 1741-1737 cm⁻¹, may be assigned to the stretching vibration of the carbonyl group (\square C=O), while that belongs to the symmetric stretching vibration of (C \square O \square C) was noticed at 1246-1170 cm⁻¹. The absorption peak observed in the region of 912-723 cm⁻¹ may ascribe to the hydrocarbon chain rocking vibration (Ali and Fadhil,2013; Gupta et al.,2106). **Fig.6** also disclosed that the spectrums of the authentic NEO blend and its MEBD are nearly the same with a bit differences in the frequencies of the absorption peaks. Besides, the bands, which appeared at 3445,2539,2352,20154,1997 and 1911 cm⁻¹ were present in the oils blend but absent in the obtained MEBD. Moreover, new absorption peaks, such as those noticed at 1435,1193 and 1119 cm⁻¹ were found in the BD and absent in the oils blend. These findings affirmed the conversion of fatty acid to fatty acid alkyl esters. The area below the absorption peaks of stretching vibration of the (\square C \square H) band, bending band of (\square C \square H), and stretching vibration of (\square C=O) were lower than those observed in the authentic oils blend. These observations might also affirm the conversion of the oils blend to its alkyl ester (Fadhil et al.,2019).

Kinetics study

Kinetics of the alcoholysis reaction of NEO mixture with the said alcohols at different temperatures is demonstrated in **Fig.7** and **Fig.8**. The pseudo-first-order kinetic model was followed to investigate the kinetics of the alcoholysis process.

$$- \ln (1 - X) = - k.t.$$

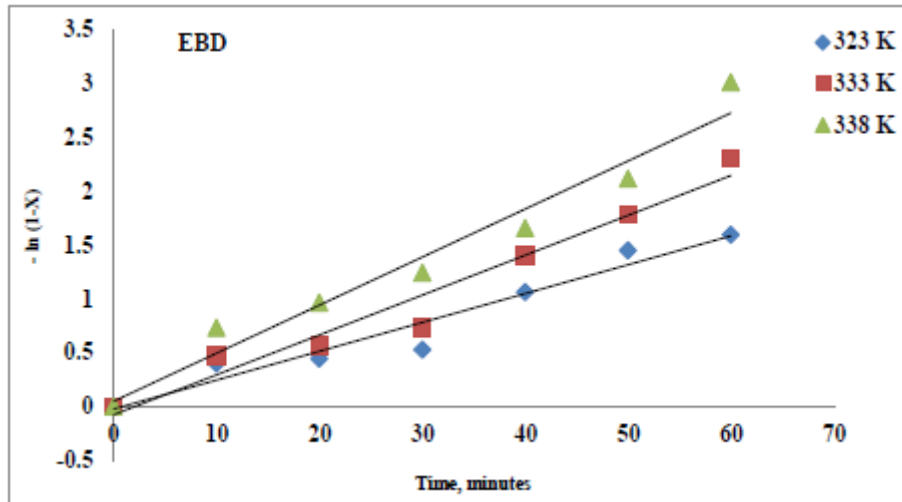


Figure 7. Plotting of - ln (1- X) versus time for ethanolysis of NEO mixture.

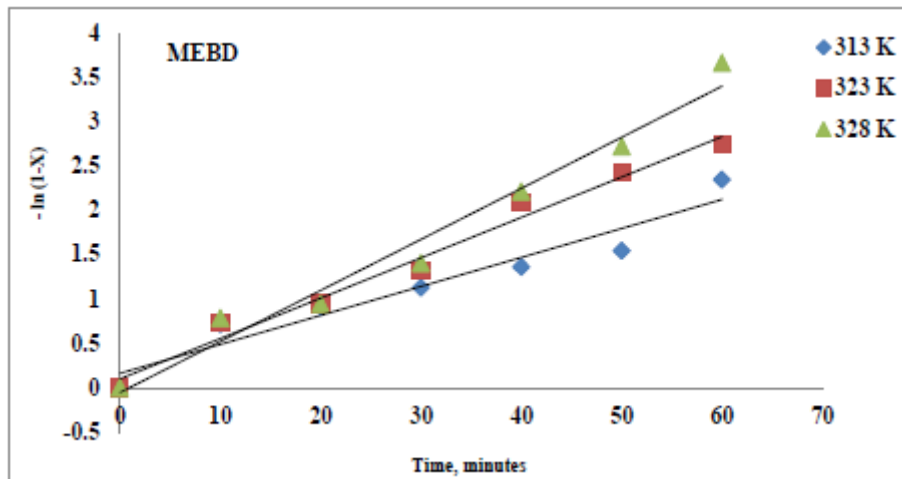


Figure 8. Plotting of - ln (1- X) versus time for transesterification of NEO mixture with mixed alcohols

