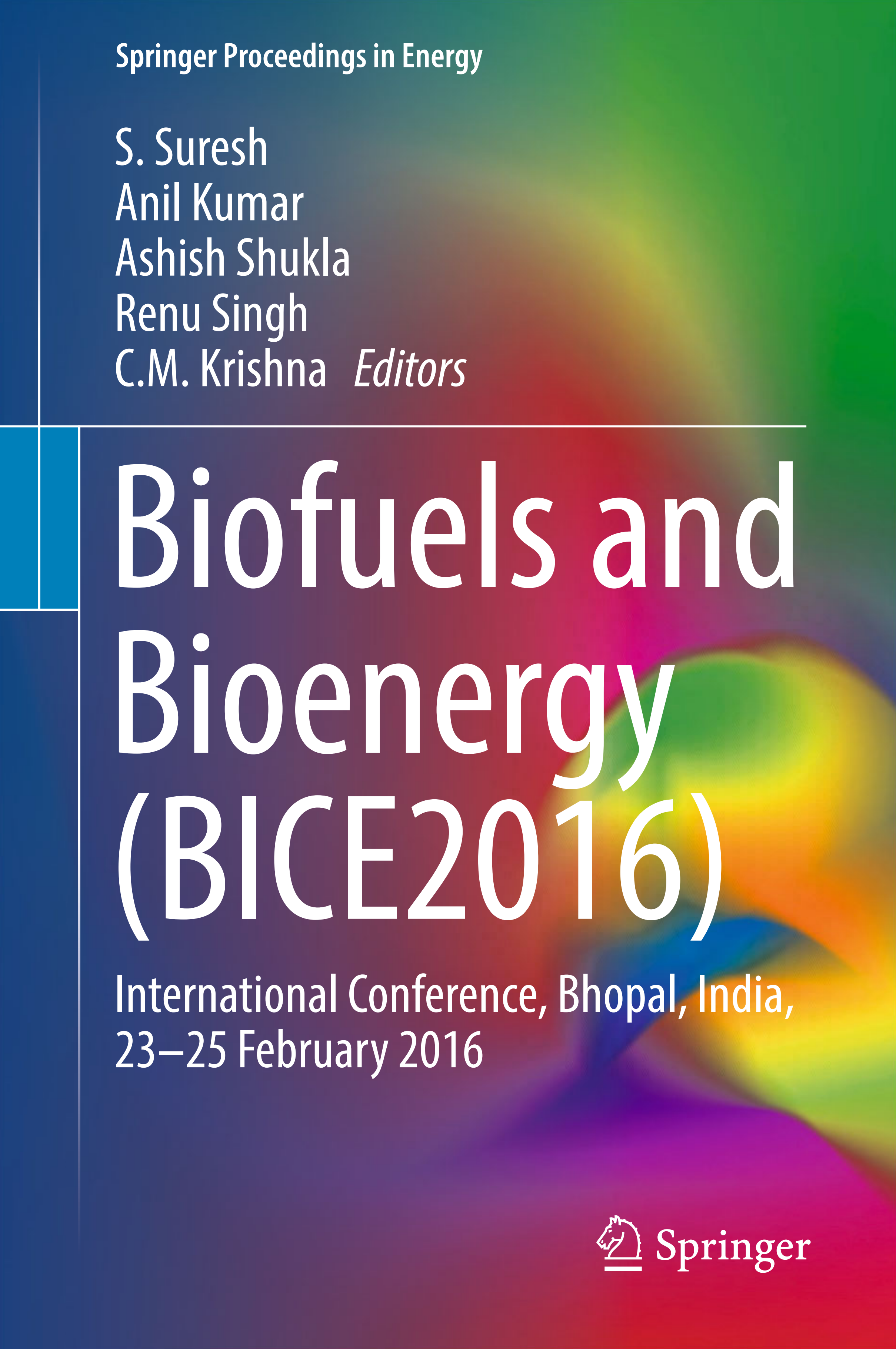

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ISSN 2352-2534 ISSN 2352-2542 (electronic)
Springer Proceedings in Energy
ISBN 978-3-319-47255-3 ISBN 978-3-319-47257-7 (eBook)
DOI 10.1007/978-3-319-47257-7

Library of Congress Control Number: 2016961679

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Contents

Waste Cooking Oil (WCO) Biodiesel Production Using Calcined Chalk as Heterogeneous Catalyst

Amit Pal, Balbir Singh and Shashank Mohan

Abstract Biodiesel is a low emission, renewable and a potential alternative of petro diesel made from vegetable oil, waste lipid and animal fat. Transesterification is a very common method to produce biodiesel from raw oil. Other three methods of production of biodiesel are: Direct use and blending of raw oils, micro-emulsion and thermal cracking. The study deals with heterogeneous catalyst based transesterification reaction for conversion of raw WCO into biodiesel. Calcium oxide used as heterogeneous catalyst was prepared from easily available and cheap white chalk ($CaCO_3$) by the process of calcinations. The heterogeneous catalyst was easily separated from the crude biodiesel produced by transesterification reaction. Further, catalyst separation did not require water washing process during purification process of biodiesel. Biodiesel production was investigated for various factors like methanol to oil molar ratio, reaction time and wt% of catalyst to oil with the help of recycled heterogeneous catalyst. Sustainable yields were obtained when the proposed catalyst was used in mechanical stirring, hydrodynamic cavitation and ultrasonic cavitation methods. The present research has the potential to ease the process of biodiesel production without environmental degradation from low quality feedstocks.

1 Introduction

Industrial development and increased transportation worldwide has created a huge demand for liquid fuel which is mainly derived from petroleum [1]. These fuel reserves being exploited extensively will not able to cater the need of future. The petroleum reserves are very limited and only available with few countries due to

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S. Suresh et al. (eds.), *Biofuels and Bioenergy (BICE2016)*,
Springer Proceedings in Energy, DOI 10.1007/978-3-319-47257-7_1

which other countries bound to import high priced crude petroleum thus facing energy and economy crisis. The environment pollution is the another curse of using petroleum based fuel due to emission of carbon monoxide (CO), nitrogen oxides, sulphur dioxide and particulate matters leading to climate change and health problems across the world. Therefore, to increase energy security for economic development and to minimize emission, the need to search for an alternative and environment friendly source of energy such as biodiesel is necessary [2]. Moreover biodiesel can be used with little or no modification in existing Compressed Ignition (C. I.) engines. Unlike fossil fuel, molecular structure of biodiesel contains oxygen which helps in increasing the rate of combustion of fuel in C. I. engines resulting in reduction in emission of CO, soot etc. [3].

