

Research paper

Synthesis of a reusable novel catalyst (β -tricalcium phosphate) for biodiesel production from a common Indian tribal feedstock[☆]



Devarapaga Madhu, Yogesh C. Sharma*

Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, Varanasi 221005, India

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ABSTRACT

In recent times, the rate of energy consumption goes on increasing and the world is desperately searching for new sources of fuel. Biodiesel (fatty acid methyl esters) is an alternative renewable energy resource for the next generation. Biodiesel has several advantages which include its non-toxic nature, it is biodegradable and it reduces greenhouse gas emissions. β -Tricalcium phosphate (β -Ca₃(PO₄)₂) catalyst was synthesized from fish waste. Fish waste contains calcium phosphate which is converted into β -tricalcium phosphate since it has low crystallinity and hydroxyl (OH) groups which decrease the potential to be a good catalyst for the synthesis of biodiesel through transesterification. This paper explores the synthesis of biodiesel using β -tricalcium phosphate (β -Ca₃(PO₄)₂) as a heterogeneous catalyst. *Pongamia pinnata* (Karanja) oil was extracted from seeds through the solvent extraction process. Intended for the development of easier transesterification process, stable and active heterogeneous β -tricalcium phosphate (β -Ca₃(PO₄)₂) catalyst was synthesized and used for the *P. pinnata* (Karanja) oil transesterification process. The synthesized heterogeneous catalyst was characterized by XRD, FT-IR, SEM and EDX to determine its structural and morphological characteristics. The catalyst exhibited good catalytic activity on reuse. Biodiesel yield was greatly dependent on operating parameters such as catalyst concentration, methanol to oil molar ratio, reaction temperature and reaction time. Effect of co-solvent on biodiesel was studied by using different co-solvents in transesterification reactions. High quality and maximum biodiesel yield (97 %) was obtained under the optimized reaction conditions (methanol to oil molar ratio, 10:1 (tetrahydrofuran (THF):methanol 1:1); reaction time 90 min; catalyst concentration 2.5 wt % and stirrer speed 650 rpm at 65 °C). Reusability of catalyst was examined up to five runs and found the catalyst was reusable up to five times without much loss of catalytic activity.

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1. Introduction

The world, with its huge population, affects the cumulative purchasing power and rapid industrialization has led to a rapid increase in the consumption of petro-fuels. The economic growth of any country is directly proportional to the increase in the production of petrochemical fuels. Humans depend mostly on petrochemical fuels like coal, natural gas, hydroelectricity and nuclear energy. At the rate in which these resources are being used, they will be consumed shortly. Petrochemical fuels have an indispensable function in the industrial economy of every nation in the world. They

are used for a variety of purposes like transportation of industrial and agricultural goods and operation of diesel tractors, pumping sets, etc. The high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the rampant use of fossil fuels make it inevitable to develop the renewable energy sources which have the characteristics of limitless duration and less impact on environmental pollution. This has invoked a recent interest in alternative sources for conventional petroleum fuels, such as the use of edible and non-edible oils derived from plants. This alternative fuel has largely been known as biodiesel. Biofuels appear to be solution to substitute fossil fuels. Biodiesel has got significant attention all over the world as a source of substitute fuel because of some of its typical properties, like non-toxicity, biodegradability, essentially free sulphur, and less release of CO [1]. Usage of biodiesel will have a balancing impact amongst agriculture, economic development and the environment.

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* Corresponding author. Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, Varanasi 221005, India. Tel. +91 542 6702865; fax +91 542 6702876.
E-mail address: ysharma.apc@itbhu.ac.in (Y.C. Sharma).

Table 1
Solvent extraction of karanja seeds using different solvent.

Solvent (10 mL/g of seed)	Weight of seed (g)	Stirring time (hr.)	Weight of crude oil (g)	Yield of oil (%)
Petroleum ether	10.03	2	4.2	41.87
	10.05	3	4.3	42.78
	10.06	4	4.4	43.73
Hexane	10.02	2	3.9	38.92
	10.03	3	4.1	40.87
	10.06	4	4.2	41.74
Diethyl ether	10.01	2	4.0	39.96
	10.03	3	4.1	40.87
	10.06	4	4.3	42.74

Commercialization is a major problem for biodiesel because of its high production cost. Total cost of biodiesel majorly depends on cost of raw materials because it takes nearly 70–85% of the total cost of biodiesel [2,3]. Estimated cost of biodiesel is approximately 1.5–3 times higher than diesel fuel due to its feedstock cost [4]. More focus on low cost feed stock and better implementation of technology will make cost of biodiesel competitive to petroleum fuels. These low cost feedstock could include enormous amount of waste lipids generated from restaurants, food processing industries, and non-edible crops. The authors have used oil of *Pongamia pinnata* extracted from its dried seeds. *P. pinnata* (karanja) is a most common plant in tribal part of north eastern India. In general, the process of transesterification involves an ester transforming into another ester by the exchange of the alkoxy group from lower molecular weight or small chain alcohols (for example methanol or ethanol) in presence of a catalyst [5]. Homogeneous as well as heterogeneous catalysts can carry out the transesterification process. However, each of them has its own drawbacks. In case of homogeneous catalysts, soap formation [6], water washings and glycerol purity have a telling impact on the cost of the process, whereas in heterogeneous systems, requirement of higher reaction temperatures and pressures greatly influence the cost of production.

Due to their fast reaction rates and less corrosive properties, bases are preferred to acid catalysts. In earlier works, fatty acid methyl esters were often manufactured with the help of alkali hydroxides (NaOH, KOH, etc.) but the process has several limitations. The catalyst cannot be reused because it is consumed during the neutralization of free fatty acid contained in the oil or side saponification reaction [7]. Apart from that, even removal of the base after reaction is problematic because the current practice of aqueous quenching with acid results in some degree of saponification and the formation of emulsions, which makes ester separation difficult. Furthermore, an alkaline wastewater stream is generated, which must be treated before its disposal [8]. Heterogeneous catalysts have many advantages such as catalyst reusability [9], ease of separation and environmental affability [10]. Therefore, in recent

Table 2
Physical and chemical properties of karanja oil.

Property	Unit	ASTM standards	Value
Color	–		Yellowish red
Acid value	mg KOH/g	ASTM D 664	8.04
Unsaponifiable matter	% w/w		2.5
Density	g/cm ³	ASTM D 1298	0.934
Boiling point	°C	–	328
Cloud point	°C	ASTM D 1510	2
Saponification value	mg KOH/g		206
Pour point	°C	ASTM D 97	–4
Kinematic viscosity(mm ² /s), at 40 °C	mm ² /s	ASTM D 445	41.3
Flash point	°C	ASTM D 93	218
Calorific value	kcal/kg	ASTM D 4809	8803
Water content	in%	ASTM D 2709	0.006%
Iodine value	–	ASTM D 2500	2.6
Copper strip corrosion	–	ASTM D 130	No corrosion observed

years, work is focused towards the development of heterogeneous catalyst systems to produce biodiesel. Mixed oxide contains more than one chemical elements in its cation or cations of single element in several oxidation states. These systems of mixed oxides provide an opportunity of choosing the cationic elements as catalytic species to catalyse related gas and liquid phase reactions. In addition to that, the adjustable surface functionalities make them more convenient to modify to the various parameters necessary for a catalytic reaction. There are reports on the esterification and transesterification of oils and fats by employing heterogeneous mixed oxides as a catalysts [11]. Metal oxides treated with sulphates such as SO₄²⁻/ZrO₂ [12], SO₄²⁻/TiO₂ [13] and SO₄²⁻/SnO₂ [14] were used for the esterification of FFAs and oils having high acid values. Brønsted (anions) and Lewis acids (cations) of metal oxides provide the required catalytic sites for methanolysis during transesterification. The rupturing of O–H bond produces hydrogen cations and methoxides which facilitate the reaction between triglyceride molecules and methoxide anions to form fatty acid methyl esters (FAMEs) [15]. Thus, various transition metal oxides such as zirconium oxides, zinc oxides and titanium oxides are attracting the research communities. Among these solid acid catalysts, sulphated and tungstate-zirconia are prominent for triglycerides to fatty acid alkyl esters [16]. Solid acid catalyst reactions occurred at high temperature and require longer time to complete the reaction. Solid acid catalysts are not economically viable due to their high cost. This paper explores the synthesis of biodiesel using β -tricalcium phosphate (β -Ca₃(PO₄)₂) as a catalyst derived from waste fish bone via calcination. Fish bones contain hydroxy apatite [17] at lower temperature below 600 °C and β -tricalcium phosphate [18] at above 800 °C. Solid base catalysts prepared from wastes not only reduce the environmental pollution but they also reduce the total cost of reaction.