where, X is the conversion of triglyceride (TG) at any given time t , and k is the rate constant. As seen from **Fig.6** and **Fig.7**, plotting $-\ln(1 - X)$ versus time will give k which could be obtained from the slope of the curve. The obtained outcomes have revealed that increasing the reaction temperature improved the rate constant for the forward reaction. The high value of R^2 coefficient assures that the reaction followed a pseudo-first-order kinetic model. The obtained consequences were in line with results performed by other authors(Birla et al.,2012; Berchmans et al.,2013).The relationship among the reaction rate constant, temperature and activation energy can be given by the Arrhenius equation:

$$k = A e^{-E_a/RT} \dots\dots\dots(4)$$

where A is the frequency factor, E_a is the activation energy, R is the universal molar gas constant, and T is the temperature ($^{\circ}K$). As the activation energy is temperature dependent; the rate constant at any temperature can be expressed using the following Eq. :

$$\ln k = \ln A - E_a /RT \dots\dots\dots (5)$$

The linear plot of $\ln k$ versus $1/T$ has given the activation energy as depicted in **Fig.8** and **Fig.9**.The activation energy values for the transesterification of the oils blend with ethanol and mixed methanol/ethanol were 30.57 $KJ mol^{-1}$ and 32.65 $KJ mol^{-1}$, respectively. These values were relatively small, which reveals the great catalytic

activity of basic catalyst (KOH) and also support that reaction is chemically controlled and not by diffusion or mass transfer limitations (Fadhil et al.,2015).

