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COMPARISON OF HOMOGENEOUS AND HETEROGENEOUS CATALYSIS FOR SYNTHESIS OF BIODIESEL FROM *Madhuca indica* OIL

Biodiesel was developed by transesterification of Madhuca indica oil by homogeneous and heterogeneous catalysis. KOH and CaO were taken as homogeneous and heterogeneous catalysts, respectively. It was found that the homogeneous catalyst (KOH) took 1.0 h of reaction time, 6:1 methanol to oil molar ratio, 0.75 mass% of catalyst amount, 55±0.5 °C reaction temperature for completion of the reaction. The heterogeneous catalyst (CaO) was found to give optimum yield in 2.5 h of reaction time at 8:1 methanol to oil molar ratio, 2.5 mass% of catalyst amount, at 65±0.5 °C. A high yield (95–97%) and conversion (>96.5%) was obtained from both the catalysts. CaO was found to leach to some extent in the reactants and a biodiesel conversion of 27–28% was observed as a result of leaching.

Key words: biodiesel; catalyst; KOH; CaO; Madhuca indica.

Energy is a resource essential to mankind for various activities and is an indication of development and prosperity of any nation. At present, the fuel used in the transport sector is crude oil after distillation and purification. The major constituents of distilled crude oil are gasoline commonly called petrol, and diesel. While both petrol and diesel are used in internal combustion engines, the former is used in spark ignition (SI) engine vehicles and the latter is used in compression ignition (CI) engine vehicles. These fuels take a long span of time in its formation and are considered a non-renewable source of energy. Out of the various modes of transportation, road emission amounts for 80% of emissions followed by rail and air which comprises for 13 and 6% emission, respectively [1]. Combustion of diesel fuel along with lubricating oil results in emission of pollutants such as particulate matter, hydrocarbons, carbon dioxide, carbon monoxide, soot (carbon) and adsorbed heavier hydrocarbon compounds [2]. Diesel exhaust is considered to be a complex mixture that is carcinogenic to animals and humans. Benzene, toluene, ethylbenzene, and *o*-, *m*-, *p*-xylene, popularly known as BTEX compounds, are

well documented carcinogenic compounds and are also emitted from the exhaust of a diesel run CI engine [3].

The depleting fossil reserves and the pollution caused by the combustion of crude oil derived diesel fuel have led to the emergence of its substitution with a green, sustainable and renewable fuel. Oils extracted from animal or vegetable sources are unsuitable to be used as fuel in CI engines because of their high viscosity and density [4]. Transesterification of the oil is carried out to produce low viscosity mono-alcohol fatty acid esters, *i.e.*, biodiesel [5]. The fuel properties of fatty acid alkyl esters have been found to be comparable with that of mineral diesel. Biodiesel is a fuel that comes in the category of renewable and non-polluting category and has the potential for replacement of conventional “diesel” fuel [6,7].

In Indian scenario, biodiesel is derived from oil extracted from non-edible feedstock, as the edible oil is scarce and a significant amount of edible oil is imported [8]. In the present work, mahua oil (*Madhuca indica*) has been chosen for the synthesis of biodiesel. Mahua is a medium to large tree found in many parts of India. The oil is extracted from the kernel of mahua which is greenish yellow in color [9]. Mahua oil has an estimated annual production of 181,000 t in India [10]. The oil derived from mahua is used as cheap organic manure as it contains 3.5% nitrogen. Mahua oil possesses toxic and bitter saponins and

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hence its cake is used as cheap and effective wormicide to maintain the turf, lawn and golf ground free from earth worms [11]. Though mahua oil has been taken for synthesis of biodiesel, there are not many reports of it being catalyzed by heterogeneous catalysts. The catalysis of biodiesel by a heterogeneous catalyst thus holds significance. Ghadge and Rahe-man [12,13] have used homogeneous catalyst for synthesis of biodiesel using madhuca indica oil. Kaul *et al.* [14] have used KOH for synthesis of biodiesel from various feedstocks using mahua oil. Puhan *et al.* [15] have used sulfuric acid for transesterification of mahua oil and found it suitable for usage in 4-stroke direct injection natural aspirated diesel engine. Puhan *et al.* [16] used sodium hydroxide for synthesis of biodiesel from madhuca indica oil and found the fuel obtained to be comparable with that of mineral diesel. Only a minor power loss and an increase in fuel consumption were observed with the fuel obtained mahua oil.