2. Materials and methods

2.1. Raw materials and chemicals

Acetone, diethyl ether, toluene, tetrahydrofuran (THF) and hexane were of analytical grade, and purchased from Merck, India. Sulphuric acid, sodium sulphate and methanol were also purchased from Merck, India. The reagents were used without further purification. Karanja seeds were collected from local market in Varanasi, India and the oil was chemically extracted from dried seeds.

2.2. Catalyst preparation

Waste fish bones were collected from a local market in Varanasi, India. The collected fish bones were first washed several times with hot distilled water to remove gelatinous matter and flesh associated with bones, then the fish bones were kept in

Table 3
Fatty acid composition (%) of *Pongamia pinnata* oil.

Sr.	Retention time	Compound name	Composition (%)	Corresponding fatty acid	Corresponding fatty acid structure
1	19.89	Palmitic acid methyl ester	10.41	Palmitic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
2	21.75	Oleic acid methyl ester	66.30	Oleic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}=\text{CHCOOH}$
3	21.89	Stearic acid methyl ester	9.07	Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
4	23.38	cis-11-Eicosenoic acid methyl ester	3.88	cis-11-Eicosenoic acid	$\text{CH}_3(\text{CH}_2)_{16}(\text{CH}=\text{CH})\text{COOH}$
5	23.62	Arachidic acid methyl ester	5.09	Arachidic acid	$\text{CH}_3(\text{CH}_2)_{10}(\text{CH}=\text{CH})_4\text{COOH}$
6	25.27	Behenic acid, methyl ester	4.02	Behenic acid	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$

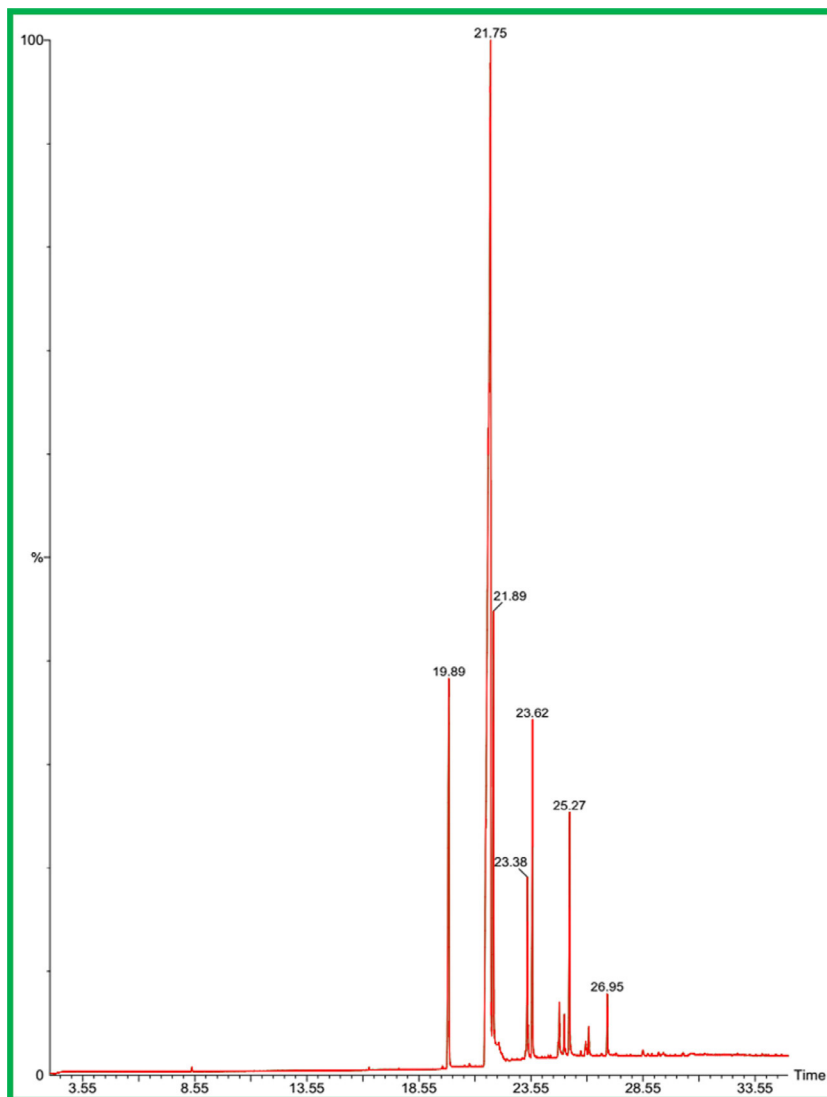


Fig. 1. GC-MS chromatogram of *Pongamia pinnata* oil.

hot air oven at 100 °C for 5 h. The dried fish bones were ground to powder and calcined in a muffle furnace at different temperatures, ranging from 600 °C to 900 °C for 4 h. The synthesized catalyst was characterized and used in the transesterification reactions. Cost of synthesized catalyst was reduced since raw material (waste fish bones) has no cost.

2.3. Characterization of catalyst

As the catalyst is a mixed oxide structure, it was characterized by X-ray diffraction (XRD). Surface structure i.e., particle arrangement of mixed oxide was observed with the Scanning Electron Microscopy (SEM).

2.4. Oil extraction

Karanja (*P. pinnata*) seeds were collected from the local market in Varanasi, India. The seeds were dried in a hot air oven at 105 °C for 90 min to remove water content. Karanja seeds were poured in ball mill apparatus and ground into powder. Karanja oil was extracted using this flour through solvent extraction process [19,20]. Low cost methodology was adopted for the extraction of oil from *P. pinnata* [21], *calophylluminophyllum* [22], and *Citrullu scolocynthis* [23]. Soxhlet apparatus fixed with 500ml round bottom flask and a condenser for cooling was used for the extraction of oil Table 1.

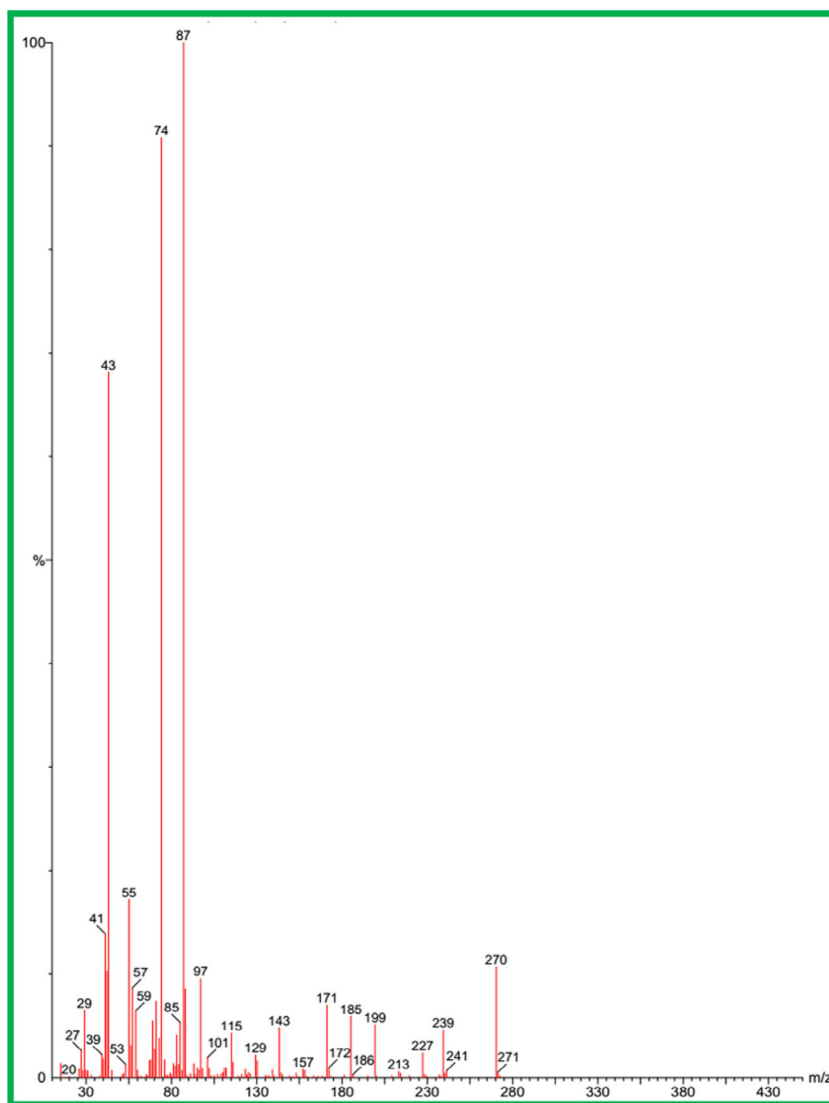


Fig. 2. GC-MS spectrum of palmitic acid methyl ester.