Biodiesel is mono alkyl esters of fatty acids which are derived from vegetable oils (edible and non-edible) and animal fats. The feed-stocks from which more than 95% of biodiesel is produced in world are in edible category as theses are only largely and mainly produced. The properties of biodiesel prepared from such oils proved to be compatible to be used with petroleum diesel [4]. But the use of edible oil for producing biodiesel will cause scarcity of edible oil in the market. Whereas waste cooking oil is not suitable for human consumption and thus it can be a potential source of feedstock for biodiesel production.

There are different methods through which biodiesel can be produced viz. blending of raw oils and direct use, micro-emulsion, pyrolysis and transesterification. Vegetable oils are nothing but a combination of organic compounds. It ranges from simple straight chain compound to complex proteins structure and fat-soluble vitamins while the petroleum diesel fuel is saturated non-branched molecules with carbon atoms in a range of 12–18 [1]. The problem implies with the vegetable oil is its higher viscosity and higher flash point contributing to its lower volatility and the reactivity of unsaturated hydrocarbons [5]. Vegetable oil has a higher viscosity in the range of 35–60 cSt in comparison with the diesel with low viscosity of 4 cSt at 40 °C [6], which creates short-term troubles like starting problem in cold weather, gumming and clogging of filters, pipelines and injectors, knocking problem in engine and long-term troubles like choking of injectors, engine wear etc. [7] when used in existing unmodified direct and indirect diesel engine. When the vegetable oils are used in C. I. engines directly or by diluting it with petro diesel than that method is called direct use and blending of raw oils.

Micro-emulsion is a special class of colloidal dispersion that has attracted a wide attention because of their ability to solubilise material which was not soluble otherwise. Micro-emulsions were found to have lower fuel viscosity and better spraying patterns of fuel during combustion process. However the micro-emulsions have lower cetane number and lower calorific value which makes it unsuitable for use in C. I. engine for long time [6, 8, 9].

Pyrolysis refers to the chemical changes of long chain and saturated vegetable oils or natural fatty acids and animal fats using thermal energy in presence of air [10]. There have been lots of studies on the pyrolysis of triglycerides to obtain products appropriate for diesel engine. Alkanes, alkadines, alkenes, aromatics and carboxylic acids are produced from triglycerides on thermal decomposition.

The products of pyrolysis are chemically alike to petroleum gasoline and diesel. The main disadvantage of Pyrolysis is that it is an energy intensive process and higher cost of production [11].

Transesterification means the exchanging of alkoxy group of an ester compound with alcohol [1]. The reaction needs alcohol to react with vegetable oil (triglycerides) in the presence of a catalyst. Methanol is commonly used alcohol due to its low cost and quick reaction with triglycerides [10]. Transesterification is the very often used method for production of biodiesel. Biodiesel produced through transesterification has higher cetane value, higher efficiency of combustion and low emissions. However the main disadvantage associated with transesterification is safe disposal of by-products (glycerol and waste water) [8, 12, 13]. The reactions mostly use an acid or a base catalyst.

2 Biodiesel Production Process with Catalyzed Reaction

The given flowchart (Fig. 1) shows transesterification process using alkali catalyzed in general. The major shortcoming of alkali catalyst is its rapid reaction with free fatty acids to form soap. Equation (1) represents saponification reaction between FFA and alkali catalyst to form water and soap.

$$\underset{\text{(FFA)}}{R_1-\text{COOH}} + \underset{\text{sodium hydroxide}}{\text{NaOH}} \rightarrow \underset{\text{(soap)}}{R_1\text{COONa}} + \underset{\text{(water)}}{H_2O} \tag{1}$$

The reaction is not desirable because NaOH reaction with free fatty acid produces the soap and the soap lowers the biodiesel yield and the esters separation from the glycerol become more difficult and slow. It also combines with the catalyst and there is more need of catalyst to complete the reaction, hence the process will become costly [14]. The water already present in the oil along with water produced in saponification reaction reacts with triglycerides to form diglyceride and free fatty acids. These undesirable reactions can be avoided by employing acid catalyzed transesterification reaction. Acid catalyst directly transforms free fatty acid in oil into biodiesel [15, 16]. This acid catalyst based reaction has not gain much attention as the alkali-catalyzed transesterification due its slow rate and a need of high methanol to oil molar ratio [17]. The oils with high value of FFA undergo pre-treatment process (before being converted into biodiesel) where the oil undergoes neutralization process in the presence of acidic catalyst. Some drawbacks of transesterification reaction using alkali catalyst are that it needs neutralization and separation from the reaction mixture. The recovery of glycerol is also a difficult process, removal of catalyst from the product requires water washing and alkaline waste water requires treatment which increases the cost of biodiesel production [18]. To avoid the formation of soap and making the purification process simple and cheap, enzymatic catalysts like lipases are used to effectively catalyze the reaction [18]. But due to longer reaction time and higher cost, enzymes are not used

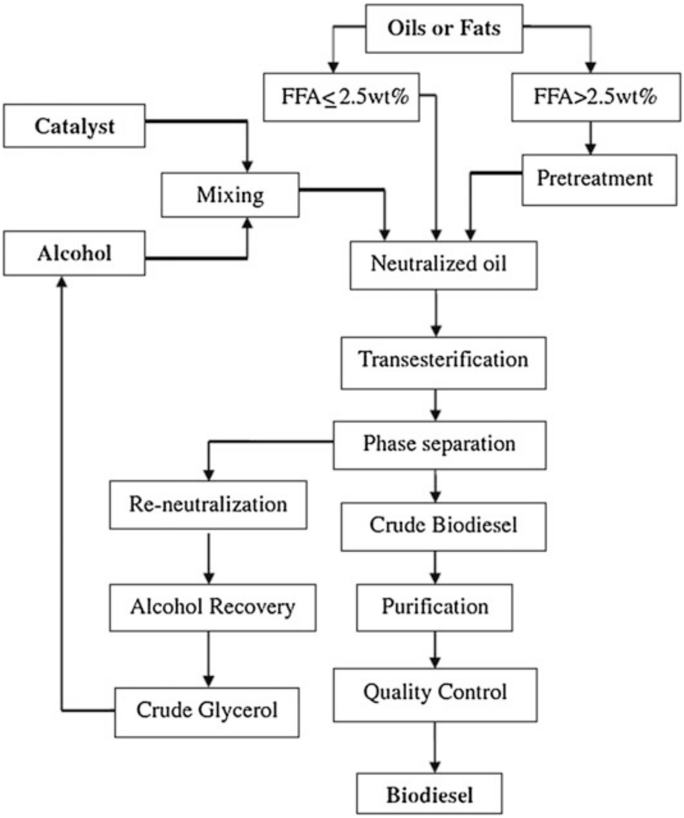


Fig. 1 Simplified process flow chart of alkali-catalyzed biodiesel production [11]

commercially [19]. Another range of catalyst is heterogeneous catalyst (alkaline or acidic) which shows easy recovery from the product of reaction by simple filtration method without water washing and eliminating the need of pre-treatment of feedstocks with high FFA content [20].