There are studies on homogeneous and heterogeneous catalysis for synthesis of biodiesel [17-20]. However, not many studies have been done as a comparative study of their performance. The present work deals with the synthesis carried out by homogeneous and heterogeneous catalysis. KOH and CaO have been tried as homogeneous and heterogeneous catalysts, respectively, to check their feasibility to obtain high yield and conversion of triglycerides to biodiesel.

EXPERIMENTAL

Materials

The mahua oilseed was procured from Ranchi, Jharkhand, India. The oil was extracted from the kernel by a mechanical expeller and thereafter by a Soxhlet extraction apparatus. After expelling the oil from the kernel, the oil was filtered with Whatman 41 filter paper of 20-25 μm pore size. For the Soxhlet extraction method, the Buchi extraction system mode of extraction was adopted using cyclohexane as solvent [21]. The Buchi extraction system comprised of extraction, rinsing and concentration. 5.0 g of crushed kernel was weighed and kept in a thimble and subjected to Soxhlet extraction with 80 ml of the solvent, i.e. cyclohexane and the oil was extracted. 5 ml of liquid sample was then mixed with 10 g anhydrous sodium sulfate before extraction. The solvent cyclohexane was removed by rotary evaporator. After extraction and evaporation of solvent, the container was dried at 105 $^{\circ}\text{C}$ for 1 h till the sample weight was constant. The oil obtained from the kernel of mahua

by mechanical expeller and Soxhlet extraction was 38%. The extracted oil was then used for synthesis of biodiesel.

CaO was prepared from the eggshells collected from a student hostel canteen. The eggshells were washed with tap and distilled water until the organic matter which adheres to the inner surface of the eggshells was removed. The washed eggshells were dried in a hot air oven at 105 $^{\circ}\text{C}$ for 24 h. Thereafter, the dried eggshells were grinded to powder in agate mortar and calcined in an open furnace at 900 $^{\circ}\text{C}$ for 2 h.

The chemicals used were of analytical grade. Potassium hydroxide (KOH) was purchased from Qualigens Fine Chemicals, Mumbai, India. Synthesis grade methanol of $\geq 99\%$ assay and $\leq 0.2\%$ water content, ortho-phosphoric acid (85% pure), sodium sulfate dry purified, and sulphuric acid (H_2SO_4) 98% GR grade were procured from Merck Limited, Mumbai, India. Double distilled water was prepared in the laboratory. Weighing was done on an electronic balance (Vibra) of 0.1 mg accuracy.

Instrumentation

The characterization of mahua oil was done on Gas Chromatograph (GC) for determination of their fatty acid profile. The instrument GC (Perkin Elmer XL Autosystem GC) was equipped with FID detector with 14 ml carrier packed column. Temperature was raised from 60 to 240 $^{\circ}\text{C}$ with 4 $^{\circ}\text{C min}^{-1}$ and keeping 5 min for hold. The conversion of oil to fatty acid methyl esters was determined using a JEOL AL300 ^1H -Fourier transform-nuclear magnetic resonance (FT-NMR) instrument. CDCl_3 was used as a solvent at 300.40 MHz. Characterization of the heterogeneous catalyst was carried on differential thermal analysis/thermogravimetric analysis (DTA-TGA); DTA-TGA experiments were conducted with a Structured Text analyzer, model No. STA 409, Mettler Geratebau GMBH (Germany), under nitrogen flow. Phase characterization of the raw and calcined catalyst was studied on an X-ray diffractometer (XRD) (Scifert and Co. Model ID-3000) using $\text{CuK}\alpha$ radiation.

Yield and methyl ester quantification

The extent of the transesterification of mahua oil was determined by ^1H -FT-NMR spectroscopy. The formula for estimation of conversion of oil to methyl esters is calculated as given by Knothe [22]:

$$C(\%) = \frac{2A_{\text{ME}}}{3A_{\alpha\text{-CH}_2}} \times 100 \quad (1)$$

where C is the conversion of feedstock to its respective ester, A_{ME} is the integration value of the protons of the methyl esters (the strong singlet peak), and $A_{\alpha\text{-CH}_2}$

is the integration value of the methylene protons. Factors 2 and 3 are attributed to the fact that methylene carbon possesses two protons and the alcohol (methanol derived) carbon has three attached protons. Knothe [23] reports methyl ester (ME) protons to peak at 3.66 ppm and the protons on the carbons next to the glyceryl moiety (α -CH₂) to peaks at 2.3 ppm. Beside this, a triplet appears at 0.8 ppm that is related to terminal methyl hydrogens. A strong signal at 1.2 arises from the methylene of carbon chain. A multiplet is observed at 1.6 ppm from the β -carbonyl methylenes. Presence of unsaturated compounds owing to allylic, bis-allylic and olefinic hydrogens appears at 2.0, 2.8, and 5.3 ppm respectively [24].

