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Oxidation stability and cold flow properties of biodiesel synthesized from castor oil: Influence of alkaline catalysts type and purification techniques

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ABSTRACT

This study investigates the effects of catalyst type and washing procedures on the oxidation stability and cold flow parameters of biodiesel produced from castor oil. Castor oil was synthesized using two different catalysts; calcium oxide on alumina support (CaO-Al₂O₃) and potassium hydroxide (KOH) at a temperature of 60C, methanol to oil molar ratio of 6:1 and catalyst loading of 1 wt% of oil for 60 min. The resulting biodiesel was purified using water washing and dry washing methods ion exchange resin. The oxidation stability and cold flow behaviour of the biodiesel produced (cloud point, pour point, cold filter plugging point, and low-temperature flow test) were determined. The findings showed that the oxidation stability and cold flow properties of biodiesel is independent of washing methods but varies with catalyst type. The heterogeneously catalyzed transesterification by CaO-Al₂O₃ exhibited higher oxidation stability with an induction period of 4.4 h as against 3.5 h for the potassium hydroxide (KOH) catalyzed biodiesel. However, the values obtained in this study were above the ASTM standard of 3 h minimum. With regards to cold flow properties, the KOH-catalyzed process exhibited better cold flow properties than CaO-Al₂O₃ catalyzed biodiesel. It can be deduced from this study that the biodiesel samples will exhibit very good ignition performances when used in ignition compression engines in the low temperate region due to their satisfactory cold flow behaviour. Copyright © 2022 Elsevier Ltd. All rights reserved.

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1. Introduction

Biodiesel is a green sustainable alternative fuel petroleum diesel. It is produced via transesterification of plant or animal oils with alcohol in the presence of a catalyst [1–3]. Biodiesel production from first-generation feedstock such as edible plant seed oil has been criticized as a potential for food crisis because it competes with food supply, it has been deemed as a possible cause of edible oil shortage. Using less expensive second-generation feedstock, such as non-edible oils, is one technique to lower the cost of biodiesel production. Non-edible vegetable oils obtained from oilbearing seeds have the potential to provide cost-effective feedstock for biodiesel production [4]. The conventional and most commonly used homogenous alkaline catalyzed transesterification using NaOH and KOH results in the generation of a large quantity of wastewater since the process requires a huge amount of water for purification. These catalysts are not reusable and sometimes causes soap formation in the presence of a higher amount of free fatty acid [4]. The high cost of biodiesel synthesis can be minimized using a heterogeneous catalyst and inexpensive feedstock. Heterogeneous catalytic transesterification of vegetable oil provides a clean and efficient approach for the conversion of low-quality feedstocks into high-quality biodiesel [5–6]. Heterogeneous catalysts are distinguished by their ease of recovery, tolerance of high free fatty acid feedstock, elimination of the risk of soap production, and minimization of biodiesel washing [7]. Among different available solid heterogeneous catalysts, MgO, SrO BaO and CaO are most