2.5. Pre-treatment of crude karanja oil

Pre-treatment process was carried out to remove the impurities present in the crude karanja oil. Minute suspended solid particles were removed with Whatman filter paper. Moisture content was removed with rotavapor and the obtained karanja oil was used for the synthesis of biodiesel. The physical and chemical properties of karanja oil were determined and have been shown in Table 2.

2.6. Determination of fatty acid composition

Table 3 represents the fatty acid composition of the oil after pre-treatment process was done. Fatty acid composition was analysed by using Gas Chromatography Mass Spectra (GC-Mass Spectrometer Perkin Elmer, Mass range: 20 to 620 Daltons (amu)). The method employed to determine the fatty acid composition was esterification reaction (methanol as solvent and H_2SO_4 as homogeneous catalyst) followed by transesterification, where the fatty acid composition present in the *P. pinnata* oil get converted into corresponding methyl esters and these methyl esters were analysed with GC-MS. Sample was prepared with 0.03 mL of above oil (af-

ter transesterification) mixed with 2.1 mL of hexane for the GC-MS analysis. Fig. 1 represents the GC-MS chromatogram of *P. pinnata* oil in which X-axis corresponds to retention time and Y-axis corresponds to percentage of relative abundance. Using the known compound spectrum from the NIST 2011 library, unknown compound spectrum was predicted with the help of Turbo Mass software. GC-MS analysis showed that the fatty acid composition present in the *P. pinnata* oil were, Palmitic acid methyl ester (Fig. 2), Oleic acid methyl ester (Fig. 3), Stearic acid, methyl ester (Fig. 4), cis-11-Eicosenoic acid methyl ester (Fig. 5), Arachidic acid methyl ester (Fig. 6), Behenic acid, methyl ester (Fig. 7) respectively. Table 3 represents the fatty acid composition and their corresponding structures with retention time. Extracted the *P. pinnata* oil consisted both saturated as well as unsaturated fatty acids.

2.7. Esterification

Before starting the transesterification, the acid value of karanja oil was determined so that it can be ascertained whether esterification process is required or not. Free fatty acid (FFA) value plays a significant role in the conversion of oil to biodiesel. For a high

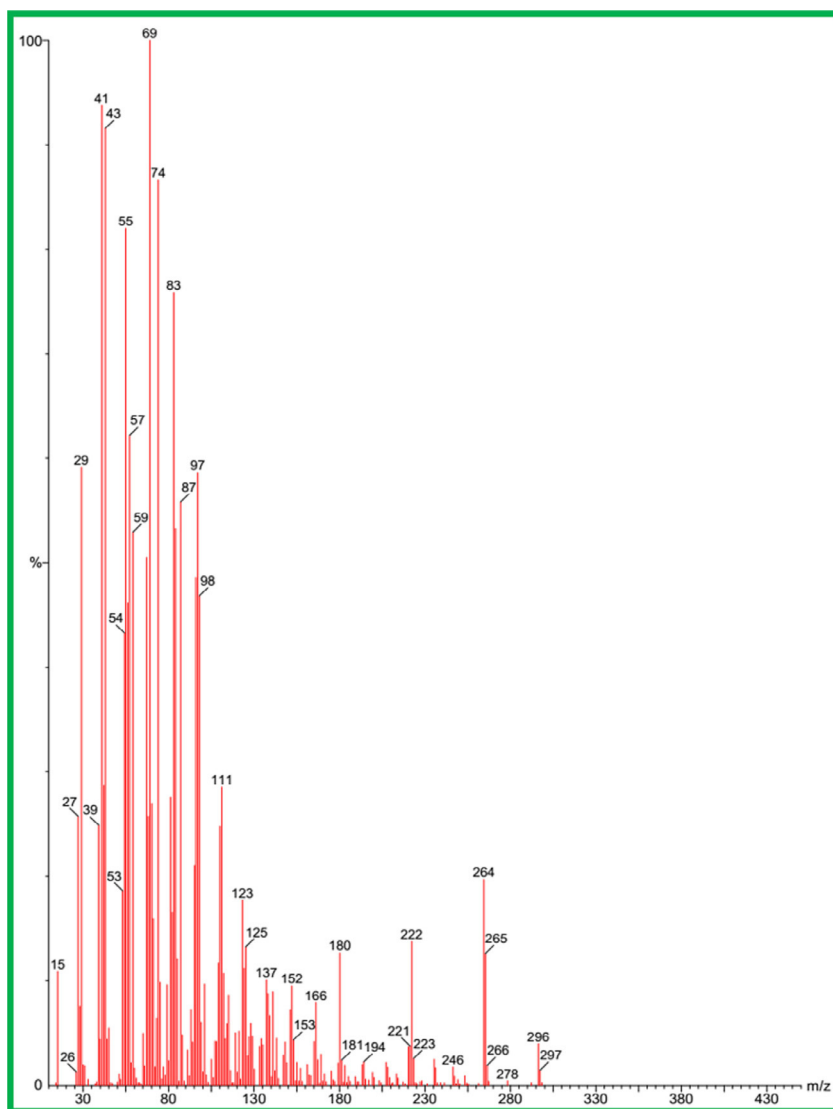


Fig. 3. GC-MS spectrum of oleic acid methyl ester.

conversion of biodiesel, the feedstock should have a free fatty acid content lesser than 3% [24]. Acid value of karanja oil was determined according to standard equation (1) and was found to be 8.04 mg KOH/g. Extracted karanja oil with high acid value (8.04 mg KOH/g) needs to undergo the esterification step before conducting transesterification step to reduce its acid value. In acid esterification [25], 6:1 oil:methanol molar ratio was poured into the 3 necked round bottom flask and the set up was kept in serological water bath. The temperature of the reaction was kept at 65 °C. The reaction mixture was then poured into a separating funnel to remove excess alcohol, sulphuric acid and water content, finally rotavapor evaporation was conducted to remove minor contents of water and alcohol from oil feedstock. The treated oil displayed acid value less than 0.5 ± 0.21 mg KOH/g, further transesterification reaction was conducted.

The acid value and free fatty acid conversion were calculated as followed:

$$\text{Acid Value (mg KOH/g)} = V_{\text{KOH}} * 56.1 * C_{\text{KOH}} / m_{\text{sample}} \quad (1)$$

$$\text{Free Fatty Acid Conversion (\%)} = \frac{(AV_1 - AV_2) / AV_1 * 100}{*100} \quad (2)$$

Where AV_1 (mg KOH g^{-1}) is the acid value of original oil sample, and AV_2 (mg KOH g^{-1}) is the acid value of catalysed product.

2.8. Transesterification

After esterification step, acid value of karanja oil was decreased from 8.04 mg KOH/g to 0.7 ± 0.18 mg KOH/g since free fatty acid content in the oil must be less than 3% for the transesterification reaction using base as catalyst [26]. Transesterification of karanja oil with methanol was carried out in a transesterification reactor with 250 mL three-neck round bottom flask fitted with an overhead stirrer and water-cooled reflux condenser. The reactor was also equipped with water bath with digital temperature controller for heating purpose. To start the optimum reaction conditions, catalyst (2 wt % relative to karanja oil weight) was placed into the reactor; necessary amount of methanol (methanol to oil molar ratio of 7:1) was added to the catalyst using the dropping funnel and both were kept under mixing until the reaction temperature reached 65 °C. The start of the reaction was considered to be after the addition of all the raw materials (karanja oil) into the reactor; at that time, mixing of the reactants was changed from medium to vigorous stirring. The biodiesel yield was calculated by using the

