6.1 Introduction

Current industrialization and cumulative purchasing power is due enormous population of the world, this huge population is accountable for more consumption of petroleum derived fuels. Many countries, almost all over the world depend on the energy from petroleum derived fuels but these resources are finite and at current usage rate, these resources will be consumed shortly. Economic growth in industrial sector mostly depends upon the petrochemical fuels. Huge energy demand from fossil fuels for technologically advanced world will produce more environmental pollution. This environmental pollution has summoned current attention in alternative sources for petroleum derived fuels. Alternative renewable energy resource is the conversion of edible and non-edible oils into biodiesel which encompasses the features of unlimited era and reduction in environmental pollution. World is looking for use of clean energy like biodiesel since it possesses non-toxicity, easily biodegradability, essentially free from sulphur, and less release of CO gas [Balat, 2011]. Biodiesel as a fuel can improve the economic status, agricultural development, employment opportunity and reduce environmental pollution. Total cost of biodiesel is the major challenge for manufacturers to commercialization the biodiesel since cost of raw material is too high [Chen et al., 2008; Tanaka et al., 2012] which is the reason that total cost of biodiesel may rise 1.5-3 times than the conventional petroleum diesel [Muppaneni et al., 2012]. Low

cost feedstock as well as advanced tools to reduce the total cost can make biodiesel inexpensive than the petroleum fuels. Waste lipids extracted from restaurants, food processing industries, and non-edible crops have high potential to reduce the total cost of biodiesel. Transesterification process using homogeneous as well as heterogeneous catalysts is common method for the synthesis of biodiesel but in each case they have drawbacks since probability of soap formation occurs in case of homogeneous catalyst [Cai et al., 2015] and high temperature is needed in the case of heterogeneous catalysts. Base catalysts are preferred as compared to acid catalysts since acid catalysts possess more corrosive properties than the base catalysts. Synthesis of biodiesel from heterogeneous catalysts has its own advantages: they have catalyst reusability [Madhu et al., 2014], easily separable and environmental friendliness [Feyzi et al., 2013]. As a result, more scientists focused to develop the heterogeneous catalysts for the synthesis of biodiesel. Present study explored the synthesis of biodiesel using *pongamia pinnata* oil (extracted from its seeds) as feedstock and β-tricalcium phosphate (β-$Ca_3(PO_4)_2$) as a solid base catalyst prepared from waste fish bone through calcination. The waste fish bones consist of hydroxyapatite [Boutinguiza et al., 2012] at below 600 °C calcination temperature and the formation of β-tricalcium phosphate [Chakraborty et al., 2011] at above 800 °C. Synthesized catalyst hasshown high catalytic activity and gave high biodiesel yield when the catalyst was reused up to five times since reusability can reduce the total cost of biodiesel.

6.2 Results and discussions

6.2.1 FT-IR analysis of biodiesel

Synthesized biodiesel was characterized with Fourier Transform Infrared Spectroscopy (FT-IR Spectroscopy) to determine the functional groups present on the synthesized biodiesel (Figure 6.1). Sharp absorption band, occurred at 1741 cm^{-1} was due the presence of C=O group in synthesized biodiesel. Absorption bands at 2923 cm^{-1} and 2853 cm^{-1} were indicated the existence aliphatic hydrocarbon, CH$_2$ group on biodiesel. Intense peak was observed at 1459 cm^{-1}, was due the existence of CH$_2$ and CH$_3$ groups. Absorption band at 720 cm^{-1} was assigned to CH$_2$ groups and C-O stretching frequency was observed at 1168 cm^{-1}.
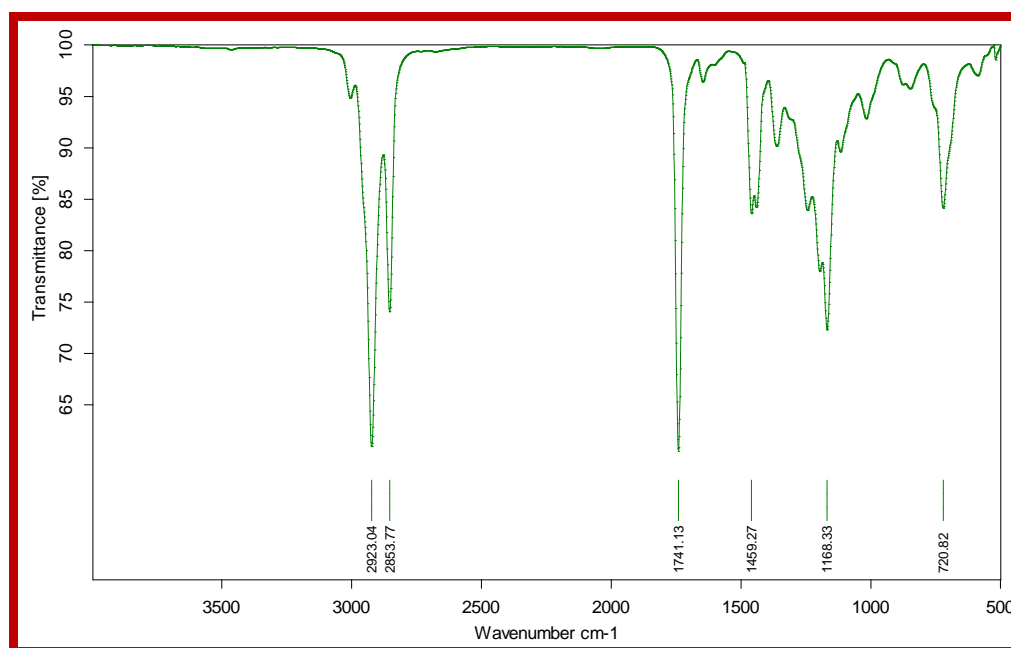