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often used for biodiesel production. However, the most frequently used heterogeneous catalyst is calcium oxide (CaO), this is obviously due to its relative abundance and lower cost [8]. Calcium oxide impregnated with alumina has been reported to increase the catalyst active site, activity, reduce catalyst leaching and ease of separation from the glycerol phase and extender catalyst life span [9–10]. The reaction with this catalyst is also characterised by a shorter reaction time and easily operated at a relatively lower reaction temperature [11]. Oxidation stability is used to predict the shelf life of biodiesel under normal storage conditions [12]. The presence of unsaturated alkyl esters, which easily oxidize to aldehydes, ketones, esters, peroxides, alcohols and acids is primarily responsible for the formation of insoluble gums and sediments resulting in low oxidation stability [13]. The acids formed causes an increase in the acid number, whereas the alcohol formed lowers the flashpoint of the biodiesel [14]. Cold flow gualities are important biodiesel attributes, particularly in cold-weather areas like Russia and Canada. Three cold flow metrics that are utilized internationally are cloud point (CP), pour point (PP), and cold filter plugging point (CFPP). However, in North America, filed test results do not correspond well with these properties, making the lowtemperature flow test (LTFT) significant in this region [15]. [16] blended biodiesel from varied feedstock to create blends with varying fatty acid profiles and investigated their oxidation stability and cold flow properties. [17] studied the effect of storage duration on the oxidation stability of biodiesel produced from diverse feed suppliers. [12] studied the effect of the catalyst manufacturing process on the oxidation stability and cold flow characteristics of biodiesel generated from Jatropha curcas. According to [13], metal contaminants lowered the oxidation stability of biodiesel/diesel blends, with copper having the highest influence among the tested metals. [18] evaluated the impact of feedstock composition on biodiesel cold flow characteristics and oxidation stability, as well as the impact of purification water acidity on these variables. Senra et al. [19] studied the impact of glycerol-derived additives on biodiesel cold flow properties. The authors reported that the additives work as dilution, stop crystallization, and improve properties. Bencheikh et al. [20] studied the effect of blending diesel with waste cooking biodiesel on cold flow properties. The authors reported that blending 80% diesel with 20% waste cooking biodiesel reduces CP, PP, and CFPP by 17, 21, and 21 °C, respectively. Similarly, the investigation by [21,22] also reported the cold flow behaviour of biodiesel from different vegetable oils.

The Castor plant (Ricinus communis L) is a member of the family Eurphorbiaceae. The plant is reportedly grown in tropical and subtropical regions of the world. In Nigeria, the plant is to grow well in a different part of the northern region as a weedy plant. The plant bears seeds that contain a substantial amount of oil (55-69%). Castor seed contains a high amount of potently poisonous protein (ricin). Castor oil possesses a high viscosity and excellent lubricity when compared with other plant oils [23]. Castor oil is ricinoleic vegetable oil. It has a molecular weight of 928.5 g/mol and is composed of 89-90 per cent ricinoleic acid. Because of the presence of hydroxyl groups in the oil, it is known to stabilize to oxygen, preventing the production of hyperperoxides and inductively preventing oxidation reactions. Because of its great oxidation stability, castor oil is a second-generation biodiesel feedstock with significant commercial potential [17,16]. To the best of the author's knowledge, no research has been conducted on the effect of alkaline catalyst type or washing procedure on the oxidation stability and cold flow characteristics of castor biodiesel. The purpose of this research is to investigate the effect of alkaline catalysts and purification processes on the oxidation stability and cold flow parameters of biodiesel derived from castor seed oil.

2. Materials and methods

2.1. Materials

Freshly extracted castor oil, CaO supported on Al_2O_3 catalyst was obtained from the National Research Institute for Chemical Technology (NARICT), Zaria. Analytical grade KOH pellets were adopted. The castor oil was filtered through cheesecloth to remove insoluble impurities. Mixed ion exchange resin (indion ion exchange) was purchased from Makurdi, Nigeria. The KOH was chosen due to its solubility in methanol and is one of the most commonly used alkaline catalysts for homogenous transesterification [4]. Calcium oxide impregnated with alumina has been reported to increase the catalyst active site, activity, reduce catalyst leaching and ease of separation from the glycerol phase and extender catalyst life span [9–10]. The reaction with this catalyst is also characterised by a shorter reaction time and easily operated at a relatively lower reaction temperature [11].

3. Methods

3.1. Transesterification

The prepared oil was weighed (250 g) and deposited in the reactor. It was then preheated to the reaction temperature of 600C. To avoid methanol loss due to evaporation, the reaction was carried out below the boiling point of methanol, 65C. The catalyst was weighed (1 wt. per cent oil) and dissolved in a calculated volume of methanol (6:1 methanol to oil molar ratio), which was then transferred to the preheated oil and left to react at 60 °C for 60 min with vigorous stirring. Following transesterification, the diesel-glycerol mixture was transferred to a separation funnel and allowed to separate into two distinct layers, with biodiesel on top and glycerol on the bottom. Separating the biodiesel (methyl esters) from the glycerol was accomplished by first draining the glycerol and then the biodiesel in separate conical flasks. This was done in two batches, one KOH-catalyzed and the other CaO supported on Al₂O₃.