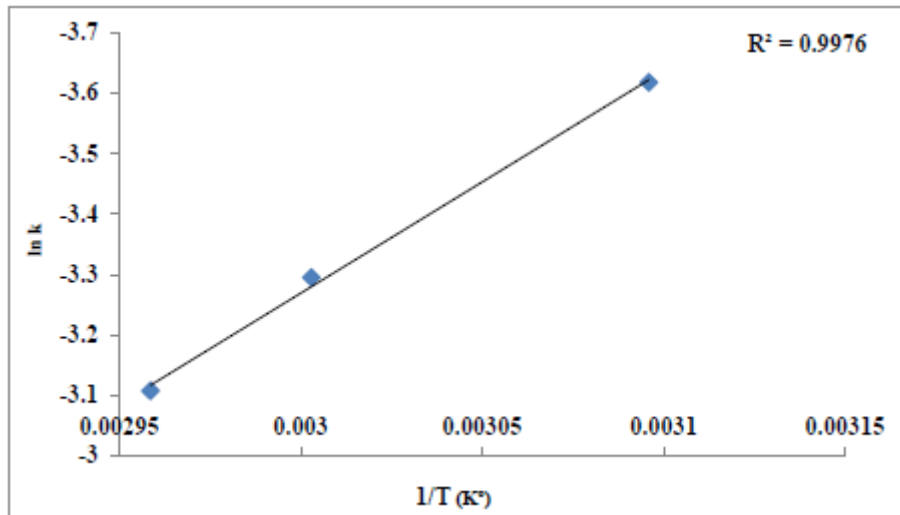


Figure 8. Arrhenius plot, $\ln k$ versus $1/T$ for ethanolysis of NEO mixture

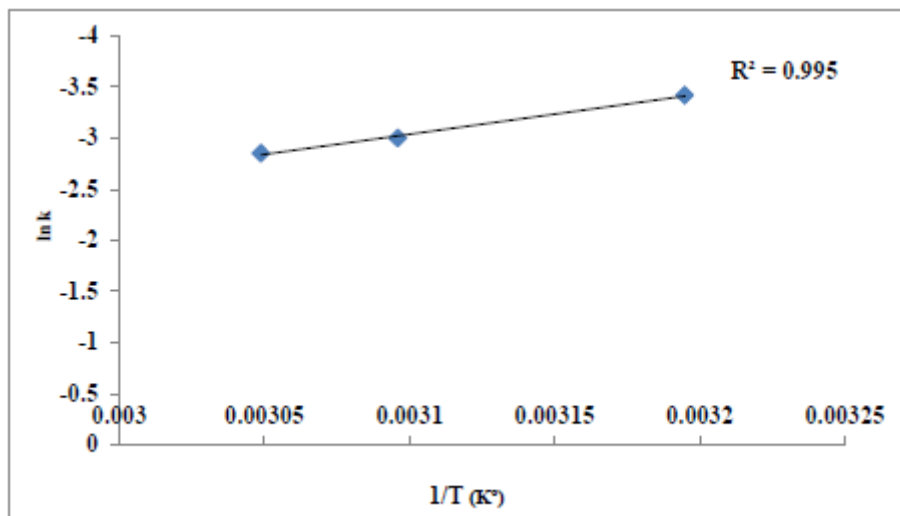


Figure 9. Arrhenius plot, $\ln k$ versus $1/T$ for transesterification of NEO mixture with mixed alcohols

Properties assessment of biodiesels

Basic physicochemical features of both EBD and MEBD produced from mixed non-edible oils were assessed according to ASTM standards, and compared with those of BD from CBO as established in **Table 2**. The results in **Table 2** exhibited that properties of the prepared fuels, were lower than those of the parent oils mixture, suggesting that alcoholysis reaction has positively changed features of the feedstock to more useful fuels. Moreover, properties fulfilled the limits given by ASTM D 6751 except the density and kinematic viscosity of the EBD. Besides, the density and kinematic viscosity of the produced fuels were superior to those of BD derived from CBO. This outcome is due to the presence of BAO and WFO, which possess much lower density and kinematic viscosity than the CBO.

Table 2. Physicochemical properties of biodiesels produced from mixed NEO

Property	BD from CSO	EBD	MEBD	ASTM D6751
Yield (wt.%)	94.55	95.11±1.0	96.33±1.0	-
Ester content (w/w %)	94.01	96.64±1.0	96.89±1.0	96.50
Density @15.6 °C g/mL	0.9202	0.9121± 0.0011	0.8940± 0.0011	0.9000
Kinematic viscosity @ 40 °C mm ² /s	9.22	8.89± 0.25	4.33±0.11	3.0 – 6.0
Flash point °C	145	±1.0160	120±1.0	130.0
Acid value mg KOH/g	0.08	0.38± 0.01	0.39± 0.01	0.50
Refractive index @ 20°C	1.4611	1.4509± 0.0010	1.4505± 0.0010	-
Pour point °C	<-15	-8	-7.0	-
Total glycerin content (wt.%)	0.08	0.14± 0.10	0.12± 0.01	0.24
Soaps (ppm)	0.62	0.98± 0.11	0.85± 0.01	5.0
Water content (%)	< 0.01	< 0.01	< 0.01	

Table 2 also shows that the properties of MEBD were superior to those of EBD. This achievement could be accredited to the ester level of each BD and the kind of alcohol used in the synthesis of BD. Blending results of MEBD with PD at various percentages are listed in Fig.10. The BD and PD can be blended at any percentages causing an improvement in their properties. Fig.10 shows that the density, kinematic viscosity, flash point and pour point of PD have been increased with the increment of BD content in the prepared blends, while the acid number decreased. These consequences could have belonged to the molecular mass of BD, which is higher than that of PD (Fadhil et al.,2019). Based on the above results, EBD and MEBD produced from the suggested oils mixture are suitable fuels for diesel engines or/and they can be successfully mixed with PD.