3 Homogeneous Catalyst

Homogeneous catalyst is of same phase as the reactants that is liquid. Homogeneous catalysts are dissolved in a solvent with the substrates. Homogeneous base catalysts (NaOH, KOH, CH_3ONa, and CH_3OK etc.) and homogeneous acid catalysts (H_2SO_4, HCl, $Fe_2(SO_4)_3$ etc.) are used for transesterification reaction. These catalysts have well defined active sites, moderate activity level and reasonably well understood reaction mechanism. After gravity separation of glycerol, the crude biodiesel is cleaned by water washing process, dry washing or membrane extraction process to remove any residual catalyst, free glycerol, unreacted alcohol and soap that were formed during transesterification reaction.

4 Heterogeneous Catalyst

These catalysts are in the form of metal oxides in solid state. In contrary to the homogenous system, heterogeneous catalysis involves adsorption of reactants and desorption of products to take place on the surface of the solid catalyst for the reaction to take place at increased rate. To get the desired properties of catalyst, heterogeneous catalysts can be easily tuned so that the presence of free fatty acid or water does not adversely affect the reaction steps during transesterification [21]. Active sites are not well defined and the reaction mechanism is poorly understood. Compared with the former one, solid acid-catalysts is cheaper, offer some advantages for eliminating separation, corrosion, toxicity, and environmental problems, but the reaction rate is slower [22].

5 Materials

Vegetable oils derived from Soybean, Groundnut, Rapeseed, Palm, Olive etc. are very commonly used for frying of food items in hotel and food industries. But after heating above a critical temperature for deep frying, they become unsuitable for further cooking, as their further consumption as food by human beings may lead to cholesterol formation in them. Presently, the WCOs are still lower cost feedstock making biodiesel production more competitive to the production of petroleum based diesel fuel. WCO was brought from 5 star hotel ITC Maurya Sheraton, Delhi. Various properties of biodiesel produced from WCO are represented in Table 1.

Methanol was purchased from nearby local market and white dustless chalk pieces (black board chalk) of Apsara Company containing high quality calcium carbonate are used to produce calcium oxide (CaO). Table 2 presents the details of constituents used for production of biodiesel. Experiments were carried out for different molar ratio of 6:1, 9:1 and 12:1 for 3, 4 and 5% catalyst by weight of oil.

Table 1 Properties of WCO biodiesel

Property	WCO biodiesel
Phase (physical)	Liquid
Colour	Oily
Specific gravity @ 25 °C	0.8849
Kinematic viscosity, mm^2/s @ 40 °C	56.94
Molecular weight (g/mol)	870
Pour point (°C)	6
Cloud point (°C)	12

Table 2 Oil, alcohol and catalyst used for mechanical stirring and ultrasonic cavitation

Molar ratio (alcohol/oil)	WCO (g)	Methanol (g)	Catalyst (CaO)		
			3%	4%	5%
6:1	100	22	3 g	4 g	5 g
9:1	100	33	3 g	4 g	5 g
12:1	100	44	3 g	4 g	5 g

6 Preparation of Heterogeneous Catalyst (CaO) from White Chalk ($CaCO_3$)

A process where ores or solids are brought to a thermal decomposition in presence of air during a thermal treatment process is known as calcinations. The calcinations process generally occurs at temperatures below the melting point but above the thermal decomposition temperature. Thermal decomposition temperature is defined as the temperature at which the standard Gibbs free energy for calcinations reaction is zero. For Calcium carbonate decomposition process, the chemical reaction is shown in (2).

$$\mathrm{CaCO_3} \xrightarrow{\text{Heating at } 850\,^\circ\mathrm{C}} \mathrm{CaO} + \mathrm{CO_2(gas)} \tag{2}$$

White chalk pieces were kept in muffle furnace at 850 °C for 2 h. Thermal decomposition started at these temperatures to drive out CO_2 gas and residual is CaO as shown in Fig. 2. The chalk pieces (CaO) were allowed to cool in furnace itself and stored in an airtight container to avoid exposure to air.

7 Preparation of WCO, Catalyst and Methyl Alcohol Mixture

First of all waste cooking oil WCO is cleaned by filtering to remove any impurities. Then the clean raw oil is heated up to a temperature of 110 °C to remove any water content if present in oil to avoid formation of soap during reaction. Then the oil is allowed to cool up to 60 °C temperature. Catalyst (CaO) (crushed to powder form) in 3, 4 and 5% by weight of oil and mixed with methyl alcohol (CH_3OH) with in a molar ratio of 6:1, 9:1 and 12:1.

8 Transesterification by Mechanical Stirring

CH_3OH and recycled powered CaO mixture is poured in a beaker. Then the WCO sample is poured into the beaker. The beaker is now kept on the hot plate of mechanical stirrer. It functions as a source of heat to maintain the temperature of the

Fig. 2 Chalk pieces heated in muffle furnace at a temperature of 850 °C

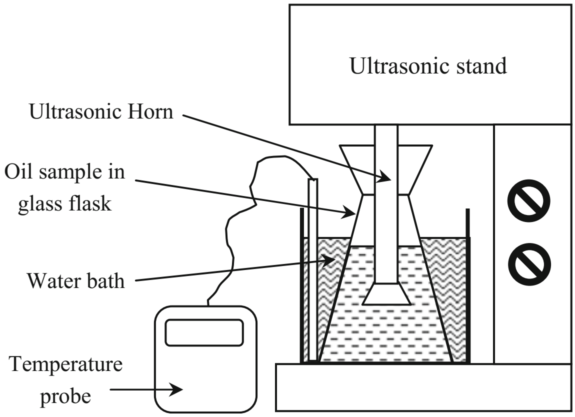
solution to 55–60 °C. The transesterification reaction is carried by conventional mechanical stirring method. A magnetic capsule is dropped in the mixture and rotated with the help of mechanical stirrer. The solution is allowed to stir with a speed of 300 rpm. During the reaction the temperature of mixture is maintained from 55 to 60 °C for the reaction time period of 3, 3½, 4 and 4½ h. After the completion of reaction the sample in the beaker is poured in a separation flask for 2–3 h for the separation. Catalyst CaO, soap, Fatty acid methyl ester (FAME) and methanol settled down in order as per their specific weight (catalyst at the bottom and methanol at the top).