3.2. Biodiesel purification

There were two washing procedures used: wet washing and dry washing. The biodiesel was cleaned to eliminate excess methanol and other contaminants for the wet washing process. An equivalent volume of heated distilled water (45 °C) was added to the biodiesel in a separation funnel, tilted slowly, and allowed to separate. As the water subsided, it percolated through the biodiesel, removing impurities. After that, it was allowed to settle naturally, splitting into two layers of biodiesel and water. The bottom layer of water was drained away, leaving the cleaned biodiesel behind. This method was repeated until the pH of the wash water was close to neutral, indicating that the catalyst had been completely washed away. The washed biodiesel was transferred to a beaker and heated on a heating mantle at 100 Celsius to remove the remaining moisture. To purify the produced biodiesel using the dry wash process, ion exchange resin was used. 50 g of mixed ion exchange resin was ionized in 100 ml of 10% (v/v) concentrated hydrochloric acid solution for 30 min before being rinsed in 1000 ml of distilled water. The resin was cleaned with methanol before use to remove any leftover water molecules. Following the passage of 20 ml of biodiesel through it to remove any remaining methanol, the purified biodiesel sample was passed through it twice under gravity to allow for ion exchange and purification.

3.3. Biodiesel characterization

The physico-chemical properties of the biodiesel samples produced were determined using standard procedures and correlations as discussed below; The cetane number of the biodiesel samples were evaluated from saponification and iodine values using correlations reported by [24]. The Iodine value (IV) and Saponification value (SV) were determined as reported by [3].

$$Cetanenumber(CN) = CI - 1.5 \tag{1}$$

where,

$$CetaneIndex(CI) = 46.3 + \frac{5458}{SV} + 0.225IV$$
(2)

The calorific value was computed from saponification and iodine values using correlations reported by [24].

$$Calorific \, value(CV) = 49.43 - 0.015IV - 0.041SV \tag{3}$$

3.4. Oxidative stability determination

The oxidative stability of the biodiesel was examined using the Metrohm 873 Biodiesel Rancimat Instrument in compliance with the EN 14,214 standard protocol. Purified air was channelled through the sample heated to 110Celsius into a determination unit containing distilled water at a constant flow rate of 10 L/h. The conductivity of the sample was constantly recorded and plotted overtime on a computer, and the induction period (IP) was determined as the intersection of two tangent lines along the conductivity curve.

3.5. Cold flow behavior

Cloud (CP) and pour points (PP) were obtained according to ASTM D2500-91 and ASTM D97-96 method respectively. CFPP and LTFT were computed using the correlation reported by Dunn [15].

$$CFPP = 1.0(CP) - 4.5$$
 (4)

$$LTFT = 1.0(CP) + 5 \tag{5}$$

4. Results and discussion

4.1. Characterization of biodiesel

The properties of the castor biodiesel samples produced are shown in Table 1. Iodine value (IV) is the measurement of the total degree of unsaturation of biodiesel fuel. It provides a useful guide in preventing various engine problems. Iodine value is based on alkyl double bonds reactivity. Higher iodine value is an indication of the possibility of the formation of various degradation products which can lead to a decrease in the quality of lubrication and affect the engine operational performance negatively. The iodine value in

Table 1

Physico-chemical properties of castor biodiesel samples.