Figure 6.1 Represents FI-IR spectrum of synthesized biodiesel.

6.2.2 Effect of reaction parameters on biodiesel yield

6.2.2.1 Effect of molar ratio and catalyst concentration on the biodiesel yield

Figure 6.2 represents the combined effect of catalyst concentration and methanol to oil molar ratio with and without co-solvent. Effect of catalyst concentration and methanol to oil molar ratio on biodiesel yield was studied by taking catalyst with different concentrations ranging from 1.0 wt % to 5.0 wt % and different methanol to oil molar ratios, ranging from 4:1 to 14:1, by keeping other parameters constant. Effect of co-solvent was observed in each and every experiment by adding tetrahydrofuran (THF): methanol (1:1) ratio to the reaction mixture since the co-solvent diminishes the immiscibility between the alcohol layer and oil layer which render the reaction mixture to become more homogeneous. Biodiesel yield increased sharply from 48 % to 66 % without co-solvent and 56 % to 79 % with co-solvent when the methanol to oil molar ratio was raised from 4:1 to 10:1 at 1.0 wt % catalyst concentration since the methanol to oil molar ratio increases, biodiesel yield also increases [Freedman et al., 1986] because more the mass transfer, more will be the contact between the reactants molecules. As the catalyst concentration increased from 1.0 wt % to 4.0 wt %, the yield also increased but in each case 10:1 was the optimum methanol to oil molar ratio to get high biodiesel yield. High biodiesel yield, 96 % was obtained with the addition of 4.0 wt % of catalyst concentration at 10: 1 methanol to oil molar ratio in the presence of co-solvent. Biodiesel yield did not increased significantly when methanol to oil molar ratio was raised from 10:1 to 14:1. This could be attributed

as excess of methanol dissolved in glycerol will shift the equilibrium towards reverse direction [Gaanty Pragas et al., 2009]. Effect of catalyst concentration on biodiesel yield was examined and increment in biodiesel yield was observed when the catalyst concentration increased up to 4.0 wt % from 1.0 wt %, but beyond 4.0 wt % biodiesel yield got decreased, this reduction in biodiesel yield is due formation of suspension which led to trouble in mixing of reaction mixture. High yield 96 %, and high quality biodiesel was obtained in the presence of co-solvent at 10: 1 alcohol: oil molar ratio and 4.0 wt % catalyst concentration.
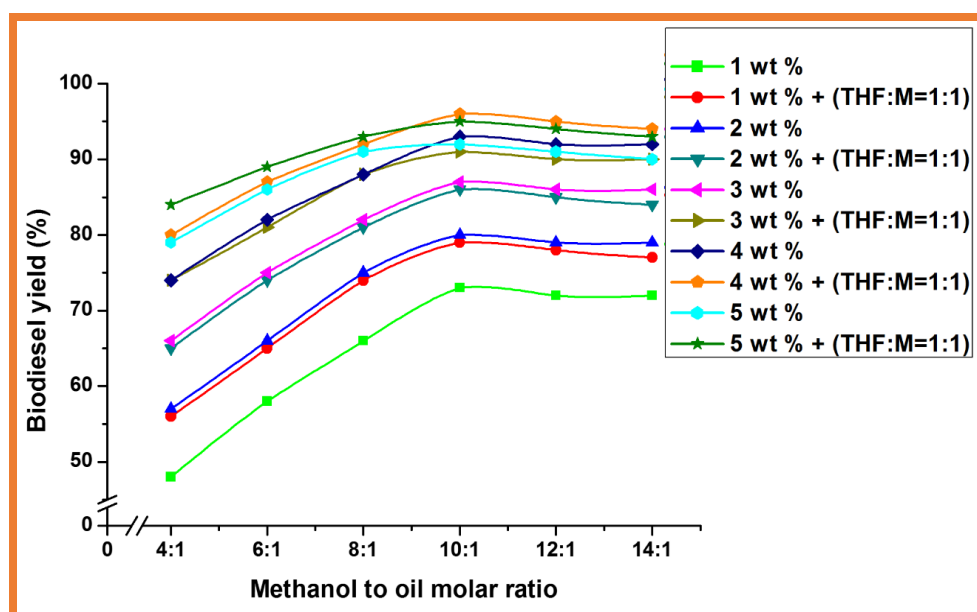