The insoluble catalyst and glycerine recovered by filtration, dried in an oven at 250 °C, sieved and catalyst reused in subsequent reactions. The remaining solution was put into the beaker. The extra methanol present in biodiesel has been removed by distillation process and left over is biodiesel. Biodiesel so produced is measured.

9 Transesterification by Ultrasonic Cavitation

The process of formation of vapour cavities in the mass of liquid i.e. formation of small bubbles or voids in the mass of liquid is known as Cavitation [23]. In this process a bubble in a fluid is forced to oscillate in size or shape due to some form of energy input, as in a case of acoustic field. Such cavitation is often employed in

Fig. 3 Ultrasonic generator



ultrasonic cleaning baths [24]. The transesterification reactions were carried out in an ultrasonic reactor. Ultrasonic horn type processor is shown in Fig. 3.

In horn type reactor, horn is attached with the transducer which produces ultrasonic irradiation in the mixture. Horn type reactor has been used for this experiment. The ultrasonic cavitation generates ultrasonic processor frequency of 25–28 kHz. The transducer horn is clamped in a separate stand having jack type table to support the beaker and for its proper adjustment so that sufficient length of horn is dipped in the sample without touching the boundaries of the beaker. The mixture of oil, methanol and catalyst is kept inside the ultrasonic processor transducer. Adjust the beaker so that ultrasonic horn sufficiently dips in the solution. Reaction time was varied for different samples from half an hour to 2 h with an increment of half an hour. After the completion of reaction the biodiesel is separated in the same way as in mechanical stirring method.

10 Experimental Results

Figures 4, 5 and 6 shows comparison of biodiesel yield for mechanical stirring transesterification process at molar ratio 6:1, 9:1 and 12:1 of methanol to alcohol respectively for varying concentration of recycled heterogeneous catalyst and reaction time. % yield of biodiesel produced was found to increase sharply with increase in reaction time from 3 to 4 h and then achieve almost constant yield with increased reaction time.

Figure 4 shows percentage yield for 5% catalyst by weight for 4 h reaction time was 20% higher than that for 4% catalyst and 2.4% higher than for 3% catalyst for 6:1 molar ratio. The maximum yield was around 85% for 5% CaO catalyst by weight.

Fig. 4 Effect of reaction time and catalyst concentration on biodiesel yield using MR 6:1 in mechanical stirring

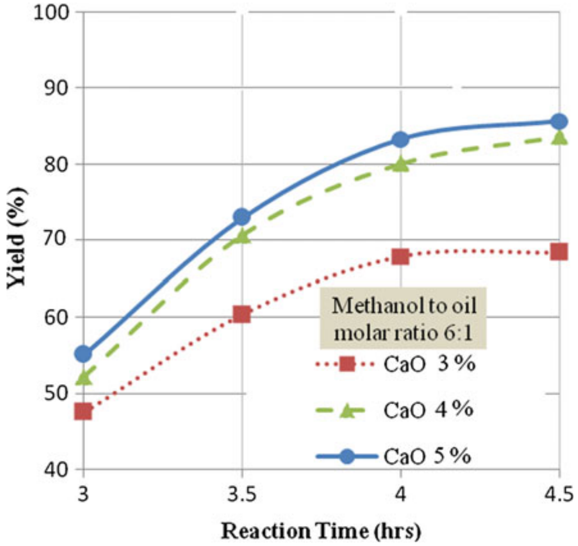


Fig. 5 Effect of reaction time and catalyst concentration on biodiesel yield using MR 9:1 in mechanical stirring

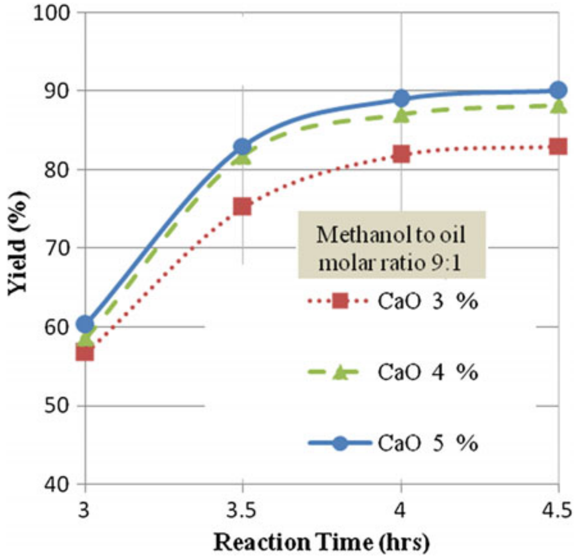


Figure 5 shows percentage yield for 5% catalyst by weight for 4 h reaction time was 7% higher than that for 4% catalyst and 2% higher than for 3% catalyst for 9:1 molar ratio. The maximum yield was around 90% for 5% CaO catalyst by weight.

Figure 6 shows percentage yield for 5% catalyst by weight for 4 h reaction time was 6.5% higher than that for 4% catalyst and 2% higher than for 3% catalyst for 12:1 molar ratio. The maximum yield was around 92% for 5% CaO catalyst by weight.

Fig. 6 Effect of reaction time and catalyst concentration on biodiesel yield using MR 12:1 in Mechanical Stirring

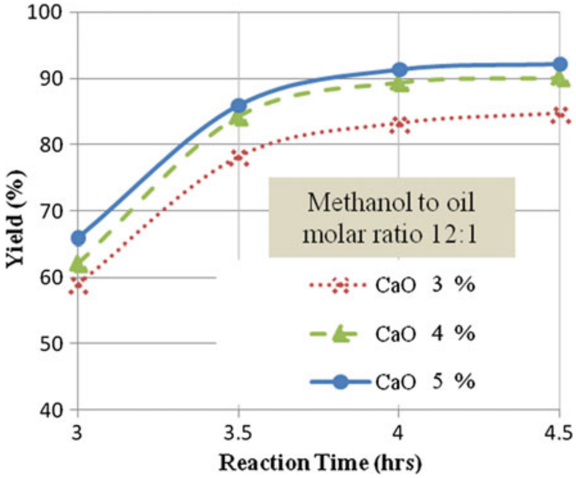
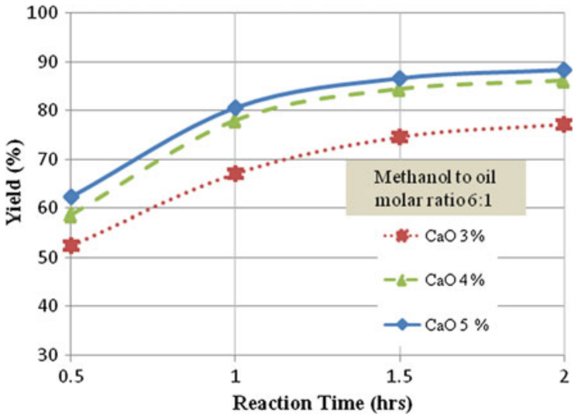