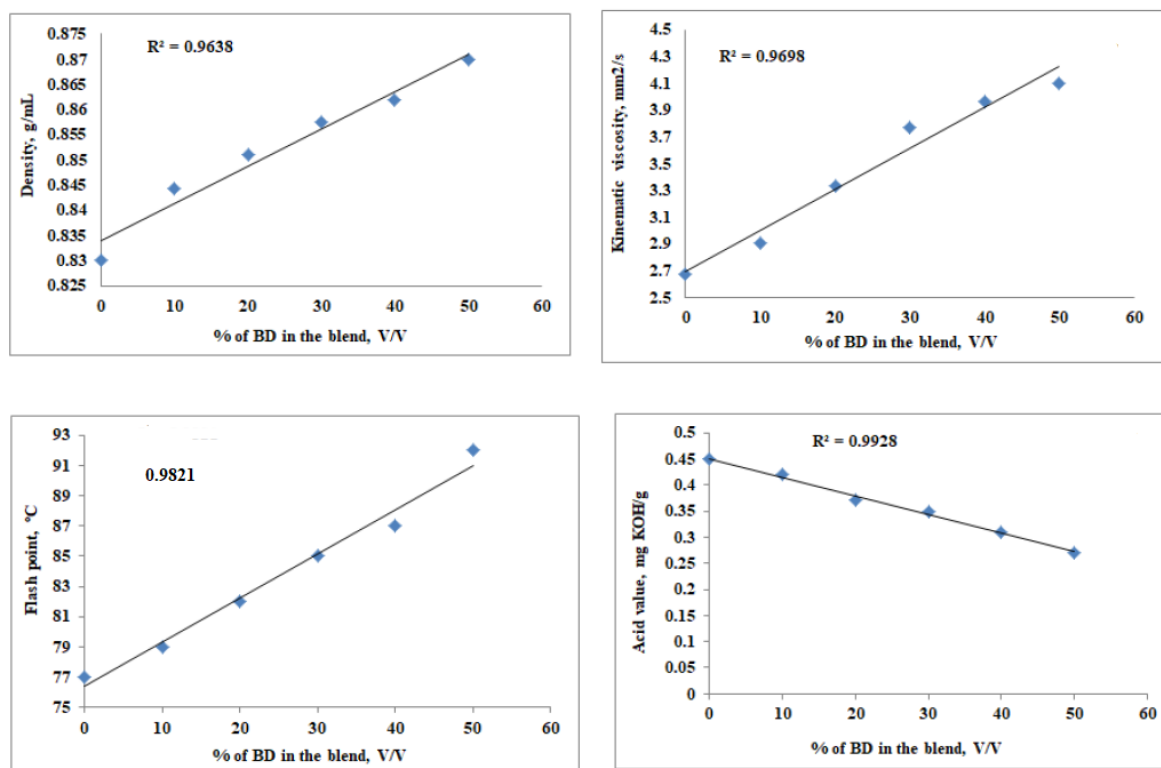


Figure 10. Effect of BD blending with petro diesel on properties of the latter

Conclusion

This paper introduces a new non-edible feedstock, namely a mixture of CBO, BAO and WFO for the synthesis of BD. This oils mixture was utilized for the production of EBD and MEBD by direct KOH-catalyzed TE process as a consequence of its low acid number. Additionally, the fuel properties of the obtained fuels lied within the limits specified by ASTM D 6751 except the density and kinematic viscosity of the EBD. The BD and conventional diesel fuel blends met the specifications fixed by ASTM D7467-17 standard. Both the ¹H

NMR and FTIR spectroscopy affirmed the conversion of non-edible oils mixture to more valuable products. Finally, transesterification of the oils blend with ethanol and mixed alcohols followed the pseudo-first-order-kinetics.