The yield of biodiesel is determined by the following equation given by Leung and Guo [25].

$$\text{Yield(\%)} = \frac{\text{Weight of product}}{\text{Weight of raw oil}} \times 100 \quad (2)$$

The “weight of the product” includes the fatty acid methyl esters (*i.e.*, biodiesel), and the remaining mono-, di-, and triglycerides that remained unreacted after separation of glycerol and catalyst.

Experimental procedure

The method adopted for the synthesis of biodiesel is transesterification reaction in an indigenous built batch reactor. The experimental set up comprised of the following apparatus and instrument: round bottom flask (1 L capacity), heating mantle, mechanical stirrer, water condenser, and thermometer. After completion of the reaction the products formed were kept in a separating funnel. The schematic diagram of the batch reactor for the experimentation is shown in Figure 1.

All the experimental data were done in duplicate. The standard error obtained in calculation of conversion and yield of biodiesel was ± 2 -3% for the duplicate set of experiments.

RESULTS AND DISCUSSION

The fatty acid profile of the oil is depicted in Table 1. Saturated fatty acids (palmitic acid, stearic acid,

and arachidic acid) were found to be present in substantial amount comprising of 33.3%. The monounsaturated fatty acid (oleic acid) was 46.3% and the polyunsaturated fatty acid (linoleic acid) was 17.9%.

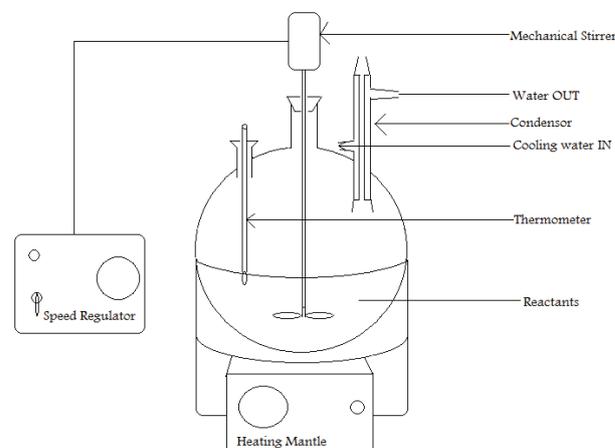


Figure 1. Transesterification reaction in batch reactor.

Thermal decomposition of the eggshell

23.0 mg of powdered eggshell was taken for DTA/TGA analysis. The temperature ranged from 28.7 to 897.0 °C. Figure 2 depicts the decomposition temperature of eggshell. The weight loss of eggshell as observed from TGA occurred from 700 to 850 °C. This indicated that, though decomposition of calcium carbonate started at 700 °C, complete decomposition occurred at 850 °C. At 850 °C, the calcium carbonate of eggshell decomposed to calcium oxide and carbon dioxide. Release of CO₂ confirms the formation of calcium oxide which acts as a catalyst in biodiesel synthesis. A small exothermic curve is observed at 350 °C. The DTA curve is observed to start at 500 °C and continue to fall till 850 °C. This shows the process to be endothermic.

Crystallinity of the heterogeneous catalyst

The property of the raw eggshell before and after calcination was studied. Upon calcination at 900 °C, the eggshells turned completely white in appearance, which was an indication that carbon dioxide

Table 1. Fatty acid composition of the mahua (*Madhuca indica*) oil

Fatty acid	Systematic name	Formula	Structure	Content, mass%
Palmitic	Hexadecanoic	C ₁₆ H ₃₂ O ₂	16:0	17.8
Stearic	Octadecanoic	C ₁₈ H ₃₆ O ₂	18:0	14.0
Oleic	<i>cis</i> -9-Octadecenoic	C ₁₈ H ₃₄ O ₂	18:1	46.3
Linoleic	<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic	C ₁₈ H ₃₂ O ₂	18:2	17.9
Arachidic	Eicosanoic	C ₂₀ H ₄₀ O ₂	20:0	1.5
Total saturated fatty acids				33.3
Total unsaturated fatty acids				64.2