Fig. 7 Effect of reaction time and catalyst concentration on biodiesel yield using MR 6:1 in ultrasonic cavitation



Figures 7, 8 and 9 shows comparison of biodiesel yield for ultrasonic cavitation transesterification process at molar ratio 6:1, 9:1 and 12:1 of methanol to alcohol respectively for varying concentration of recycled heterogeneous catalyst and reaction time. % yield of biodiesel produced was found to increase sharply with increase in reaction time from 0.5 to 1 h and then increases gradually up to 1.5 h and then achieve almost constant yield for increased reaction time.

Figure 4 shows percentage yield for 5% catalyst by weight for 1.5 h reaction time was 12% higher than that for 3% catalyst and almost equal to that for 4% catalyst for 6:1 molar ratio. The maximum yield was around 87% for 5% CaO catalyst by weight.

Figure 6 shows percentage yield for 5% catalyst by weight for 1.5 h reaction time was 10.5% higher than that for 3% catalyst and 3% higher than for 4% catalyst for 9:1 molar ratio. The maximum yield was around 93.5% for 5% CaO catalyst by weight.

Fig. 8 Effect of reaction time and catalyst concentration on biodiesel yield using MR 9:1 in ultrasonic cavitation

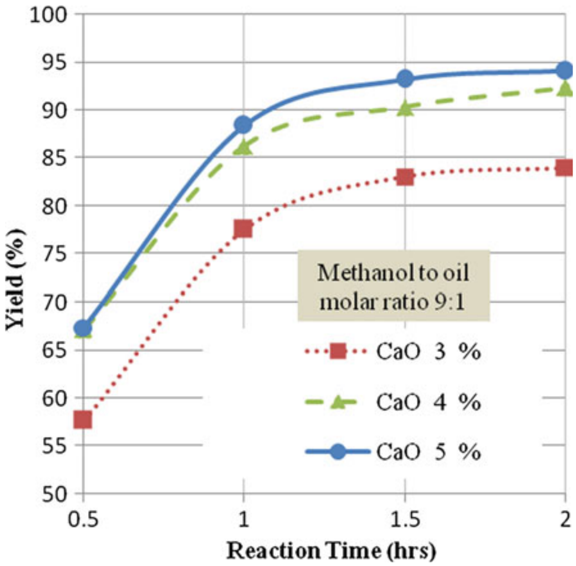


Fig. 9 Effect of reaction time and catalyst concentration on biodiesel yield using MR 12:1 in ultrasonic cavitation

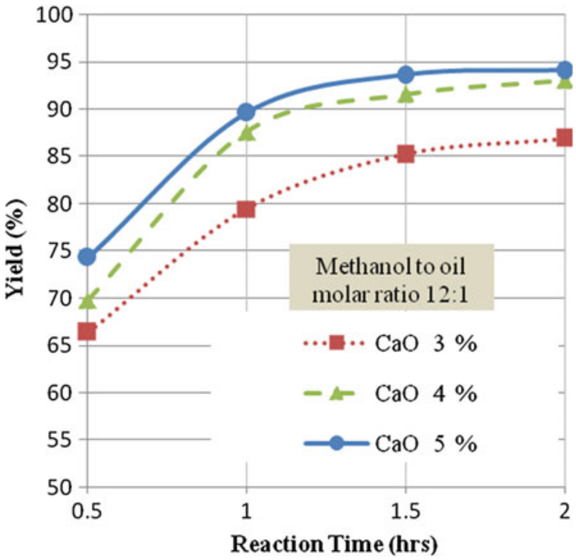


Figure 6 shows percentage yield for 5% catalyst by weight for 1.5 h reaction time was 8.5% higher than that for 3% catalyst and 2.5% higher than for 3% catalyst for 12:1 molar ratio. The maximum yield was around 94% for 5% CaO catalyst by weight.

11 Discussion

An increase in molar ratio (methanol to oil) of 12:1 has given maximum yield for every variation of catalyst concentration. A further increment in molar ratio does not increase the yield in all the methods of production.

An increase in catalyst concentration has given maximum yield for every variation of different molar ratio of methanol. A further increase in catalyst quantity does not increase the yield in all the methods of production. Increase in catalyst quantity beyond 5% raised the viscosity of solution, so the hindrance in the mixing of reactants.

12 Conclusion

Heterogeneous base catalyst has proved to be economical, environmental friendly, easily recyclable, ease in separation and low cost of separation in comparison with homogeneous catalyst, whereas the catalyst preparation is difficult and expensive task. Heterogeneous catalyst transesterification reaction was slow when comparing with homogeneous catalyst. It is probably due to inadequate mass transfer of reactants in the solution, thus improper and inefficient contacts of reactants with the catalyst to complete the reaction. However the rate of reaction increases in ultrasonic cavitation method of transesterification reaction. CaO catalyst leads to sustainable yield even at molar ratio of 12:1 whereas most of the commonly used heterogeneous catalyst requires high molar ratios up to 20:1.

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Synthesis of Biodiesel from Karanja Oil Using Modified Mordenite as a Heterogeneous Catalyst

Shikha Gangil, Virendra Singh Dhakar, Yashwant Parihar, Divya Bhagat, Priyanka Bhawate and Bharat Modhera

Abstract The catalytic performance of alkali leached modified mordenite has been obtained for transesterification of Karanja oil using a rota mantle as experimental setup at 60 °C. Dealumination was found in the alkali leaching calcined catalysts. It was found significant effect on the physical structure and chemical composition of the catalysts. The alkali leached modified mordenite processed transesterification gave the highest methyl ester yield 95.14% with NaOH loading (20% by wt) of in 3 h.