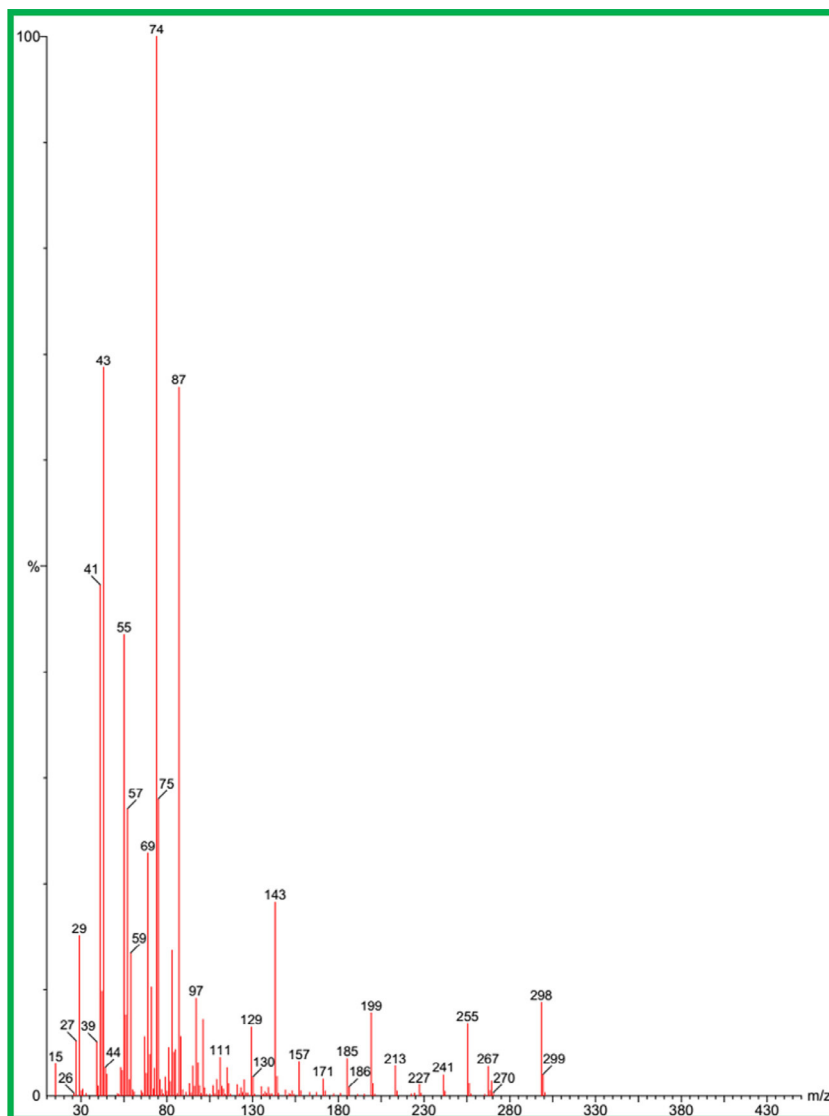


Fig. 4. GC-MS spectrum of stearic acid, methyl ester.

following well known equation:

Biodiesel yield(%)

$$= \frac{\text{Weight of fatty acid methyl ester/}}{\text{Weight of karanja oil used}} * 100\% \quad (3)$$

3. Results and discussion

3.1. Characterizations of synthesized catalyst

3.1.1. XRD analysis

The powder X-ray diffraction (XRD) analysis of the catalyst was carried out with a Shimadzu diffractometer model XRD6000. The diffractometer employed Cu-K α radiations to generate diffraction patterns from the powder crystalline samples at ambient temperature. The XRD diffraction spectra of the prepared catalysts are shown in Fig. 8. The results showed the formation of β -tricalcium phosphate from waste fish bones by increasing calcination temperature from 500 °C to 900 °C. Fish bones contain both hydroxyapatite and β -tricalcium phosphate which was clearly shown in Fig. 8. Conversion of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) into β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) was observed when the calcina-

tion temperature was raised from 500 °C to 900 °C. The XRD intensity peaks of the calcined fish bones at 990 °C indicated the presence of β -tricalcium phosphate due to the noticeable peaks observed in the spectra (JCPDF file 70–2065). The prominent peaks were located at 2θ 21.8, 26.4, 31.02, 34.3, 39.8, 46.9 and 51.4°. Insignificant portion of hydroxyapatite peaks was seen according to JCPDF file (74–0565) at 28.9, 32.8 and 49.4°.

3.1.2. SEM/EDX analysis

The surface morphology of the prepared samples was studied by SEM (Scanning Electron Microscopy) and their images are demonstrated in Fig. 9. The surface structure of β -tricalcium phosphate derived from waste fish bone was found to be porous. The particles were homogeneously well distributed with regular shapes. The calcination temperature effects the porous nature of catalyst and it was observed that the porous nature of catalyst increased by increasing calcination temperature. The β -tricalcium phosphate catalyst is exceedingly agglomerated with almost sphere-shaped particles partaking average size of 150 nm. The microstructure of the synthesized catalyst possesses an average size of 150 nm which increases the catalytic activity for the production of biodiesel in the tranesterification step. Ele-

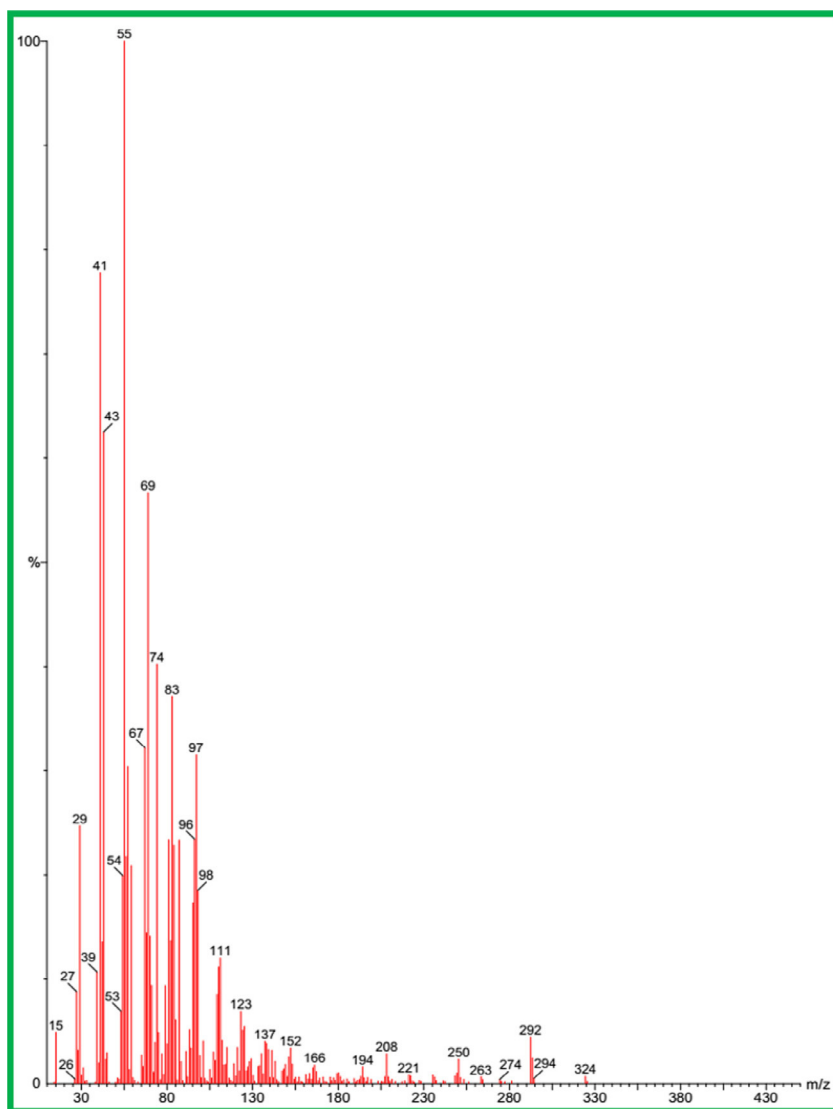


Fig. 5. GC-MS spectrum of cis-11-eicosenoic acid methyl ester.

Table 4
Weight% and atomic% of β -tricalcium phosphate.

Element	Weight%	Atomic%
O	41.10	60.82
P	25.30	19.34
Ca	33.60	19.85
Total	100.00	

mental and chemical characterizations of β -tricalcium phosphate were determined by using energy-dispersive X-ray spectroscopy (EDX) as shown in Fig. 10. The EDX indicated presence of Ca, P and O in the catalyst, β -tricalcium phosphate. Their values were found to be 39.59%, 39.59% and 39.59% respectively as shown in Table 4. The EDX spectrum results clearly indicated in Table 4 that the weight percentages of calcium phosphorus and oxygen were 62.14%, 62.14%, and 62.14%.

3.1.3. TG/DTA/DTG analysis

Thermal stability of uncalcined waste fish bone at high temperature was analyzed with thermo-gravimetric analysis

(TG/DTA/DTG) (Fig. 11). 10.200 mg of uncalcined waste fish bone was used for TG/DTA/DTG analysis. The weight loss of uncalcined waste fish bone was observed from room temperature, 27 °C to 1200 °C which was shown in TG curve. The total weight loss of uncalcined waste fish bone was found to be 46.46 %. Sharp weight loss in TG curve occurred up to 200 °C was due to the dehydroxylation and the high weight loss, ~ 33.34% at 200 < T < 500 was supposed to be there due to loss of organic matter present in waste fish bone. There was no further weight loss after 900 °C, indicating that formation of β -tricalcium phosphate base catalyst from hydroxyapatite [27].

3.1.4. FT-IR analysis

Fourier transform infrared spectroscopy (FT-IR) is a well known analytical technique to determine the functional groups present in a compound. The sharp vibration band at 560 cm^{-1} was assigned to existence of PO_4^{3-} . The broad peak at 1644 cm^{-1} assigned to adsorbed water and sharp vibration peak at 962 cm^{-1} corresponding to PO_4^{3-} . The absorption bands at 962 cm^{-1} , and 1087 cm^{-1} , were attributed to hydroxyapatite since presence of minor amount of hydroxyapatite along with the β -tricalcium phosphate (Fig. 12).