this study was low (11.42–18.18 $gI_2/100 g$) as compared to EN stipulated value of 120as the maximum. The low iodine values obtained signifies that the castor biodiesels have relatively good oxidation stability. The results are satisfactorily better lower than 108 and 126.6 gI₂/ 100 g reported for corn oil biodiesel [25] and soyabean oil biodiesel [26]. The saponification values were generally close to the value obtained for coconut oil biodiesel (126.225 mg/KOH) and lower than those reported for cashew nut oil biodiesel (187.94 mgKOH/g) by [27]. The saponification values and iodine value are related to cetane number and calorific value. The cetane numbers of the biodiesel is a measure of the ignition quality of diesel fuel. It is a valuable indicator of the quality of diesel fuel [28]. A higher cetane number is desirable as fuel with a higher cetane number ignite more easily when injected into the diesel engine [29]. The cetane numbers of the biodiesel samples were within 79.063 - 87.41 which is well above the minimum standard specification of 47. This is an indication that the biodiesel samples will exhibit very good ignition performances when used in an ignition compression engine. According to Bajpai and Tyagi (2006) [28], biodiesel has a higher cetane number than petrol diesel due to its higher oxygen content. This means that while using biodiesel, the engines will run more smoothly and quietly [30]. The cetane numbers observed in this study is also obviously higher than the 48 reported for Jatropha biodiesel [31]. The viscosity of a fluid is a measure of its resistance to deformation when subjected to shear stress. The Viscosity of biodiesel samples ranges from 4.22 to 4.33 mm²/s which is appreciably within 1.9-6.0 mm²/s stipulated for ASTM standard. According to Musa et al.[2], lower viscosity than required specification can lead to volumetric fuel loss and increasing wear of engine parts while too high viscosity is the major cause of mechanical inefficiencies. The calorific value of a fuel assesses its energy content. The calorific value of biodiesel lies between 39 and 41 MJ/Kg. The calorific values were higher than those obtained for algae biodiesel (41.36 MJ/kg) and cashew nut oil biodiesel (37.20 MJ/kg) as reported by [32] and [28] respectively.

4.2. Influence of washing methods and catalyst type on oxidation stability

The induction period, which is the amount of time required for a biodiesel sample to produce rapid oxidation when subjected to elevated temperature and oxygen aeration, is used to evaluate biodiesel oxidation stability [12]. Table 1 displays the induction period (IP) for biodiesel samples synthesized by various techniques. Wet washing of biodiesel with warm water is widely utilized due to pollutants' solubility in water, process simplicity, low cost, and availability. The technique is characterized by emulsion formation and generation of a large volume of wastewater [33]. Because samples purified using different wash techniques have the same IP (4.4 and 3.5 h) for CaO-Al₂O₃ and KOH catalyzed reactions, respectively. The results for the two wash methods employed in this investigation reveal that the oxidation stability of Castor Methyl Esters (CME) is independent of the washing method. Considering the

Properties	кон		CaO-Al ₂ O ₃ ,		ASTM (D6751-20)Specification
	Wet	Dry	Wet	Dry	
Iodine Value (mgKOH/g)	18.18	11.421	18.73	15.228	EN 120 max
Cetane Number	87.41	80.39	83.82	79.06	47 min.
Saponification Value (mgKOH/g)	124.82	148.67	136	154.28	-
Calorific Value (MJ/kg)	43.977	43.089	43.505	42.799	-
Viscosity	4.22	4.31	4.33	4.30	1.9-6.0
Induction Period (hours)	3.5	3.5	4.4	4.4	Min. 3

influence of catalyst type; the CaO-Al₂O₃ catalyzed transesterification exhibited a higher IP of 264 min (4.4 h) as against an IP of 208 min (3.5 h) exhibited for KOH catalyzed biodiesel samples. This indicates that the heterogeneous catalyst resulted in improved oxidation stability (CaO-Al₂O₃). The presence of hydroxyl groups on the castor oil feed's triglyceride chain, which stabilizes it to oxidation, could explain these findings. These acids decrease biodiesel stability by producing peroxides and hydroperoxides. These side reactions are not conceivable for transesterification employing a heterogeneous catalyst (CaO- Al₂O₃) due to a lack of alkaline hydroxides [34]. As a result, the end outcome was more stable. All samples (both KOH and CaO-Al₂O₃ catalyzed) met the ASTM criteria of 3 h minimum IP (ASTM D6751).