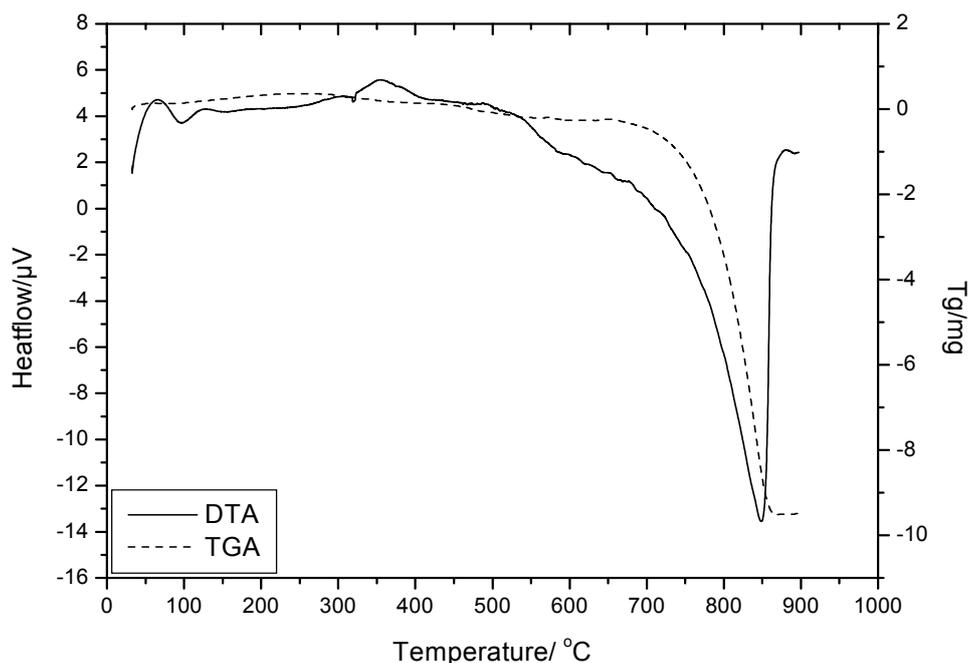


Figure 2. Thermogram of raw eggshell.

escaped and the product constituted of calcium oxide. The peaks were compared to the Joint Committee on Powder Diffraction Standards (JCPDS) file (PDF release 1997, International Centre for Diffraction Data (ICDD)). XRD spectra of raw and calcined eggshell samples were obtained with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV, 30 mA, scan speed of $1.0^\circ/\text{min}$, and scan range of $10\text{--}90^\circ$.

For the raw eggshell, the main peaks were observed at 2θ 29.48° and other peaks were observed at 2θ 48.60 , 51.82 , 57.58 and 68.16° . These peaks were characteristic of calcium carbonate. The peaks for the calcined catalyst appeared at 2θ 32.32 , 37.45 and 53.93° which were characteristic of calcium oxide. Calcium hydroxide was also observed at 2θ 14.77 and 17.87° . The crystalline size of the catalyst was calculated from the XRD data using the Scherrer's formula, given by Qin *et al.* [26]:

$$D \approx \frac{0.89\lambda}{\beta \cos \theta} \quad (3)$$

The crystalline size of the uncalcined catalyst was calculated and found to be 29.7 nm whereas, the crystalline size of the catalyst upon calcination reduced to 0.952 nm. This shows that crystallinity of the eggshell decreased on calcination. This has been attributed to the presence of water in CaO [27].

Experimentation and optimization of variables

Esterification using H_2SO_4 . Mahua oil was initially analyzed for its viscosity and acid value as per

ASTM D445-06 and ASTM D664-07 methods respectively. The value obtained for viscosity was 29.35 cSt at 40°C . The acid value determined was 22.90 mg KOH/g. A high acid value which is due to free fatty acids (FFA) is a deterrent in the conversion of fatty acids to fatty acid methyl esters. The FFA will react with the alkali catalyst and will cause saponification. Hence, it is suggested to reduce the acid value to less than 2% which corresponds to 4 mg KOH/g [7]. As mahua oil possessed a high acid value, acid esterification was done to make it suitable for the alkaline transesterification reaction. Hence, a two-step process - acid esterification followed by alkaline transesterification - was adopted to develop biodiesel from mahua oil. The parameters which can affect the esterification and alkaline transesterification reactions are alcohol to oil molar ratio, catalyst amount, reaction temperature and time. These parameters were studied separately for acid esterification and alkaline transesterification reactions of the mahua oil.