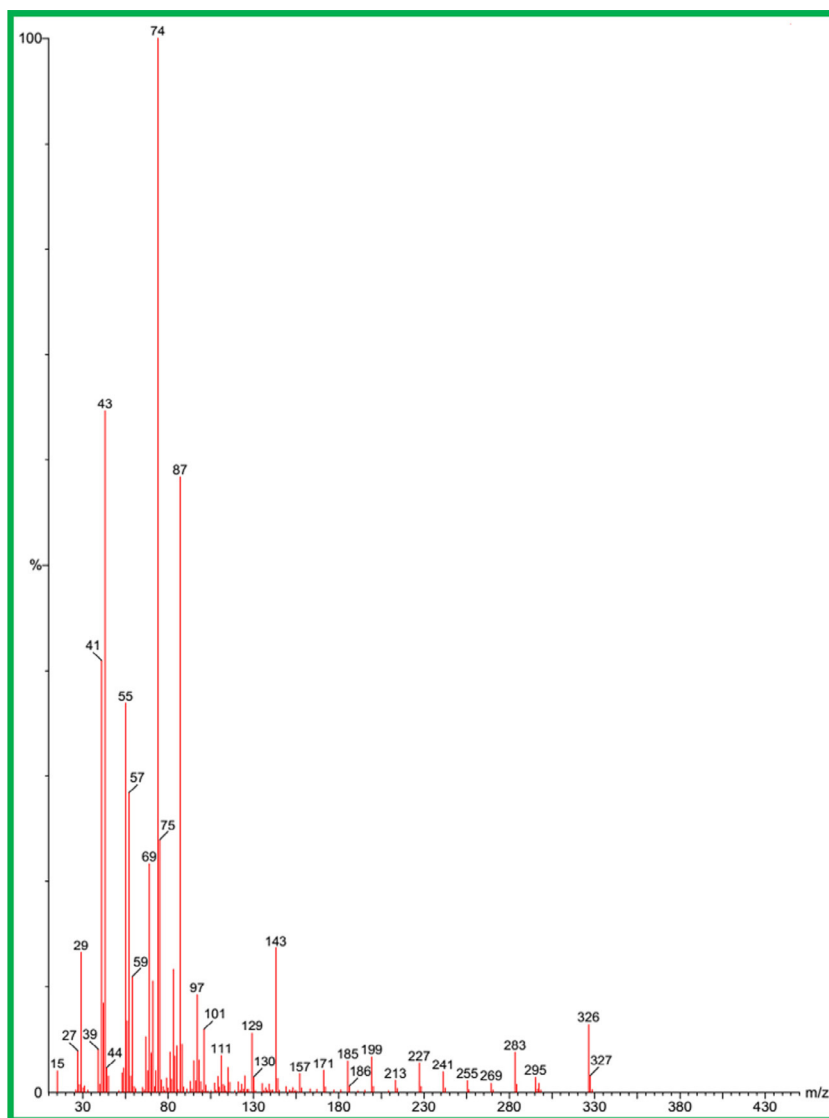


Fig. 6. GC-MS spectrum of arachidic acid methyl ester.

3.2. Characterization of biodiesel

Synthesized biodiesel was characterized with proton NMR spectroscopy. Fig. 13, represents the NMR spectrum of biodiesel synthesized from karanja oil. In each different experimental condition, the conversion of karanja oil to biodiesel was calculated according to well-known equation (2). In the present study, transesterification process was explored to synthesize biodiesel from karanja oil under different operating conditions such as methanol:oil molar ratio, catalyst concentration (wt %), reaction time (min), reaction temperature ($^{\circ}\text{C}$) and stirrer speed (rpm) using β -tricalcium phosphate as a catalyst. These are the most important biodiesel parameters which significantly affected the biodiesel yield [28]. In each experimental setup, the effect of biodiesel parameters on biodiesel yield was studied when one of the biodiesel parameter was varied while other biodiesel parameters were kept constant. According to stoichiometric ratio, synthesis of biodiesel through the transesterification process needs 1 mole oil and 3 moles of alcohol but the whole process of transesterification proceeds reversibly due to which transesterification needs extra alcohol to shift the reaction product side.

$$C = 100(2 * A_{\text{CH}_3}) / (3 * A_{\text{CH}_2}) = 100(2 * 2.24) / (3 * 1.7) = 87.8\% \quad (4)$$

3.3. Effect of co-solvent on biodiesel

Different co-solvents were added to the reaction mixture at fixed methanol:co-solvent (1:1) molar ratio to study the effect of co-solvent on biodiesel yield while other parameters such as catalyst concentration (2.5 wt %), methanol to oil molar ratio (10:1), reaction temperature (65°C) and stirrer speed (650 rpm) were kept constant. In reaction mixture, alcohol (as solvent) and oil form two phase system. This immiscibility of alcohol and oil can be reduced by using co-solvent [4,29], so that reaction mixture immediately shifts towards the product side (biodiesel). Different co-solvents such as acetone, diethyl ether, toluene, tetrahydrofuran (THF) and hexane were used to determine the effect of co-solvents on biodiesel yield since these co-solvents contributed to form reaction mixture to be more homogeneous (Fig. 14). The highest yield (94 %) was observed in case of tetrahydrofuran (THF) since tetrahydrofuran (THF) facilitates the two phase system into one phase system or facilitates to form more homogeneous form of the reaction

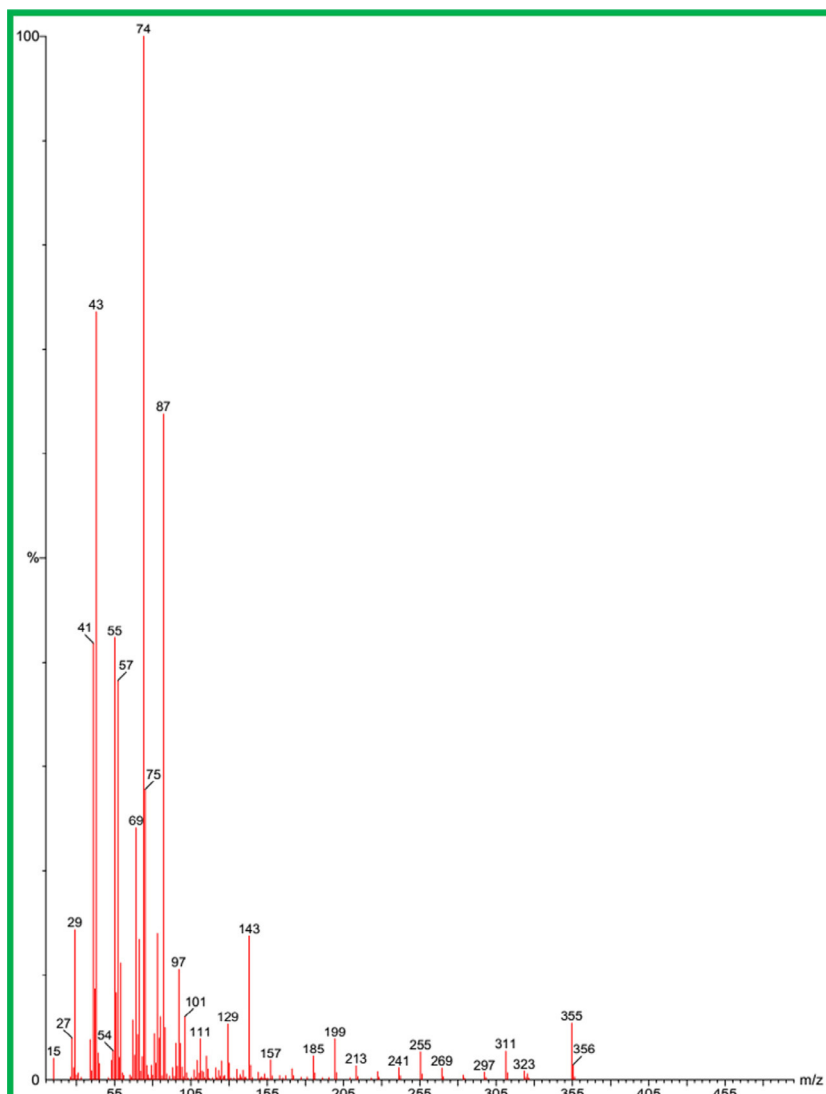


Fig. 7. GC-MS spectrum of behenic acid, methyl ester.

mixture. In the case of acetone and diethyl ether, the biodiesel yield was less due to evaporation. After completion of the reaction, tetrahydrofuran (THF) was recovered for reuse. Tetrahydrofuran (THF) was chosen as co-solvent in all transesterification reactions due to its significant effect on the biodiesel yield and it does not contaminate the biodiesel. Co-solvent was removed with the rotavapor and it was recovered.