1 Introduction

With the decreasing conventional source of petroleum fuel, it will increase to concern about alternate sources and environmental impacts. That's why, it is crucial to grow eco-friendly biodegradable and renewable alternate source of energy to eliminate this problem.

In this regard, biodiesel proves to be a better alternate of energy. Biodiesel, a combination of long-chain fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs) biodiesel can be formed by several methods; transesterification has become the most popular method today. It possesses various benefits like better performance for production of biodiesel in less requisite, etc. [1]. Biodiesel is currently produced by using homogeneous acid or base catalyst. These catalysts include some undesirable features: costly process steps of catalyst/products separation; need to get rid of FFA and water from the feedstock [2].

Generally, Biodiesel was produced with a homogeneous catalyst such as NaOH or KOH. It produces methyl ester with high yield under mild reaction conditions: temperature of 60 °C, atmospheric pressure and reaction time of 1 h. But, before use of this product as a diesel fuel, the base catalyst must be separated from it. Due

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S. Suresh et al. (eds.), *Biofuels and Bioenergy (BICE2016)*,
Springer Proceedings in Energy, DOI 10.1007/978-3-319-47257-7_2

to high basicity of process wastewater, it will environmentally toxic. The total cost of the biodiesel production based with including separation process is not sufficiently viable as compared to the production cost of petroleum diesel oil. For example, soyabean oil transesterification with ETS-10. Zeolites has been studied, conversion in more than 90% was achieved at a reaction temperature of 100 °C [3]. To remove problem corresponding to homogeneous catalyst, people are focusing to the development of heterogeneous catalyst. The heterogeneous catalytic transesterification embraces under Green Technology due to the following reasons: (1) catalyst can be recycled/reused, (2) there is zero waste water or very less amount of waste water produced during the process and (3) separation of biodiesel and glycerol is very easy. During homogeneous catalytic transesterification the glycerol produced is of low quality and requires lengthy process and distillation for purification. Heterogeneous catalyst production rate of biodiesel is slightly slow as compared to homogeneous catalyst but production is economically feasible with recycling nature of catalyst and no more extra utilities requirement [4]. Chemistry of heterogeneous catalyst reported, includes metal hydroxides, metal oxides, metal complexes such as magnesium oxide, calcium oxide, zirconium oxide, hydro calcites, zeolites and supported catalysts. These types of catalysts have been examined as solid catalysts which overwhelmed some of the weakness on use of homogeneous catalysts. Alkaline earth oxide catalysts activity order was observed as BaO > SrO > CaO > MgO [5]. Another concern with biodiesel production is the availability of feedstock. In countries like US and Europe, the main sources for biodiesel production are generally edible oils like soyabean, rapeseed and sunflower. In India, non-edible oils like Karanja and Jatropha are being encouraged on a very large scale, as these can be grown on negligible and waste lands. Saras Vieira et al. modified the ZSM-5 with the citric acid at different concentration and temperature which result as the increase in external surface area and reduction in both Bronsted and Lewis acid sites with the increase in Si/Al ratio from 11 to 15 at 60 °C temperature, sample showed the better result with highest Bronsted acidity result and greatest increase in surface area [6]. Wang et al. performed Na^+ ion exchange process with modifying the low Al zeolites Beta as an effective catalyst in transesterification of triolein in excess methanol. Which resulted that at least eight cycles of transesterification on reaction by reflux method the Na-Zeolite exhibits any significant decrease in catalysts in transesterification of triolein [7]. Wang et al. showed that modified zeolites MCM-22 prepare with NaOH ion exchange process gives the conversion yield of triolein to biodiesel as high as 94.5% achieved in 1 h [8]. Liu et al. showed that calcium meth oxide has excellent catalytic activity and better stability in transesterification of soyabean to biodiesel with methanol and the optimum conditions: 1:1 volume ratio of methanol to oil, addition of 2% $Ca(OCH_3)_2$ catalyst, 65 °C and about 2 h of reaction time. It has the potential to replace homogeneous catalyst [9]. Intarapong and Iangthanarat told that 20% KOH/Mordenite is an better catalyst for palm oil transesterfication with methanol, showing highest activity with methyl ester yield of 96.7 wt% in the tested catalyst. Further, he explained that activity of uncalcined catalyst is better than calcined catalyst [10]. Bhagiyalakshmi et al. synthesized Na-ZSM-5 in alkaline medium and impregnated with cerium oxide by using cerium nitrate as a source for cerium. The maximum yield of transesterification process was resulted to be 90% under the conditions: oil:methanol molar ratio: 1:12; temperature: 60 °C; time: 1 h; catalyst: 5 wt%. Then reaction is catalyzed with ceria and the maximum yield of 93% over 15% Ce-ZSM-5 might be due to the availability more ceria for transesterification [11]. Selvabala et al. experimented that solid catalyst present lower activity as compared to other catalyst in transesterification reaction. This lower activity is compensated by higher reaction temperature. For this much temperature a large amount of energy is required. So research must be done to increase the catalyst efficiency under lower operating temperature [12]. Jiang et al. [13] showed that Na_3PO_4 had excellent activity and stability during transesterification reaction. During the transesterification of rapeseed oil to be biodiesel, the yield attained 95% with a mass ratio of catalyst to oil of 3%, molar ratio methanol: oil of 9:1, reaction temperature of 70 °C and reached equilibrium after 20 min. The dissolution of catalyst in solution was very less. Karmee and Chadha used Hb-zeolite, ZnO and montmorillonite K-10 catalysts for non-edible oil crude Pongammia Pinnate transesterfication with methanol (1:10 Molar ratio of oil: methanol), 0.575 g catalyst (0.115 wt% of oil) in 5 g oil at 120 °C. They found that the highest conversion rate of 83% was obtained with ZnO, while montmorillonite K-10, Hb-zeolite catalyst gave low conversion rates of 47 and 59% respectively in 24 h of reaction time [14].

Chauhan and Sharma [5] synthesized $[Et_3NH]Cl–AlCl_3$ for biodiesel production. Chloro aluminate ionic liquid was showed it is very capable for biodiesel production with high biodiesel yield 98.5% under the operating conditions: soybean oil 5 g, methanol 2.33 g, catalyst $[Et_3NH]Cl–AlCl_3(x(AlCl_3) = 0.7)$, reaction time 9 h, temperature 70 °C. Suppes et al. studied that catalyst used for the alcoholysis of soybean shows less activity as compared to the activities of faujasite NaX and ETS-10 zeolites. Conversion to methyl esters in excess of 90% were achieved at temperature of 150 and 120 °C with residence times of 24 h. At 100 °C, the ETS-10 provided a conversion of 92% in 3 h. Pretreating the ETS-10 catalyst at 500 °C for 4 h was instrumental in increasing the activity of the ET-10 catalyst [15]. Corma et al. experimented alcoholysis of triglycerides with using basic solid catalysts such as Cs-MCM-41, Cs-sepiolite and hydrotalcites. The reaction was carried out at 240 °C and 5 h of reaction time. Hydrotalcites gave a good conversion of 92% followed by Cs-sepiolite (45%) and Cs-MCM-41 (26%) [16].