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References

- Al-dobouni, I. A., Fadhil, A. B., and Saeed, I. K. (2016). Optimized alkali-catalyzed transesterification of wild mustard(*Brassica juncea* L.) seed oil. *Energy Sources, Part A*. 38:2319–2325.
- Al-Tikrity, E.T.B., Fadhil, A.B., Ibraheem, K.K.(2017). Biodiesel production from bitter almond oil as new Feedstock. *Energy Sources part a*;39:649-656. non-edible oil.
- Al-Tikrity, E.T.B., Fadhil, A.B., Albadree, M.A.(2016). *Cyprinus carpio* fish oil: A novel feedstock for biodiesel production. *Energy Sources, Part A* 38 (22),3367-3374.
- Armendáriz, J., Lapuerta, M., Zavala, F., García-Zambrano, E., Ojed, M.C. (2015). Evaluation of eleven genotypes of castor oil plant (*Ricinus communis* L.) for the production of biodiesel. *Industrial Crops and Products* 77, 484–490 .
- Bindhu, C.H., Reddy, J.R.C., Rao, B.V.S.K., Ravinder, T., Chakrabarti, P.P., Karuna, M.S.I., et al. (2012). Properties and evaluation of biodiesel from *Sterculia foetida* seed oil. *J Am Oil Chem Soc*. 89,891–6.
- Birla, A., Singh, B., Upadhyay, S. N., Sharma, Y.C. (2012) . Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Bioresource Technology* 106 : 95–100.
- Berchmans, H.J., Morishita, K.; Takarada, T. (2013) . Kinetic study of hydroxide-catalyzed methanolysis of *Jatropha curcas*–waste food oil mixture for biodiesel production. *Fuel* ,104 : 46–52.
- Barbosa, D. da-Costa, T. Serra, S.M.P. Meneghetti, M.R. Meneghetti,(2010). Biodiesel production by ethanolysis of mixed castor oil and soybean oil. *Development of biodiesel from castor oil*, *Fuel* 89 : 3791–3794.
- Borras, E., Amigo, J.M., Van den Berg, F., Boque, R., Busto, O. (2014). Fast and robust discrimination of almonds (*Prunus amygdalus*) with respect to their bitterness by using near infrared and partial least squares-discriminant analysis. *Food Chemistry* 153 : 15–19.
- Barbosa, D.C., Serra, T.M., Plentz Meneghetti, S.M., Meneghetti, M., R. (2010). Biodiesel production by ethanolysis of mixed castor and soybean oils. *Fuel* 89,3791–4 .
- Cortes, V., Talens, P., Barat, J. M., Lerma-García, M.J. (2018). Potential of NIR spectroscopy to predict amygdalin content established by HPLC in intact almonds and classification based on almond bitterness . *Food Control* 91 : 68-75.
- Damanik, N., Ong, H.C., Chong, W., Silitonga, A.,(2017). Biodiesel production from *Calophyllum inophyllum*-palm mixed oil. *Energy Sources, Part A*. 39,1283-1289.
- Dias, J.M., Maria, C.M., Alvim-Ferraz, Almeida, M., F. (2009). Production of biodiesel from acid waste lard. *Bioresour Technol.* 100,6355–61.
- Fadhil, A. B., Aziz, A. M., and Altamer, M. H.(2016). Biodiesel production from *Silybum marianum* L. seed oil with high FFA content using sulfonated carbon catalyst for esterification and base catalyst for transesterification. *Energy Convers. Manage.* 108:255–265.
- Fadhil, A.B., Al-Tikrity, E.T., Albadree, M.A.(2017). Biodiesel production from mixed non-edible oils, castor seed oil and waste fish oil. *Fuel* 210, 721-728.
- Fadhil, A. B., and Ahmed, A. I. (2016). Production and evaluation of biodiesel from mixed castor oil and waste chicken oil, *Energy Sour.*, 38(Part A), 2140–2147.
- Fadhil, A. B., and Ahmed, A., I. (2018). Production of mixed methyl/ethyl esters from waste fish oil through TE with mixed methanol/ethanol system. *Chemical Engineering Communications* 205 (9):1157–66.
- Fadhil, A. B., Saleh, L. A. Altamer, D. H. (2019). Biodiesel production from spent fish frying oil via alkali-catalyzed transesterification. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*. <https://doi.org/10.1080/15567036.2019.1604893>.
- Fadhil, A.B., Mohammed, H.M. (2018). Co-solvent transesterification of bitter almond oil into biodiesel: Optimization of variables and characterization of biodiesel. *TRANSPORT* 33(3) 686–698.