3.4. Effect of reaction parameters

3.4.1. Effect of molar ratio and catalyst concentration on the biodiesel yield

Fig. 15 represents the effect of methanol to oil molar ratio and catalyst concentration on biodiesel yield with and without addition of co-solvents. In order to examine the effect of alcohol to oil molar ratio on the yield of biodiesel fuel, different molar ratios were taken at different catalyst concentrations. In order to observe the effect of co-solvent, since it reduces the separation between the immiscible layers of alcohol and oil, we conducted each experiment with co-solvent and without co-solvent. In each experiment, optimum solvent and co-solvent ratio was taken i.e., tetrahydrofuran (THF):methanol (1:1) as shown in Fig. 11. At fixed catalyst concentration, it was clearly observed that the methanol:oil molar ratio was to be increased from 4:1 to 10:1 because increase in molar

ratio increased the biodiesel yield [30]. Alcohol and oil interaction increases when we increase the methanol:oil molar ratio because the greater the mass ratio of reactant, it will increase the interaction between the molecules. The sharp increase in the biodiesel yield occurred with and without addition of co-solvent when the molar ratio was raised from 4:1 to 10:1, beyond this molar ratio there was no significant effect on the biodiesel yield. The biodiesel yield decreased when we raised methanol to oil molar ratio (with and without addition of co-solvent) from 10:1 to 12:1, since reverse reaction between the glycerol and ester or glycerides starts in the reactor. In order to examine the effect of catalyst loading on the biodiesel yield, a number of experiments with different catalyst concentrations over the range of 1–3 wt % were carried out. The same (as in the case of alcohol:oil molar ratio) increment trend in biodiesel yield was observed when we increased catalyst concentration from 1 wt % to 2.5 wt %. At the same time, molar ratio plays vital role but it was observed that the alcohol:oil molar ratio of 10:1, with and without addition of co-solvent was optimum molar ratio since excess of molar ratio decreases the biodiesel yield [31,32]. There was no further increase in biodiesel yield when we increased catalyst from 2.5 wt % to 3 wt % because formation of emulsion takes place and it increases the viscous nature of reaction mixture which led to the difficulty in mixing of reaction mix-

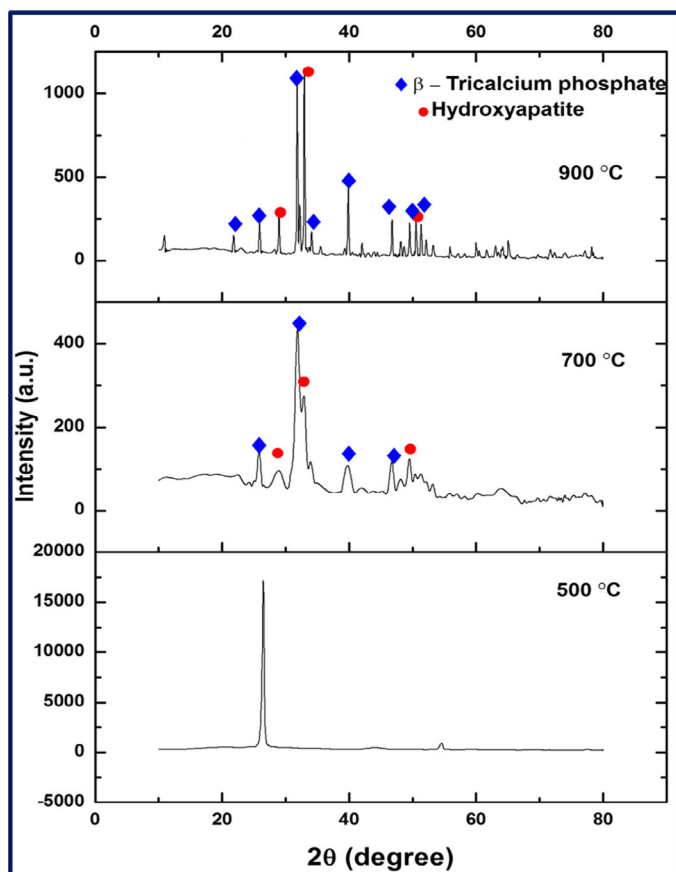


Fig. 8. XRD patterns of β -tricalcium phosphate at different calcination temperatures.

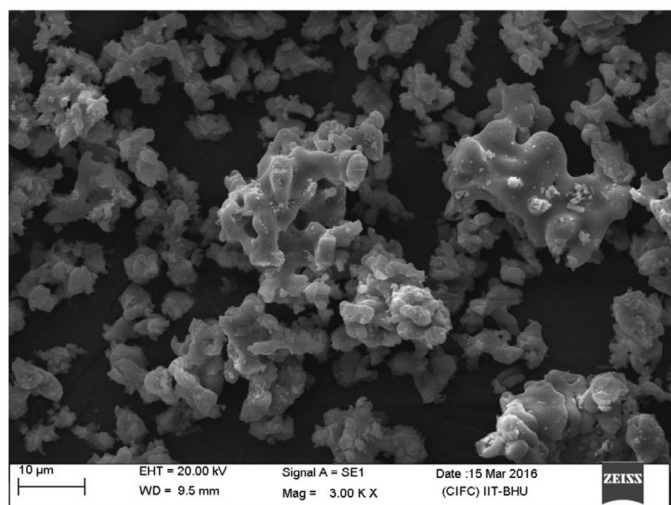


Fig. 9. SEM of β -tricalcium phosphate base catalyst derived from waste fish bone.

ture. High yield (97 %) and high purity biodiesel was obtained with co-solvent at 2.5 wt % catalyst concentration and 10:1 alcohol:oil molar ratio.

3.4.2. Effect of reaction temperature on biodiesel yield

Fig. 16 represents the combined effects of temperature and co-solvent on biodiesel yield. It was observed while the other parameters such as catalyst concentration (2.5 wt %), reaction time (90 min), stirrer speed (650 rpm) and methanol to oil molar ratio (10:1) molar ratio were kept constant and reaction temperature

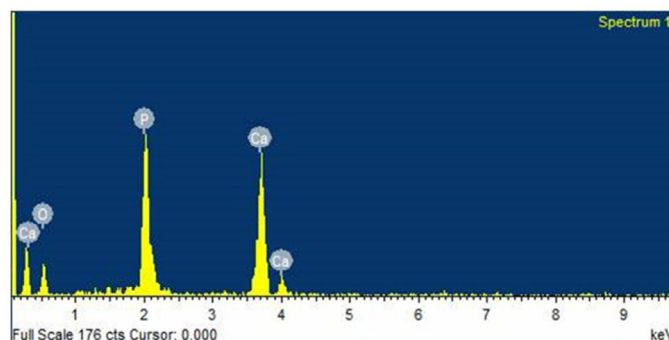


Fig. 10. EDX spectrum of β -tricalcium phosphate.

was varied. Temperature of the reaction was found to have a considerable influence on biodiesel yield. Thus, the experiments using β -tricalcium phosphate catalyst were conducted at 35 °C, 45 °C, 55 °C, 65 °C and 75 °C. By increment in temperature from 35 ° to 65 °C, the biodiesel yield also increased from 64% to 91% without co-solvent and 67 % to 97 % with co-solvent but the optimum temperature was found to be around 65 °C. Insignificant decrease in biodiesel yield was observed when temperature was raised 65 °C. This decrease in biodiesel yield after 65 °C temperature was due to the evaporation of alcohol. Therefore, the temperature of the reaction was optimized at 65 °C for the other study when the time of the reaction was kept constant. Biodiesel yield was significantly increased when we added tetrahydrofuran (THF) as co-solvent.

3.4.3. Effect of mixing rate on biodiesel yield

Effect of stirrer speed on biodiesel yield was studied at stirrer speed between 350 rpm and 850 rpm while the other parameters such catalyst concentration (2.5 wt %), methanol to oil molar ratio (10:1), co-solvent (tetrahydrofuran (THF):methanol molar ratio 1:1) and reaction temperature (65 °C) were kept constant. Reaction mixture exists as a two-phase system and as we increased the stirrer speed, the immiscible nature oil and alcohol significantly decreased and homogeneous mixture i.e., single phase was formed and it favors the reaction mixture towards the product side (biodiesel). Biodiesel yield significantly increased when the stirrer speed increased from the 350 rpm to 650 rpm. Co-solvent accelerates this two phase system into one phase system and this co-solvent supported to produce higher biodiesel yield at minimum stirrer speed. As we increased stirring speed beyond 650 rpm, there was no significant increase in yield as shown in Fig. 17. Biodiesel yield got decreased after 650 rpm due to the high stirrer speed hindered the contact between the reactants and the methanol.