Sulfuric acid was taken as a homogeneous catalyst for esterification of free fatty acids present in the mahua oil. The initial experiment was done with 6:1 methanol to oil (M:O) molar ratio, 0.9 mass% of catalyst, 45°C in 1 h of reaction time. The other molar ratios (M:O) taken for acid esterification were 8:1, 10:1 and 12:1. It was found that the 6:1 molar ratio lowered the acid value of mahua oil to 2.07 mg KOH/g. Further increase in molar ratio resulted in generation of unreacted methanol. H_2SO_4 used as acid catalyst was varied from 0.5 to 2.0% (v/v ratio with oil). Conversion

of FFA to methyl esters increased with the increase in catalyst amount. With 0.5% H_2SO_4 , the acid value reduced to 11.40 mg KOH/g which further reduced to 6.50 with 1.3% of H_2SO_4 . The acid value of mahua oil was further reduced to 2.07 mg KOH/g with 1.5% (v/v) H_2SO_4 . Further increase in the catalyst amount resulted in darkening and loss of the product. Temperature variation study was conducted in the 45 to 65 °C range. It was found that 55 ± 0.5 °C was optimum for maximum reduction of acid value (2.07 mg KOH/g) of mahua oil. Lower temperature could not reduce the FFA to less than 2% (*i.e.*, <4.0 mg KOH/g) and temperature higher than 55 ± 0.5 °C showed no further reduction in FFA value. At 45 ± 0.5 °C, reduction in acid value was found to be 8.10 mg KOH/g. A further reduction in acid value was noted with increase in temperature. At 50 ± 0.5 °C, the value of FFA was 6.50 mg KOH/g which is still above the safe limit for transesterification reaction (*i.e.*, 4.0 mg KOH/g). Lower temperature could not reduce the FFA to less than 2.0% and temperature higher than 55 ± 0.5 °C showed no further reduction in FFA. 1.0 h of reaction time was optimum for the reduction of acid value. The rate of stirring was fixed at 1000 rpm to overcome the mass transfer limitation of the reactants.

Transesterification using KOH and CaO. After lowering of the acid value, alkaline transesterification with KOH and CaO was done to convert the oil to fatty acid methyl esters. Parameters that need to be optimized for alkaline transesterification are same as those done for acid esterification. These include the molar ratio, amount of catalyst, temperature, rate of stirring, and reaction time. For the homogeneous catalyst, the initial experiment was conducted with 6:1 M:O molar ratio, 0.45 mass% of catalyst (KOH), 55 °C in 1 h of reaction time. For the heterogeneous catalyst, the initial experiments were done with 6:1 M:O molar ratio, 1.75 mass% of catalyst (CaO), 55 °C and 3 h of reaction time. The stoichiometric molar ratio for transesterification is 3:1 alcohol to oil molar ratio. However, a higher molar ratio is favorable for completion of the reaction [6]. The other molar ratios employed during alkaline transesterification taking KOH as catalyst were 5:1, 7:1, 8:1, and 9:1. 6:1 (alcohol to oil) molar ratio was found to give a high conversion (>96.5%) and yield (95%) of biodiesel. This is in compliance to the fact that a high molar ratio neither increases the yield nor the conversion of biodiesel. Methanol has a polar hydroxyl group which acts as emulsifier and causes emulsification [7]. This is also in accordance with the findings of Ghadge and Raheman where 6:1 A:O molar ratio of 6:1 was found to be optimum [13]. Using CaO as catalyst, the yield of biodiesel obtained

was 78% with 6:1 molar ratio of methanol to oil. The yield rose to 85% when the molar ratio (alcohol to oil) was increased to 8:1. Further addition of methanol did not increase the yield (Figure 3). This is near to the molar ratio optimized by Wei *et al.* [20] where a molar ratio above 9:1 gave maximum yield.

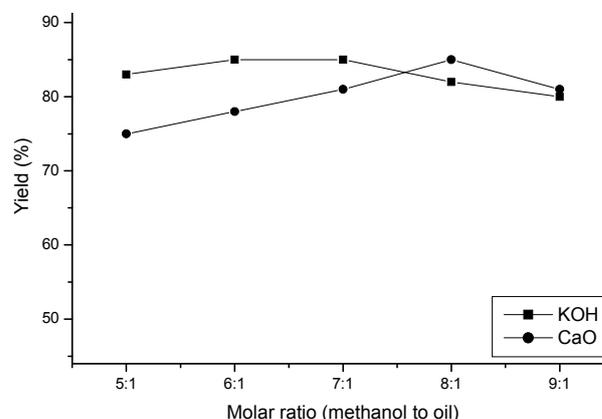


Figure 3. Effect of molar ratio on yield of biodiesel with KOH and CaO catalyst. Conditions: KOH: catalyst amount 0.45 mass%, 55 °C, 1 h; CaO: catalyst amount 1.75 mass%, 55 °C, 3 h.