2 Methodology

2.1 Materials and Methods

Mordenite, (SAR = 20) was obtained from the Qingdao Wish Chemicals Co., Ltd. China. NaOH and methanol were purchased of AR grade from Merck Specialties Pvt. Ltd. Karanja oil was obtained from local market. Table 1 shows the detail

Table 1 Composition of extracted oil for fatty acid [17]

Fatty acid	Molecular formula	Composition (%)
Oleic acid	$C_{18}H_{34}O_2$	51.61
Linolenic acid	$C_{18}H_{32}O_2$	16.66
Palmitic acid	$C_{16}H_{32}O_6$	11.64
Stearic acid	$C_{18}H_{36}O_2$	7.70
Dosocasnoic acid	$C_{22}H_{44}O_2$	4.46
Eicosanoic acid	$C_{20}H_{40}O_2$	1.33
Tetracosonaic acid	$C_{24}H_{48}O_2$	1.08

composition of Extracted oil. It was consisted of 94.48% pure triglyceride and rests were lipid associates free fatty acids. These will measure of unsaponifiable matter. The fatty acid profile of Karanja oil was recognized by gas chromatograph (GC). GC (Perkin-Elmer XL Auto system GC) was equipped with a flame ionization detector (FID) with a 14 ml carrier packed column. The temperature was raised from 60 to 240 °C with a 4 °C/min rise in temperature and then held for 5 min.

2.2 Catalyst Modification

The pure Mordenite was calcined at 600 °C for 2 h. Mordenite was modified by impregnation of various amount of Na loadings (5, 10, 15, 20, 25, and 30 wt%). Mordenite was mixed with NaOH solution for 24 h. Then, it was dried at 110 °C for 24 h before use as a catalyst in the reaction.

2.3 Catalyst Characterization

Parent Mordenite and modified mordenites were characterized by sophisticated instruments. FTIR spectrum of Mordenites was recorded on Agilent technologies in a range of 650–4000 cm^{-1}. Morphology of Mordenites were examined by Scanning Electron Microscope (SEM, JEOL/EO, Version 1.0, JSM-6390 operated at 10 kV. EDS analysis reported by the Instrument: 6390 (LA) with Detector Type: EX54175JMU.

2.4 Experimental Setup

Reaction flask with Large Capacity (Approx. 1 L capacity) and Three-Necked Morton-Type Round Bottom, separating funnel (500 mL), Bubble Condenser

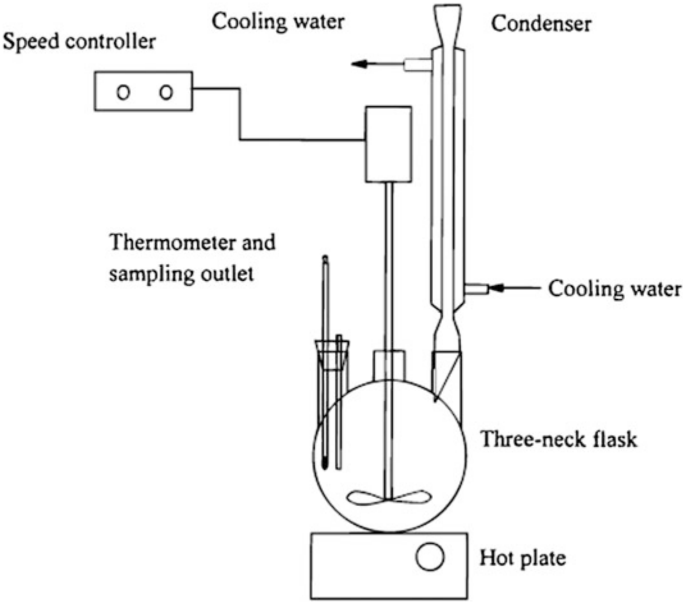

Fig. 1 Experimental setup for biodiesel production

(medium size), contact thermometer Hot plate with magnetic Stirrer and mechanical stirrer with electric motor were used for experimental set up as shown in Fig. 1 [17].

The Experimental reactions were carried out in a three-necked round bottom flask (capacity 1000 ml) having sampled outlet. The flask temperature was controlled by water bath within ±2 °C. One neck was equipped with a bubble condenser which will reduce alcohol loss through evaporation. Another neck is used to keep thermometer. Mechanical stirrer is arranged through the central neck of flask, which is connected to an electric motor along with speed controller. The reaction mixture is heated via water bath by a hot plate.

2.5 Preparation of Karanja Oil Methyl Ester

Karanja oil methyl ester (KOME) is produced by transesterification process of Karanja oil with methyl alcohol, with modified mordenite zeolite. The transesterification process was done for 60 min at reaction temperature 60 °C in a closed reactor vessel with alcohol to oil molar ratio (6:1) and mordenite 2% (by wt).

3 Results and Discussion

3.1 *Influence of NAOH Loading*

The SEM images reveal that the Mordenite and NaOH/Mordenite particles are irregular in shape. No significant difference in the morphology of the Mordenite and NaOH/Mordenite is observed. After being loaded with NaOH, the particles seem to agglomerate. Morphology of the 30 wt% NaOH/Mordenite changed to an amorphous structure due to the damaged structure of the Mordenite support. When loading NaOH to 20 wt%, the surface of the modified Mordenite still exhibits round shapes with crystallinity being almost the same as the unmodified Mordenite. An excess of Sodium at 30 wt% hide all the pores and surface of the Mordenite, which shows the growth of the particles.