3.4.4. Effect of reaction time on biodiesel yield

The reaction time for the synthesis of biodiesel was determined by carrying out reactions using β -tricalcium phosphate solid base catalyst at varying reaction time keeping other factors constant. It reveals the variation of the karanja oil based on biodiesel content with the processing time, further at optimized factors of the process, the methyl ester's yield improved during the interval ranging from 30 to 90 min, and subsequently kept almost steady, with an insignificant increase of the karanja oil biodiesel after 90 min as shown in Fig. 18. The biodiesel yield was increased as methanol:oil molar ratio increased but the trend did not go beyond the optimum methanol:oil molar ratio of the reaction. Biodiesel yield was clearly influenced by the addition of co-solvent since significance of co-solvent effect on biodiesel yield was considerably high since all the reactions were carried out at shorter time period. The time of the reaction was quite less in all the reactions since the long reaction time will consume more energy. Hence, 90 min were con-

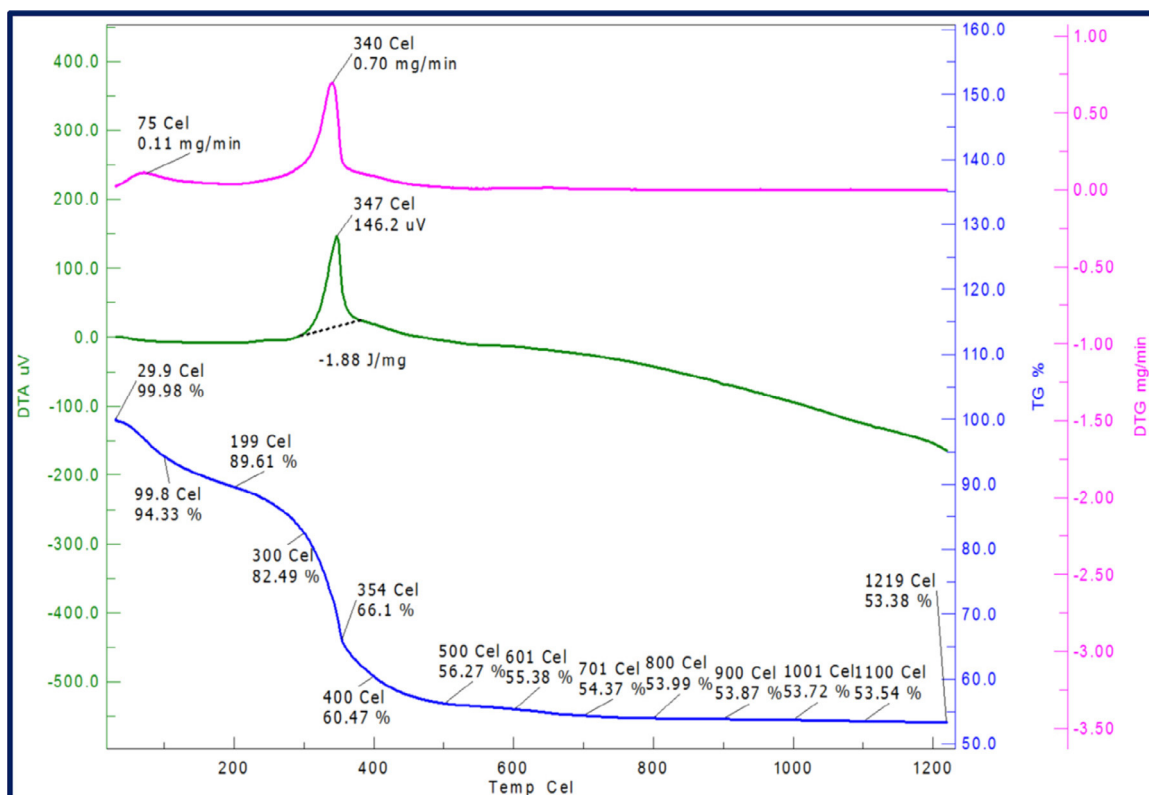


Fig. 11. TG/DTA/DTG of uncalcined waste fish bone.

sidered as an optimum reaction time for the synthesis of biodiesel via the β -tricalcium phosphate catalyst.

3.5. Reusability of catalyst

Reusability of catalyst was analysed by conducting transesterification reactions as shown in Fig. 19. Catalyst reusability was conducted with two different path ways: (i) methanol washing and (ii) methanol washing followed by recalcination. In the first method, after completion of transesterification reaction, the solid catalyst was separated through the filter paper and washed with methanol to remove polar compounds such as glycerol etc., further dried at 100 °C for 1 h to remove water content; this dried catalyst was reused in transesterification reaction. In second method, separated catalyst was washed with methanol and calcined at 650 °C for 4 h and was reused in transesterification reaction. Synthesized catalyst gave high biodiesel yield nearly 97% (in Fig. 15) but in the case of first method (in Run 1), the reused catalyst gave 86% without calcination and in second method, the biodiesel yield was 91%. Run 1 to Run 5, the biodiesel yield was high in the case of second method, since the polar compounds got adsorbed on the surface the catalyst are removed when we kept at 650 °C temperature. In the leachability test, no loss of catalyst was observed in the reaction mixture after completion of the reaction.

4. Conclusions

Biodiesel was synthesized from karanja oil through esterification and transesterification and base catalyst was prepared from fish bones and characterized with TGA/DTA, FT-IR, SEM/EDS and XRD. Karanja oil was extracted using solvent extraction and properties of extracted karanja oil were determined. Synthesized biodiesel was characterized with the proton NMR. Various parameters such as temperature of the reaction, reaction time,

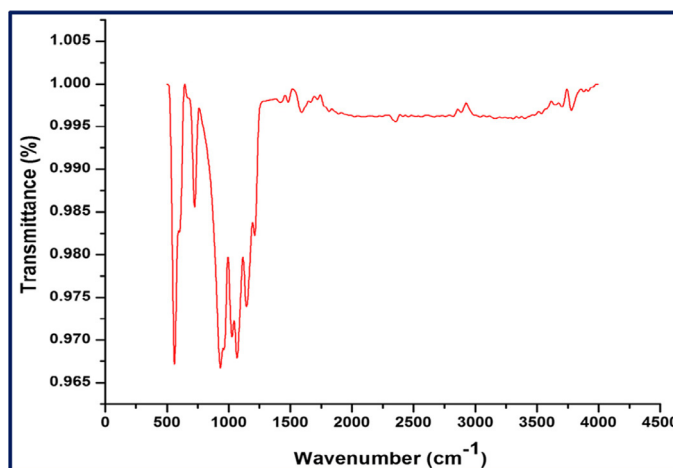


Fig. 12. FT-IR spectrum of β -tricalcium phosphate.

catalyst concentration were studied. High yield (97%) and pure biodiesel was obtained when 2.5 wt % of synthesized catalyst, methanol:oil 10:1 (tetrahydrofuran (THF):methanol 1:1) molar ratio, stirrer speed was 650 rpm, at 65 °C for 90 min. Properties of synthesized biodiesel were followed ASTM standards. Reusability of catalyst up to five times with a small loss of activity was observed.