4.3. Influence of catalyst type and wash method on cold flow properties

The cold flow properties of the tested biodiesel samples are summarized in Table 2. The cloud point of biodiesel is the temperature at which the fuel starts to form visible crystals after cooling [18]. For both wet and dry washing operations, CaO- Al₂O₃ catalyzed biodiesel samples exhibited a cloud point of -5°C. Similar results were obtained with KOH catalyzed CME. This finding suggests that the wash technique has little effect on biodiesel cloud points. The cloud point of biodiesel samples made with KOH catalyst was found to be lower $(-13^{\circ}C)$ than that of samples made with CaO-Al₂O₃ catalyst (-5C). The results obtained in this study outperform the cloud points of 0, 16, and 20 Celsius published by [15], and [12] for biodiesel made from soya bean oil, palm oil, and Jatropha curcas oil, respectively. The low cloud points observed in this work is an indication low tendency of gel formation by the biodiesel. These low values depict that biodiesel has a satisfactory ability to perform well under cold climatic conditions. The difference in cloud point value could be attributed to the difference in feedstock's employed and catalyst type.

The pour point is the lowest temperature at which fuel can flow when the container is tilted. It is an essential feature for forecasting biodiesel behaviour in cold weather circumstances [15]. The finding reveals a similar trend to those for the cloud point, with a variance in KOH, Dry. The pour point of biodiesel produced using CaO- Al_2O_3 , Dry (-17C) is the same as that of (CaO-Al_2O_3, Wet), and the wash technique does not affect biodiesel pour point. Furthermore, KOH, Wet had a lower pour point than CaO-Al₂O₃, Dry, and CaO-Al₂O₃, implying that KOH-catalyzed castor oil transesterification produced biodiesel with a higher pour point than CaO-Al₂O₃catalyzed transesterification. The pour point of virgin castor oil was higher than that of all other product biodiesel, indicating that transesterification of castor oil into biodiesel enhances its pour point. The finding in this study differs significantly with - 4 and 16C reported for corn oil methyl ester and palm oil methyl ester respectively [15]. The lowest temperature at which 20 ml of fuel may pass freely through a 45 m mesh size filter under 0.019 atm pressure in 60 s is CFPP. This property governs how a biodieselpowered engine responds when cold. It represents the temperature

Table 2

Cold flow properties of biodiesel samples.

at which crystalline fuel components cause a filter to plug [15]. The CFPP results for the biodiesel samples are shown in Table 2. CFPP values followed the same pattern as cloud point, with virgin castor oil having the highest CFPP value of -4.5C and KOH catalyzed biodiesel having the lowest (-17.5C). Greater CFPP values indicate unsatisfactory cold flow characteristics. The findings suggest that converting castor oil into biodiesel enhances the end product's cold flow qualities. It also implies that biodiesel made with the KOH catalyst has better cold flow properties than biodiesel made with the CaO-Al₂O₃ catalyst. These findings were greater than the - 6C and -14C values reported by Serrano et al. for sunflower and rapeseed biodiesel, respectively [18].

The low-temperature flow test (LTFT) is the lowest temperature at which 180 ml of test fuel may be safely drawn through a 17 m screen at 20 kPa of vacuum in 60 s [15]. This attribute determines the efficiency with which diesel fuels move through the filtering unit of a diesel engine under test conditions. The result shows that biodiesel samples produced with KOH catalyst have a lower LTFT ($-8 \, ^\circ$ C) than those produced with CaO-Al₂O₃ catalyst, which has an LTFT value of 0 $^\circ$ C. Again, in terms of LTFT, all of the biodiesel samples outperformed virgin vegetable oil. The poor cold flow properties of castor methyl esters found in this study are mostly due to a high percentage of low melting, unsaturated components (97.5 per cent wt. of methyl esters).