The amount of catalyst was varied from 0.45 to 0.95 mass%. The optimum amount of KOH for a high yield was obtained with 0.75 mass%. Less amount of catalyst resulted in lower yield, whereas, higher catalyst amount could not increase the yield further but rather reduced the yield substantially (Figure 4). This must be due to side reaction “saponification” that resulted in soap formation and lowered the yield. The finding was in accordance to that obtained by Ghadge and Raheman [13], where 0.7 w/v of KOH was observed to be optimum for synthesis of biodiesel.

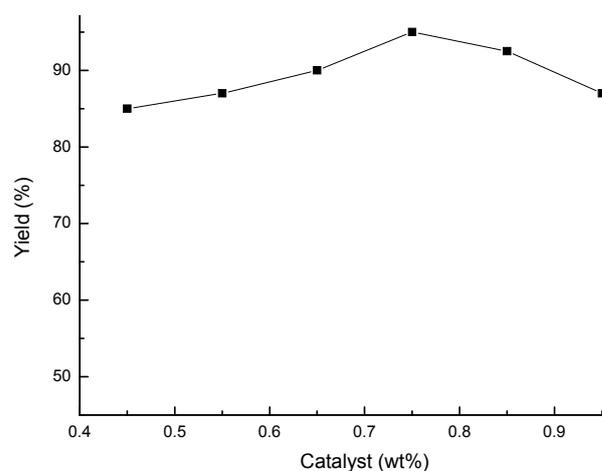


Figure 4. Effect of catalyst (KOH) amount on yield of biodiesel. Conditions: molar ratio: 6:1, 55 °C, 1 h.

Using CaO as catalyst, 80% yield was obtained with 1.5 mass% of catalyst, which increased to 85% with 1.75 mass% catalyst. Yield further rose to 87% with 2.0 mass% of calcined eggshell in form of CaO as catalyst. An optimum yield of 90% was obtained with 2.5 mass% of catalyst. Catalyst amount beyond 2.5 mass% did not show any increase in the yield of biodiesel (Figure 5). This is in compliance to the finding by Wei *et al.* where a catalyst loading of 3.0 mass% gave maximum amount of yield [20].

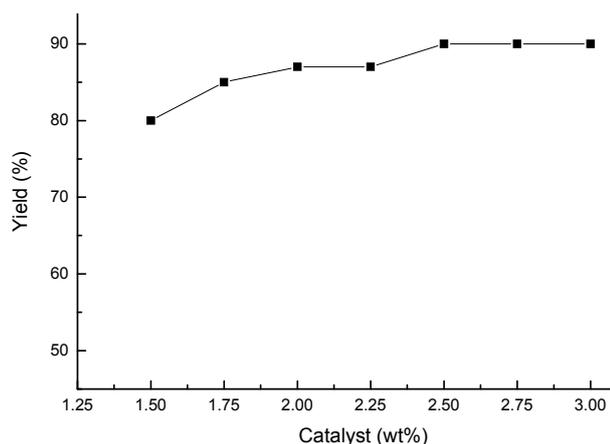


Figure 5. Effect of catalyst (CaO) amount on yield of biodiesel. Conditions: molar ratio: 8:1, 55 °C, 3 h.

Temperature was varied from 45±0.5 to 65±0.5 °C at intervals of 5 °C using KOH and CaO catalyst. Temperature of 55±0.5 °C was optimum for the best conversion of biodiesel with KOH catalyst. Yield remained same when temperature was increased till 65±0.5 °C. Yield of biodiesel however decreased when the temperature was increased further to 70±0.5 °C. Ghadge and Raheman [13] report 60 °C for a high yield (98%) of biodiesel. While using CaO as catalyst, yield of only 85% was achieved when temperature was 50±0.5 °C, which increased substantially with increase in temperature. The optimum yield of 95% was obtained at 65±0.5 °C. Temperature higher than reflux of methanol (*i.e.*, 70±0.5 °C) resulted in a decreased yield with both the catalyst, Figure 6, which can be attributed to loss of some methanol at high temperature. This is in compliance with the findings of Wei *et al.* [20] where 65 °C was found to be the optimum temperature.