FTIR spectra of the Mordenite support and the NaOH/Mordenite catalysts. The absorption peaks at 3614 and 3460 cm^{-1} are attributed to OH-stretching associated with terminal silanol groups and the H–O–H frequency of the H_2O molecule is located at a wave number of 1629–1646 cm^{-1} at a medium intensity. A set of strong intensity peaks at 1224 and 1046 cm^{-1} are ascribed to the vibration of external TO_4 (T = Al, Si) and anti-symmetrical stretching vibration of the tetrahedral (T–O bonds), respectively. The other absorption bands of 628–789 cm^{-1} correspond to the characteristic vibration of symmetrical stretching of Si(Al)–O bonds, and the bending of O–Si(Al)–O is interpreted at 437 cm^{-1}. These results confirmed the functional groups and the characteristics of the pure Mordenite support. For the fresh catalyst several absorption peaks are changed due to the Na loading. The reduction in intensity of the OH stretching vibration at 3600 cm^{-1} changes to a broadband. In addition, the set of high intensity absorption peaks at 1000–1250 cm^{-1} of the pure Mordenite support is converted into a broad peak at 800–1300 cm^{-1} for the NaOH/Mordenite catalysts. It could be inferred that the impregnation of NaOH affects the structure and composition of the Mordenite support, which shows of crystallinity loss, probably as a consequence of dealumination.

EDS analysis is recognized to the different Si/Al ratios of the mordenites as well as the amount and type of charge-balancing cations. Si/Al ratio on the NaOH/Mordenite catalyst decreased upon treatment suggesting that Si has been slightly extracted out of the Mordenite. Our results correspond with those of Guisnet et al., who noted that the decrease in crystallinity was probably due to the absence of extra frame work aluminum on the Mordenite which could be replaced by the silicon [18].

3.2 *Influence of Calcination Temperature*

Samples were calcined at different temperatures 400, 500, and 600 °C. The SEM results of the catalysts calcined at 400–600 °C is show that particles are agglomerated and irregular in shape, with a substantial variation in particle size. Inconsistency that it was observed between the effect of calcinations carried out on uncalcined and calcined catalysts is most likely attributed to a slight decrease in crystallinity of the calcined catalyst, particularly in samples calcined at a high temperature. After calcination, there was an increase in Si/Al ratio or decrease in Al atoms resulted (dealumination). Removal of framework Al after calcinations caused a change in morphology and an increase in particle size, while a decrease in surface area. Therefore, a high calcinations temperature altered the Si/Al value, which in turn changed the physical properties of the catalyst.

Effect of calcination temperature on the basic strength demonstrated that no difference in basic strength was found between the uncalcined and the calcined catalysts. However, the total basic sites of the calcined catalysts continuously decreased while the calcination temperature was increased. This could be due to the collapse of the pore structure.

3.3 Reusability of the Catalyst

The catalytic activity and reusability of the NaOH/mordenite were investigated. The spent catalysts were recovered by simple filtration and that was used to catalyze the next sample. A remarkable reduction in catalytic performance was observed yield 65.5 and 39.5 wt% of methyl ester content in the second and third runs for the NaOH/mordenite catalyst, respectively.

3.4 Results and Discussion

Table 2 and Fig. 2 show the effect of NaOH loading on Yield of KOME. The KOME yield was obtained higher for Mordenite catalyst with 20% NaOH than with 25% NaOH. 20% NaOH loading on Mordenite catalyzed process attained a maximum KOME content of 95.14% compared to 92.5% yield with 25% NaOH and 89.15% with 15% NaOH and followed by 86.12% with 30% NaOH. It was observed that the yield of Karanja Oil Methyl Ester increases with increase in the concentration of NaOH up to a certain value. After attaining the maximum value,

Table 2 Esterification of Karanja oil by modified zeolites

Run	NaOH loading (wt%)	Yield (%)
1	5	66.20
2	10	78.15
3	15	89.15
4	20	95.14
5	25	92.50
6	30	86.12

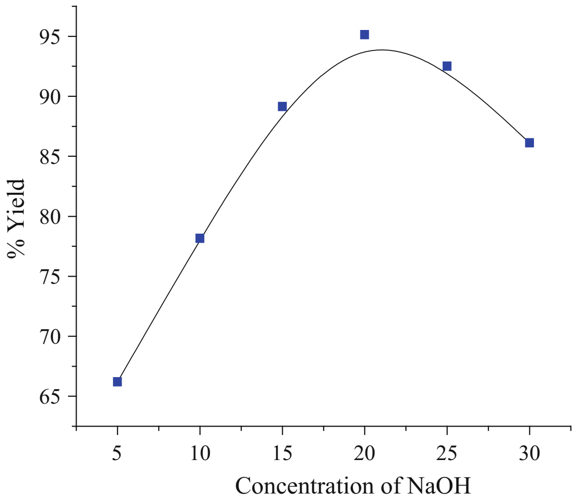

Fig. 2 Effect of NaOH loading on yield of KOME

the yield of KOME decreases with increase in concentration of NaOH. The reason behind this behavior is that the esterification process starts and the yield of KOME decreases. 66.2% yield was obtained with 5% NaOH and 78.15% yield was obtained with 10% NaOH. The maximum KOME conversion (yield 95.14%) is obtained with mordenite NaOH in 60 min at 60 °C.

Reaction conditions: Reaction time-3 h, Alcohol to Oil molar ratio-6:1, Catalyst amount (wt%) 2, Calcination Temperature-600 °C.

Table 3 lists the physico-chemical properties of the produced biodiesel in comparison with Karanja oil. The values of methyl ester flash point, viscosity, density, pour point, Cetane no. are close to the requirements of the ASTM standard. Owing to the absence of sulphur content in the biodiesel, the use of biodiesel can reduce emissions after combustion. Thus, the 20 wt% NaOH on mordenite catalyst can be a promising catalyst for the biodiesel industry.

Table 3 Physico-chemical properties of Karanja oil and KOME as per ASTM biodiesel standards

Properties	Karanja oil	KOME	ASTM biodiesel method
Kinematic viscosity (cst)	41.8	3.52	ASTM D445
Density @ 25 °C (kg/m^3)	926	891	ASTM D4052
Saponification value (mg KOH/g of oil)	184	116	ASTM D5558
FFA%	15.62	0.9	ASTM D5555
Pour point (°C)	−4	−7	ASTM D97
Flash point (°C)	208	97.1	ASTM D93
Cetane no.	40	52	ASTM D613
Colour	Dark brown	Golden yellow	–

4 Conclusion

20% NaOH/mordenite is an efficient catalyst for transesterification of Karanja oil with methanol, exhibiting the highest activity with methyl ester yield of 95.14 wt% among the tested catalysts. The activity of the uncalcined catalyst was higher than that of the calcined catalyst. At high calcinations temperatures, the pore structure of the mordenite collapsed and dealumination occurred. In addition, the basic sites decreased with increasing in calcination temperature. The leaching of the Na species was relatively low from the solid support during the reaction. Further studies need to be conducted to investigate the reusability of the catalyst after being treated with other solvents.

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