5. Conclusions

The study has attempted and succeeded in investigating the effect of the influence of alkaline catalysts type and purification techniques on oxidation stability and cold flow behaviour of biodiesel from castor seed oil. The biodiesel produced has a low iodine value (11.42–18.18 gI_2 / 100 g), saponification values. The high cetane numbers (79.063 - 87.41) obtained is well above the minimum standard specification of 47. The viscosity of 4.22 4.33 mm²/s is appreciably within 1.9–6.0 mm²/s stipulated for the ASTM standard. The calorific value of biodiesel lies between 39 and 41 MJ/Kg. The biodiesel samples purified using different (wet and dry) wash techniques have the same IP (4.4 and 3.5 h) for CaO-Al₂O₃ and KOH catalyzed reactions, respectively. This indicates that the oxidation stability of castor Methyl Esters (CME) is independent of the washing method. The CaO-Al₂O₃ catalyzed transesterification exhibited a higher IP of 264 min (4.4 h) as against an IP of 208 min (3.5 h) exhibited for KOH catalyzed biodiesel samples suggesting that heterogeneous (CaO-Al₂O₃) catalyst enhanced oxidation stability. However, both KOH and CaO-Al₂O₃ catalyzed met the ASTM criteria of 3 h minimum IP (ASTM D6751). The cloud point of KOH catalysed biodiesel was lower $(-13^{\circ}C)$ than CaO-Al₂O₃ catalysed biodiesel $(-5^{\circ}C)$ which suggests that the biodiesel has a satisfactory ability to perform well under cold climatic conditions. CFPP values followed the same pattern as cloud point, with virgin castor oil having the highest CFPP value of -4.5°C and KOH catalyzed biodiesel having the lowest (-17.5°C). The findings suggest that converting castor oil into biodiesel enhances cold flow qualities. Biodiesel produced with the KOH cat-

КОН		CaO-Al ₂ O ₃		
Washing Method				
Wet	Dry	Wet	Dry	
- 13	- 13	- 5	- 5	
- 22	- 17	- 17	- 17	
- 17.5	- 17.5	- 9.5	- 9.5	
- 8	- 8	0	0	
	KOH Washing Method Wet - 13 - 22 - 17.5 - 8	KOH Washing Method Wet Dry - 13 - 13 - 22 - 17 - 17.5 - 17.5 - 8 - 8	KOH CaO-Al ₂ O ₃ Washing Method Wet Wet Dry Wet - 13 - 13 - 5 - 22 - 17 - 17 - 17.5 - 17.5 - 9.5 - 8 - 8 0	

alyst exhibit better cold flow properties than biodiesel made with the CaO-Al₂O₃ catalyst. The LTFT (- 8C) obtained KOH catalyzed biodiesel is lower than 0 °C for CaO-Al₂O₃ catalysed biodiesel. The poor cold flow properties of castor methyl esters found in this study are mostly due to a high percentage of low melting, unsaturated components (97.5 per cent wt. of methyl esters). It can be deduced from this study that the biodiesel samples will exhibit very good ignition performances when used in an ignition compression engine as the value obtained are appreciably within stipulated for ASTM and EN stipulated standards.