As per the European Norm (EN) specification, the fatty acid methyl ester should be more than 96.5% [28]. Biodiesel with fatty acid methyl ester content less than 96.5% will lead to detrimental effects on blending with diesel fuel [29]. Hence, the biodiesel samples were analyzed on ¹H-FT-NMR at regular intervals to obtain the optimized reaction time for a high

conversion (>96.5%). 1.0 h reaction time resulted in completion of reaction with high conversion (>96.5%) and yield of fatty acid methyl esters of mahua oil with KOH as catalyst. This is in compliance with the reports on various homogeneous catalysts for alkaline transesterification reported by Sharma *et al.* [7] where the time taken varies from 30 min to 1.5 h [7]. With CaO as catalyst, the conversion of fatty acids to fatty acid methyl esters was found to increase with time. In 30 min reaction time, conversion obtained was 64%. Conversion increased to 69% in 1 h. In 1.5 h, 90% conversion was obtained which further rose to 94% in 2 h. The conversion was 97% in 2.5 h, which increased to 99% in 3 h. Hence, 2.5 h of reaction time is considered to be optimum for synthesis of biodiesel from mahua oil using CaO as catalyst. Figure 7 depicts the extent of conversion of fatty acids to biodiesel with time duration. CaO catalyzed reaction took 2.5 h reaction time for the completion of the reaction. The finding is also comparable to that of Wei *et al.* [20] where 3 h was optimum for yield > 95% with CaO as catalyst.

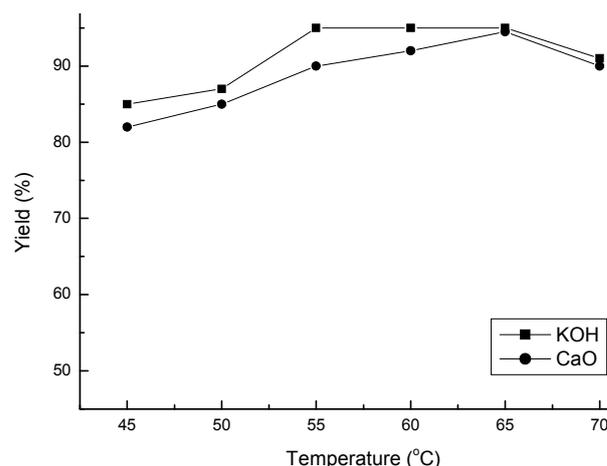


Figure 6. Effect of temperature on yield of biodiesel. Conditions: for KOH: molar ratio: 6:1, catalyst 0.75 mass%, 1 h; for CaO: molar ratio: 8:1, catalyst 2.5 mass%, 3 h.

Viscosity of mahua oil obtained from both the catalysts reduced from 29.35 to 5.80 cSt at 40 °C. Final acid value of the methyl esters were calculated and found to be 0.43 mg KOH/g for mahua oil methyl ester. The acid value and viscosity after acid esterification, and final value are shown in Table 2. It can be seen that the acid value and viscosity are within the ASTM D6751 specification. A high conversion, *i.e.*, >96.5% of mahua oil to biodiesel has been achieved which is an indication that on a blending ratio up to 20%, the fuel can be used as a supplement to mineral diesel fuel.

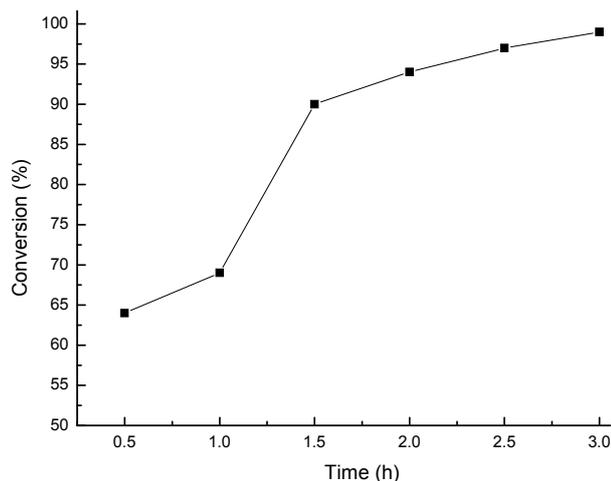


Figure 7. Effect of time on conversion of biodiesel with CaO as catalyst. Conditions: molar ratio: 8:1, catalyst 2.5 mass%, temperature 65 °C.

Table 2. Variation of parameters before and after reaction for mahua oil

State	Acid value mg KOH/g	Viscosity cSt (40 °C)
Initial	22.90	29.35
After acid esterification	2.07	12.31
After alkaline transesterification	0.43	5.80
ASTM Standards D6751		

Selectivity of mahua oil towards transesterification reaction

The selectivity of mahua oil towards transesterification reaction was found to be comparable with that obtained from *Jatropha curcas* and *Pongamia pinnata* that are most commonly employed for biodiesel development in the Indian scenario and has been depicted in Table 3. It can be seen that the yield obtained with all the three oilseeds are high (>90%) [30,31]. Also, for the first time a heterogeneous catalyst (CaO) has been tried for synthesis of biodiesel from mahua oil with yield similar to that obtained from homogeneous catalysis.