- Fu, J., Hue. B.T.B., Turn, S.Q. (2017) Oxidation stability of biodiesel derived from waste catfish oil. Fuel 202 - 455–463.
- Gaurav, D., and Sharma, M. P..(2014). Prospects of biodiesel from pongamia in India. Renewable Sustainable Energy Rev. 32,114–122.
- Gupta, Jharna, Agarwal, M., Dalai A.K. (2016). Optimization of biodiesel production from mixture of edible and non-edible vegetable oils . Biocatalysis and Agricultural Biotechnology8:112–120.
- Hadiyanto, H., Yuliantaru, I., Hapsari, R.(2018). Production of biodiesel from mixed waste cooking and Castor oil. In: MATEC Web of Conferences. EDP Sciences.
- Hassen, M. S., Imededdine, A. N., Chin, P. T., and Saud, I. A.(2014). Production and characterization of biodiesel from Camelus dromedaries (Hachi) fat. Energy Convers. Manage. 78,50–57.
- Hincapié, G., Mondragon, Fanor, Lopez, D. (2011). Conventional and in situ TEof castor seed oil for biodiesel production Fuel 90 ,1618–1623 .
- Karnjanakom, S., Kongparakul, S., Chaiya, ., Reubroycharoen, P., Guan, G., Samart, C . (2016) . Biodiesel production from Hevea brasiliensis oil using SO₃H-MCM-41 catalyst. Journal of Environmental Chemical Engineering 4 47–55.
- Keera, S.T., El Sabagh, S.M., Taman, A.R.(2018). Castor oil biodiesel production and optimization. Egyptian Journal of Petroleum 27 : 979–984.
- Khan, T.M.Y., Atabani, A.E., Badruddin, I.A., Ankalgi R.F., Khan, T.K. M., Badarudin, A .(2015). *Ceiba pentandra*, *Nigella sativa* and their blend as prospective feedstocks for biodiesel. Industrial Crops and Products 65 :367–373.
- Kudre, T.G., Bhaskar, N., Sakhare, P.Z. (2017) . Optimization and characterization of biodiesel production from rohu (Labeo rohita) processing waste. Renewable Energy 1131408-1418.
- Lamba, N., Gupta, R., Modak, J.M., Madras, G. (2014) . ZnO catalyzed TEof Madhuca indica oil in supercritical methanol . Fuel 242 (2019) 323–333.
- Liu, J., Cui, Q., Kang, Y., Meng, Y., Gao, M., Efferth, T., Fu, Y. *Euonymus maackii* Rupr. (2019).Seed oil as a new potential non-edible feedstock for biodiesel. Renewable Energy 133: 261-267.
- Ong, H. C., Silitonga, A. S., Masjuki, H. H., Mahlia, T. M. I., Chong, W. T., and Boosroh, M. H. (2013).Production and comparative fuel properties of biodiesel from non-edible oils: *Jatropha curcas*, *Sterculia foetida* and *Ceiba pentandra* . Energy Convers. Manage. 73,245–255.
- Ong, H.C., Milano, J., Silitonga, A.S., Hassan, M. H.i, Shamsuddin, A., Wang, C., Mahlia, T.M.I., Siswanto, J., (2019). Biodiesel production from *Calophyllum inophyllum*- *Ceiba pentandra* Kusumo, F., Sutrisno, J. oil mixture: Optimization and characterization. Journal of Cleaner Production 219: 183-198.
- Pisarello, M.L., Dall-Costa, B.O, Veizaaga, N.S., Querini, C.,A.. (2010).Volumetric method for free and total glycerin determination in biodiesel. Ind Eng Chem Res;49, 8935–41.
- Reshad, A.S., Tiwari, P., Goud, V.V. (2015). Extraction of oil from rubber seeds for biodiesel application: Optimization of parameters Fuel 150, 636–644.
- Silitonga, A.S., Ong, H.C., Mahlia, T.M.I., Masjuki, H.H., Chong, W.T.(2014). Biodiesel conversion from high FFA crude *jatropha curcas*, *calophyllum inophyllum* and *ceiba pentandra* oil. Energy Procedia 61 480 – 483.
- Silitonga, A.S., Ong, H.C., Masjuki, H.H., Mahlia, T.M.I. , Chong, W.T., Yusaf, T.F.(2013). Production of biodiesel from *Sterculia foetida* and its process optimization. Fuel 111 478–484.
- Silitonga, A.S., Masjuki, H.H., Mahlia, T.M.I., Ong, H.C., Kusumo, F., Aditya, H.B., Ghazali, N.N.N., Schleicher, L.(2015).oil as feedstock for biodiesel production Fuel 156 ,63–70.
- Saez-Bastante, J., Pinzi, S., Jiménez-Romero, F.J., M.D. de Castro, L.F. Priego-Capote, Dorado, M.P.(2015). Synthesis of biodiesel from castor oil: Silent versus sonicated methylation and energy studies, Energy Convers. Manage. 96 : 561–567.
- Syazwani, O.N. , Teo, S.H. , Islam, A. , Taufiq-Yap , Y.H. .(2017). TEactivity and characterization of natural CaO derived from waste venus clam (*Tapes belcheri* S.) material for enhancement of biodiesel production, Process Saf. Environ. Protect. 105: 303-315.
- Ullah, Z, Bustam, M.A., Man, Z., A., Khan, S., Muhammad, N. Sarwono, A. (2017). Preparation and kinetics study of biodiesel production from waste cooking oil using new functionalized ionic liquids as catalysts, Renew. Energy 114 :755-765.
- Verma, D., Raj, J., Pal, A., Jain, M. (2016) . A critical review on production of biodiesel from various feedstocks, J. Sci. Innov. Res. 5 (2) 51-58.
- Vanessa, F. de Almeida, A. Pedro J. García-Moreno Antonio Guadix, B., Emilia M. Guadix.(2015) .Biodiesel production from mixtures of waste fish oil, palm oil and waste frying oil: Optimization of fuel properties. Fuel Processing Technology 133 152–160.

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