CRediT authorship contribution statement

Faruk Aisha Abubakar: Supervision. **Umar Mohammed Garba:** Supervision. **Mohammed Alhassan:** Investigation and Data curation. **Usman Baro Abdullahi:** Editing. **Agi Damian Tyoor:** Writing - Original draft. **Abubakar Garba Isah:** Writing - Review and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] A.F. Lee, J.A. Bennett, J.C. Manayil, K. Wilson, Heterogeneous Catalysis for Sustainable Biodiesel Production via Esterification and Transesterification, Chem. Soc. Rev. (2014) 3–32.
- [2] U. Musa, A.A. Aboje, I.A. Mohammed, M.A. Aliyu, M.M. Sadiq, O. Olaibi Aminat, The Effect of Process Variables on the Transesterification of Refined Cottonseed Oil, Proceedings of the World Congress on Engineering 2014 Vol I, 2014.
- [3] U. Musa, F. Aberuagba, Characteristics of a Typical Nigerian Jatropha curcas oil for biodiesel production, Res. J. Chem. Sci. 2 (10) (2012) 7–12.
- [4] A. Abdullah, F. John, B. Rob, The optimization of Biodiesel Production by Using Response Surface Methodology and Its Effect on Diesel Engine, 2nd International Conference on Environment Science and Biotechnology 48 (4) (2012) 1–7.
- [5] N.P. Asri, S. Machmudah, Wahyudiono, Suprapto, K. Budikarjono, A. Roesyadi, M. Goto, Palm oil transesterification in sub- and supercritical methanol with heterogeneous base catalyst, Chem. Eng. Process. 72 (2013) 63–67, https://doi. org/10.1016/j.cep.2013.07.003.
- [6] L.R.V. Da Conceição, L.M. Carneiro, J.D. Rivaldi, H.F. De Castro, Solid acid as a catalyst for biodiesel production via simultaneous esterification and transesterification of macaw palm oil, Ind. Crops Prod. 89 (2016) 416–424.
- [7] V.V. Bobade, K.S. Kulkarni, A.D. Kulkarni, Application of heterogeneous catalysts for the production of biodiesel, Int. J. Adv. Eng. Technol. 2 (2) (2011) 184–185.
- [8] P. Verma, M.P. Sharma, G. Dwivedi, Impact of alcohol on biodiesel production and properties, Renew. Sustain. Energy Rev. 56 (2016) 319–333.
 [9] S. Sulaimana, B. Shah, P. Jamal, M.Z. Alam, Production of Heterogenous Catalyst
- [9] S. Sulaimana, B. Shah, P. Jamal, M.Z. Alam, Production of Heterogenous Catalyst for Biodiesel Synthesis, Int. J. Chem. Environ. Eng. 5 (2) (2014) 56–78.
- [10] N.S. Talha, S. Sulaiman, Overview of Catalyst in Biodiesel Production, ARPN J. Eng. Appl. Sci. 2 (1) (2016) 439–448.