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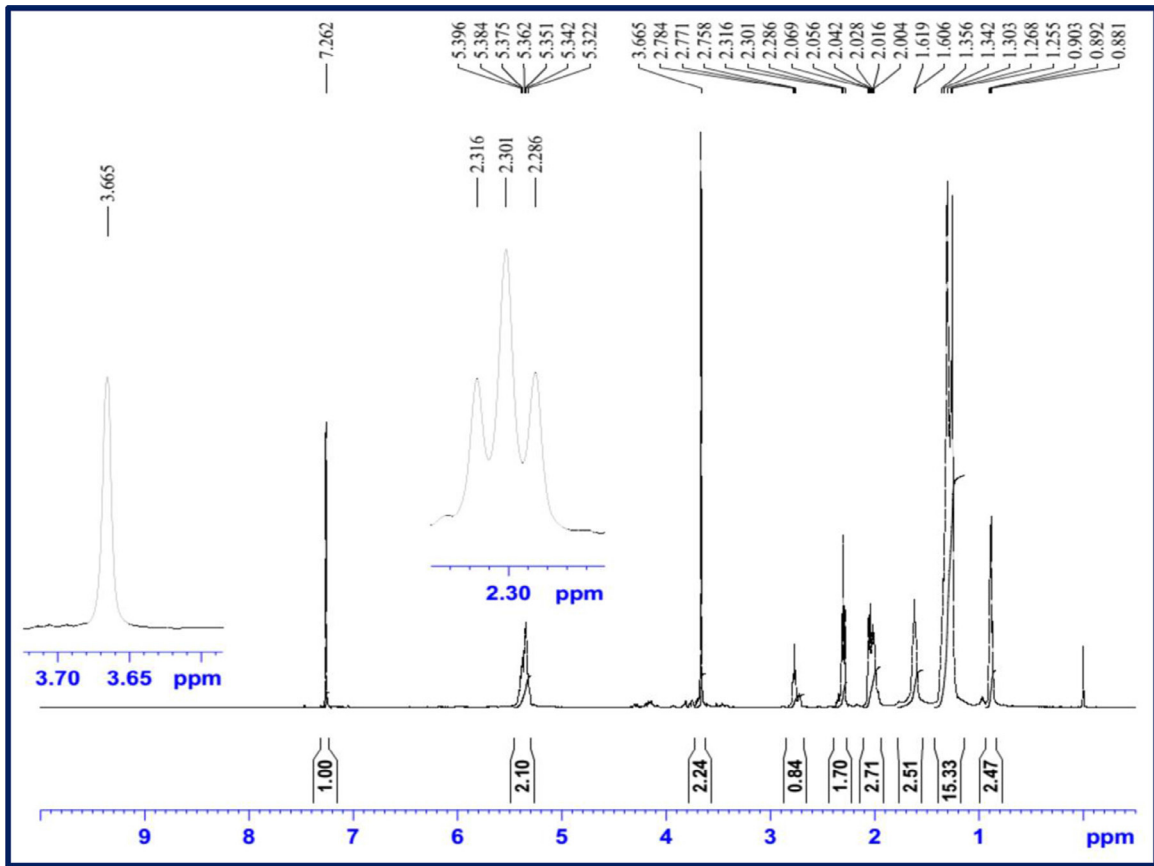


Fig. 13. NMR spectrum of synthesized biodiesel from karanja oil.

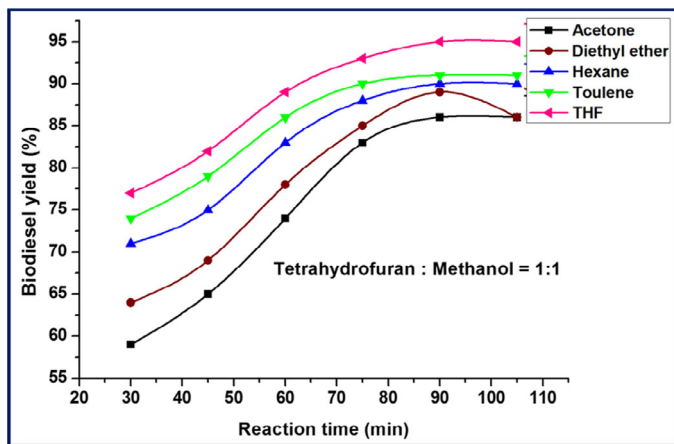


Fig. 14. Effect of co-solvent on biodiesel using different co-solvents.

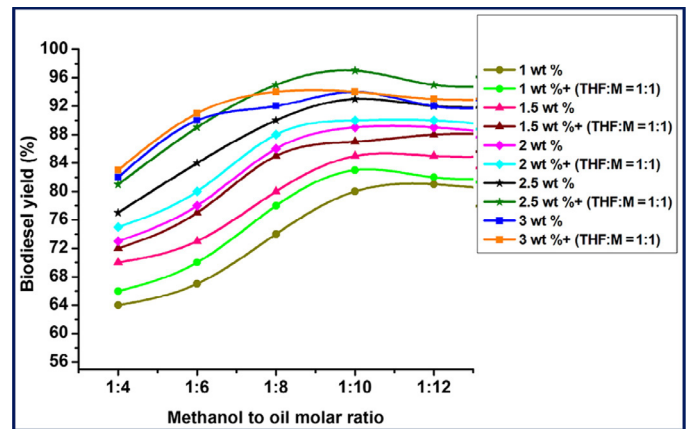


Fig. 15. Effect of molar ratio on the biodiesel production with different catalyst concentration.

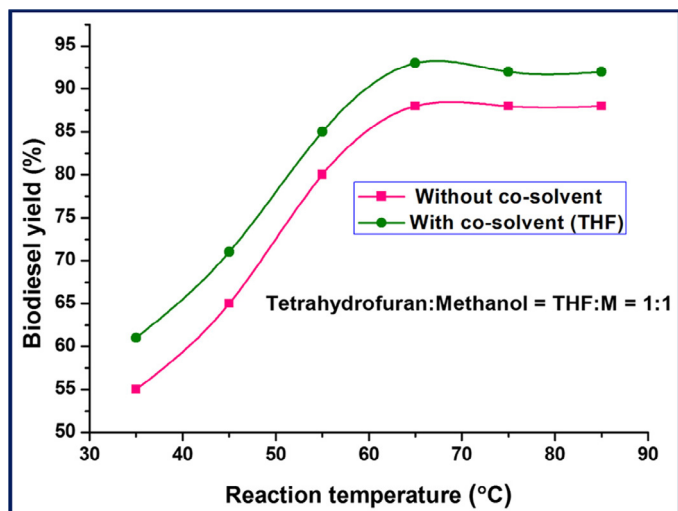


Fig. 16. Effect of reaction temperature on biodiesel yield with and without addition of co-solvent.

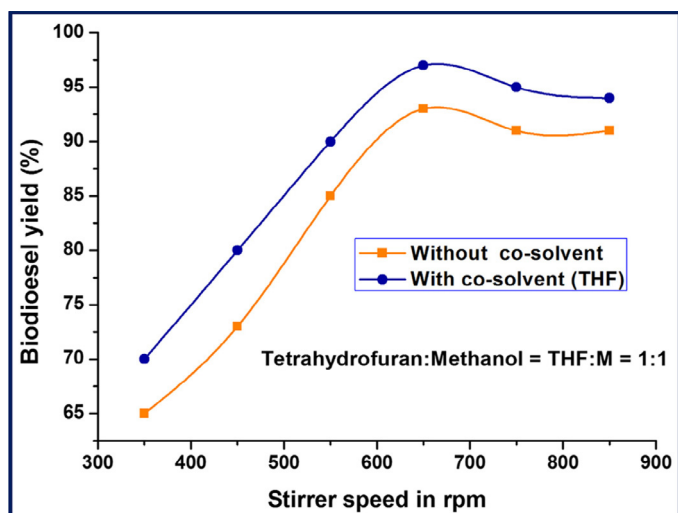


Fig. 17. Effect of mixing rate on biodiesel yield with and without addition of co-solvent.

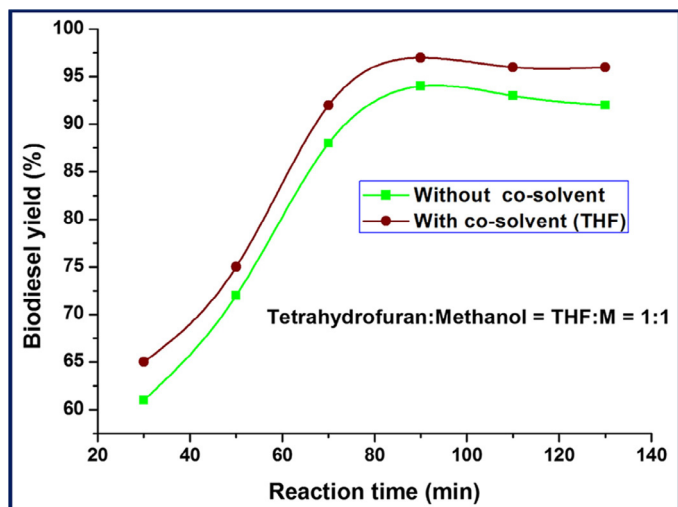


Fig. 18. Effect of reaction time on biodiesel yield with without co-solvent.

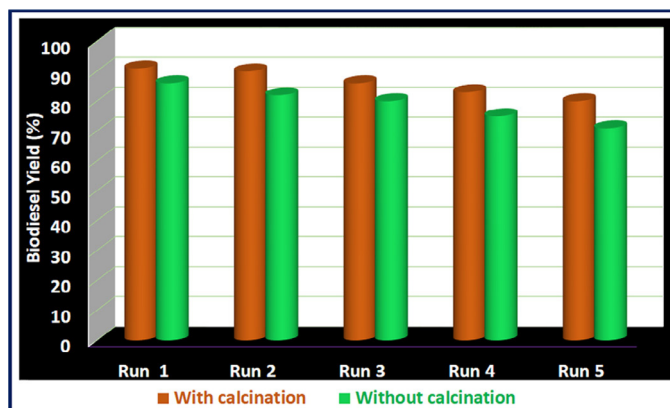


Fig. 19. Reusability of catalyst with and without addition of calcination.

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