

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

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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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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 $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$ [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% $\text{Ca}(\text{OCH}_3)_2$ 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 transesterification 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 Pongamia Pinnate transesterification 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 $[\text{Et}_3\text{NH}]\text{Cl}-\text{AlCl}_3$ 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 $[\text{Et}_3\text{NH}]\text{Cl}-\text{AlCl}_3$ ($x(\text{AlCl}_3) = 0.7$), 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	$C_{16}H_{32}O_2$	11.64
Stearic acid	$C_{18}H_{36}O_2$	7.70
Dosocanoic acid	$C_{22}H_{44}O_2$	4.46
Eicosanoic acid	$C_{20}H_{40}O_2$	1.33
Tetracosanoic 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

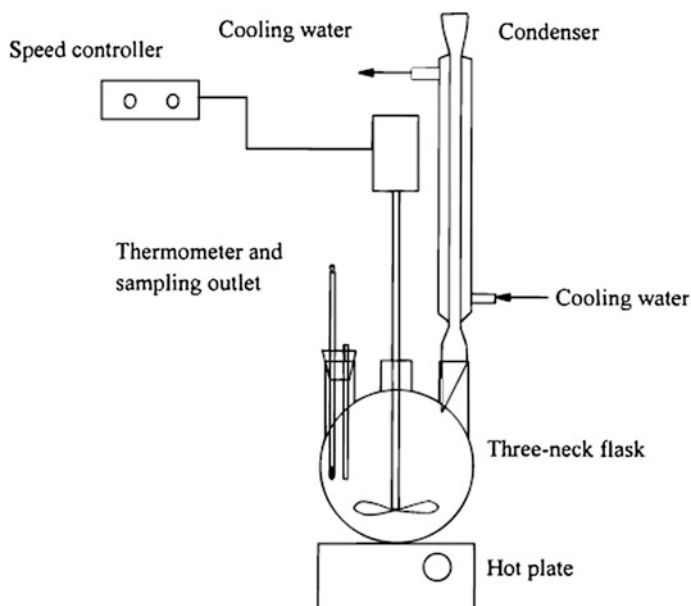


Fig. 1 Experimental setup for biodiesel production

(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 $\pm 2^\circ\text{C}$. 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 $1629\text{--}1646\text{ cm}^{-1}$ 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 ($\text{T} = \text{Al}, \text{Si}$) and anti-symmetrical stretching vibration of the tetrahedral (T–O bonds), respectively. The other absorption bands of $628\text{--}789\text{ cm}^{-1}$ 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 $1000\text{--}1250\text{ cm}^{-1}$ of the pure Mordenite support is converted into a broad peak at $800\text{--}1300\text{ cm}^{-1}$ 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 $600\text{ }^\circ\text{C}$. The SEM results of the catalysts calcined at $400\text{--}600\text{ }^\circ\text{C}$ 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.

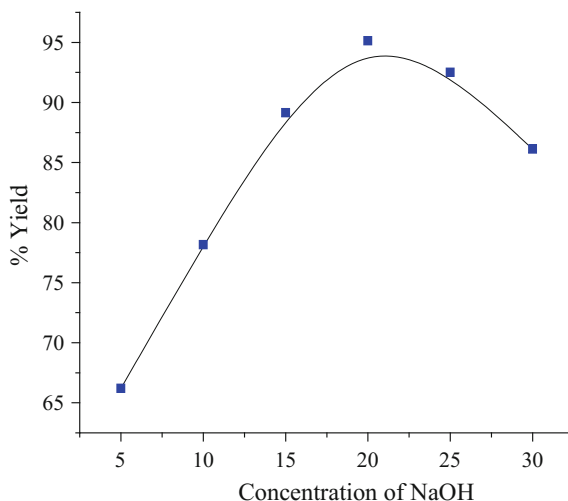
3.4 Results and Discussion

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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