- [11] M. Zabeti, W.M.A.W. Daud, M.K. Aroua, Optimization of the activity of CaO/ Al₂O₃ catalyst for biodiesel production using response surface methodology, Appl. Catal. A 366 (1) (2009) 154–159.
- [12] L.M.d.S. Freire, I.M.G.D. Santos, J.R. de Carvalho Filho, A.M.T.d.M. Cordeiro, L.E. B. Soledade, V.J. Fernandes, A.S. de Araujo, A.G. de Souza, Influence of the Synthesis Process on the Properties of Flow and Oxidative Stability of Biodiesel from *Jatropha curcas* Biodiesel, Fuel 94 (2012) 313–316.
- [13] S. Jain, M.P. Sharma, Effect of metal contents on oxidation stability of biodiesel/ diesel blends, Fuel 116 (2014) 14–18.
- [14] Y.C. Sharma, B. Singh, S.N. Upadhyay, Advancements in development and characterization of biodiesel: A review, Fuel 87 (12) (2008) 2355–2373.
- [15] R.O. Dunn, Improving the Cold Flow Properties of Biodiesel by Fractionation, Soybean -Applications and Technology (2011) 211–240.
- [16] Zuleta, E.C., Luis A. Rios, L.A and Benjumea, P.N (2012). Oxidative Stability and Cold Flow Behavior of Palm, +Sacha-inchi, Jatropha and Castor Oil Biodiesel blends, *Fuel Processing Technology*, 102, 96-101.
- [17] M. Ndana, B. Garba, L. Hassan, U.Z. GandFaruk, Effect of Storage on Stability of Biodiesel Produced from Selected Seed Oils, Int. J. of Pure and Applied Sci. and Tech. 13 (1) (2012) 10–18.
- [18] M. Serrano, R. Oliveros, M. Sánchez, A. Moraschini, M. Martínez, J. Aracil, Influence of Blending Vegetable Oil Methyl Esters on Biodiesel Fuel Properties: Oxidative Stability and Cold Flow Properties, Energy 65 (2014) 109–115.
- [19] M. Senra, S.N. McCartney, L. Soh, The effect of bio-derived additives on fatty acid methyl esters for improved biodiesel cold flow properties, Fuel 242 (2019) 719–727, https://doi.org/10.1016/j.fuel.2019.01.086.
- [20] Bencheikh, K., Atabani, A. E., Shobana, S., Mohammed, M. N., Uguz, G., and Arpa, O. (2019). Fuelsproperties, characterizations and engine and emission performance analyses of ternary waste cooking oil biodiesel-diesel-propanol blends. Susta. Energy Technol. Asses. 35, 321-334. doi:10.1016/j. seta.2019.08.00
- [21] C.B. Sia, J. Kansedo, Y.H. Tan, K.T. Lee, Evaluation on biodiesel cold flow properties, oxidative stability and enhancement strategies: A review, Biocatal. Agricultural Biotechnol. 24 (2020) 101514, https://doi.org/10.1016/j. bcab.2020.101514.
- [22] N.A. Fathurrahman, C.S. Wibowo, M. Nasikin, M. Khalil, Optimization of sorbitan monooleate and γ-Al₂O₃ nanoparticles as a cold-flow improver in B30 biodiesel blend using response surface methodology (RSM), J. Ind. Eng. Chem. 99 (2021) 271–281, https://doi.org/10.1016/j.jiec.2021.04.037.
- [23] Musa, U., Mohammed, Ibrahim. A Sadiq, M. M., Aberuagba, F and Olurinde, O.A and Obamina, R (2015). Synthesis and Characterization of Trimethylolpropane- Based Biolubricating Oil from Castor oil, Proceedings of 45th Annual Conference, Exhibition of Nigerian Society of Chemical Engineers (NSChE), Nov. 5-7, 2015, Warri, Delta State.
- [24] C.C. Enweremadu, O.J. Alamu, Development and Characterization of Biodiesel from Shea Nut Butter, Int. Agrophys. 24 (2010) 29–34.
- [25] N. El Boulifi, A. Bouaid, M. Martinez, J. Aracil, Process Optimization for Biodiesel Production from corn oil and its oxidative Stability, Int. J. Chem. Eng., Article ID 518070, 9 (2010), doi:10.1155/2010/518070
 [26] A.S. Silitonga, H.H. Masjuki, T.M.I. Mahlia, H.C. Ong, F. Kusumo, H.B. Aditiya, N.
- [26] A.S. Silitonga, H.H. Masjuki, T.M.I. Mahlia, H.C. Ong, F. Kusumo, H.B. Aditiya, N. N.N. Ghazali, *Schleichera oleosa* L oil as feedstock for biodiesel production, Fuel 156 (2015) 63–70.
- [27] E.I. Bello, A.O. Akinola, F. Out, T.J. Owoyemi, Fuel and Physiochemical Properties of Cashew (*Anacardium occidentale*) Nut Oil, Its Biodiesel and Blends with Diesel, Br. J. Appl. Sci. & Technol. 3 (4) (2013) 1055–1069.
- [28] D. Bapjai, V.K. Tyagi, Biodiesel: Source, Production, Composition, Properties and its Benefits, J. Oleo Sci. 55 (10) (2006) 487–502.
- [29] A. Demirbas, Characterization of Biodiesel Fuels, Energy Source, A 31 (11) (2009) 889–896.
- [30] A. Demirbas, Biodiesel production from vegetable oil via catalytic and noncatalytic supercritical methanol transesterification methods, Prog. in Energy and Combustion Science 31 (2005) 466–487.
- [31] T.K. Tint, M.O. Mya, Production of biodiesel from Jatropha oil (Jatropha curcas) in a pilot plant, In Proceedings of World Academy of Science, Engineering and Technology (38), 2009.
- [32] P. Nautiyal, K.A. Subramanian, M.G. Dastidar, Kinetic and thermodynamic studies on biodiesel production from Spirulina platensis algae biomass using single-stage extraction-transesterification process, Fuel 135 (2014) 228–234.
- [33] M.G. Gomes, D.Q. Santos, L.C. de Morais, D. Pasquini, Purification of biodiesel by dry washing, employing starch and cellulose as natural adsorbents, Fuel 155 (2015) 1–6.
- [34] G. Shruti, Z. Yaakob, B.N. Narayanan, S. Padikkaparambil, U.K. Surya, A.P. Mohammed, A review on the oxidation stability of biodiesel, Renew. Sustain. Energy Rev. 35 (2014) 136–153.