Table 3. Specificity of *Madhuca indica* in comparison to other oils

Oil	Catalyst	Yield, %	Reference
<i>Jatropha curcas</i>	KOH	90-95	30
<i>Pongamia pinnata</i>	KOH	96.5-97	31
<i>Madhuca indica</i>	KOH	95-97	This study
<i>Madhuca indica</i>	CaO	95-97	This study

Leaching aspects

Using the same optimized reaction conditions, the catalyst CaO prepared from eggshell was tested

for its heterogeneous nature. 2.5 mass% of CaO was dissolved in methanol (8:1 methanol to oil molar ratio) and was then filtered through Whatman 42 filter paper of 20-2.5 μm pore size. A conversion of 27.42% indicates that a minor amount of CaO does get leached in the reactants. The methanol used contains a small amount of water ($\leq 0.2\%$ water content) and CaO is known to form calcium hydroxide in presence of water. Hence, the reason attributed for some conversion of mahua oil to biodiesel may be the activity of $\text{Ca}(\text{OH})_2$ which also acts as catalyst and might have contributed in the formation of fatty acid methyl esters. Leaching of calcium using CaO as catalyst has also been observed by other researchers. Granados *et al.* [32] also reported some extent of homogeneous catalysis by CaO during synthesis of biodiesel. Granados *et al.* [32] observed the solubility to increase of CaO by an order when using glycerol-methanol and biodiesel-glycerol-methanol in comparison to its solubility in methanol. The solubility of CaO was found to be dependent on the contact time of the catalyst with methanol. In 3 h contact time duration with methanol, the solubility of CaO was 0.169 mg CaO per ml methanol. However, the contribution of homogeneous catalysis was found to be negligible in comparison to its heterogeneous contribution when the amount taken is greater than 1.0 mass%. Granados *et al.* [33] reported reuse of CaO as catalyst with adequate amount for 8 runs. In our case too, the catalyst was reutilized for 10 runs after washing and recalcination without any significant loss in the yield and conversion of biodiesel. Kouzu *et al.* [34] reported the reuse of the catalyst for 10 successive operations with fatty acid methyl ester yield of 96.5% in 2 h reaction time. Zabeti *et al.* [35] have also reported leaching of CaO in the biodiesel product but the leaching was not a deterrent in its reuse for 8 cycles.

CONCLUSIONS

Biodiesel has been developed from a non-edible feedstock, *i.e.*, mahua oil (*Madhuca indica*) using a homogeneous (KOH) and heterogeneous catalyst (CaO). The biodiesel developed from both the catalysts showed similar characteristics of viscosity and acid value. A high yield and conversion of mahua oil to biodiesel were achieved by optimizing parameters such as the molar ratio (methanol to oil), amount of catalyst, reaction time, and temperature. The mahua oil possessing a high free fatty acid value (22.90 mg KOH/g) underwent acid esterification with H_2SO_4 using the optimized parameters. Using the optimized reaction conditions, a high yield (95-97%) and conversion (>96.5%) was obtained from both the catalysts. CaO

was found to leach in the reactants and 27-28% conversion of mahua oil to biodiesel was observed from the filtrate of methanol from catalyst.

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NAUČNI RAD

UPOREDNO PROUČAVANJE SINTEZE BIODIZELA IZ *Madhuca indica* HOMOGENOM I HETEROGENOM KATALIZOM

Biodizel je dobijen transesterifikacijom ulja Madhuca indica homogenom i heterogenom katalizom. KOH i CaO su korišćeni kao homogeni i heterogeni katalizatori, respektivno. Utvrđeno je da homogeni katalizator (KOH) obezbeđuje završetak reakcije za jedan čas pri molskom odnosu metanol-ulje 6:1, količini katalizatora 0,75% i temperaturi 55±0,5 °C. Optimalni prinos biodizela sa heterogenim katalizatorom (CaO) se dobija za 2,5 h pri molskom odnosu metanol-ulje 8:1, količini katalizatora 2,5% i temperaturi 65±0,5 °C. Sa oba katalizatora dobijaju se visok prinos (95-97%) i stepen konverzije (>96,5%). Uočen je odredeni stepen luženja CaO i stepen konverzije od 27-28% kao rezultat ovog luženja.

Ključne reči: biodizel; katalizator; KOH; CaO; Madhuca indica.