Figure 6.2 Represents the effect of molar ratio and catalyst concentration on the biodiesel yield.

6.2.2.2 Effect of reaction temperature on biodiesel yield

Effect of temperature on biodiesel yield was studied with and with addition of co-solvent while the other parameters such as methanol to oil molar ratio (10:1),

reaction time (114 min), stirrer speed (650 rpm) and catalyst concentration (4.0 wt %) were kept constant. Transesterification reactions were carried out using *Pongamia pinnata* oil as a feedstock and β-tricalcium phosphate as a solid base catalyst at 35 °C, 45 °C, 55 °C , 65 °C, 75 °C and 85 °C temperatures as shown in Figure 6.3. Biodiesel yield was increased from 61 % to 92% without co-solvent and 68 % to 96 % with co-solvent when the reaction temperature raised 35 ° to 65 °C. Reaction temperature was increased beyond 65 °C, there was no increment in biodiesel yield but comparatively biodiesel yield was decreased due the evaporation of alcohol. Temperature of the transesterification reactions was optimized at 65 °C since at this temperature high yield and pure biodiesel was occurred.
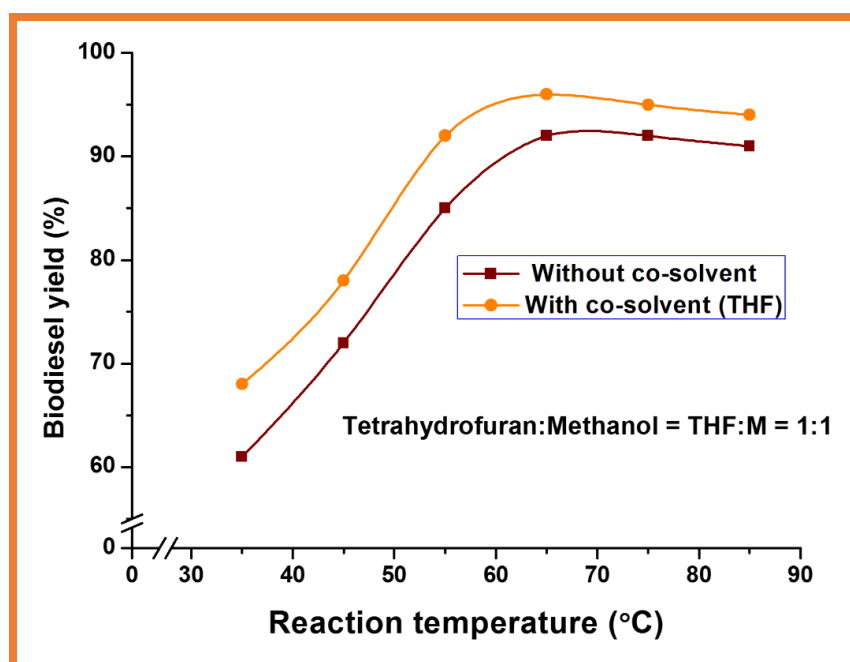

Figure 6.3 Represents the effect of reaction temperature on biodiesel yield.

6.2.2.3 Effect of mixing rate on biodiesel yield

In order to examine the effect of stirrer speed on biodiesel yield, a series of experiments were conducted from 350 rpm to 850 rpm while other parameters such as catalyst concentration (4.0 wt %), methanol to oil molar ratio (1:10), reaction temperature (65 °C) and co-solvent (tetrahydrofuran (THF): methanol (1:1) ratio) were kept constant. Biodiesel yield gradually increased as the stirrer speed increased from 350 rpm to 650 rpm due the vanishing of two phase system of reaction mixture and the mixture becoming more homogeneous. This homogeneity of reaction mixture sifted the equilibrium towards the product side. Homogeneousness of reaction mixture not only got accelerated by stirrer speed, but also co-solvent since the biodiesel yield (94 %) was high at minimum stirrer speed (650 rpm). When stirrer speed was increased beyond 650 rpm, there was no significant increase in biodiesel yield due the evaporation of methanol and less interaction between the reactants and the methanol at higher stirrer speed as shown in Figure 6.4.
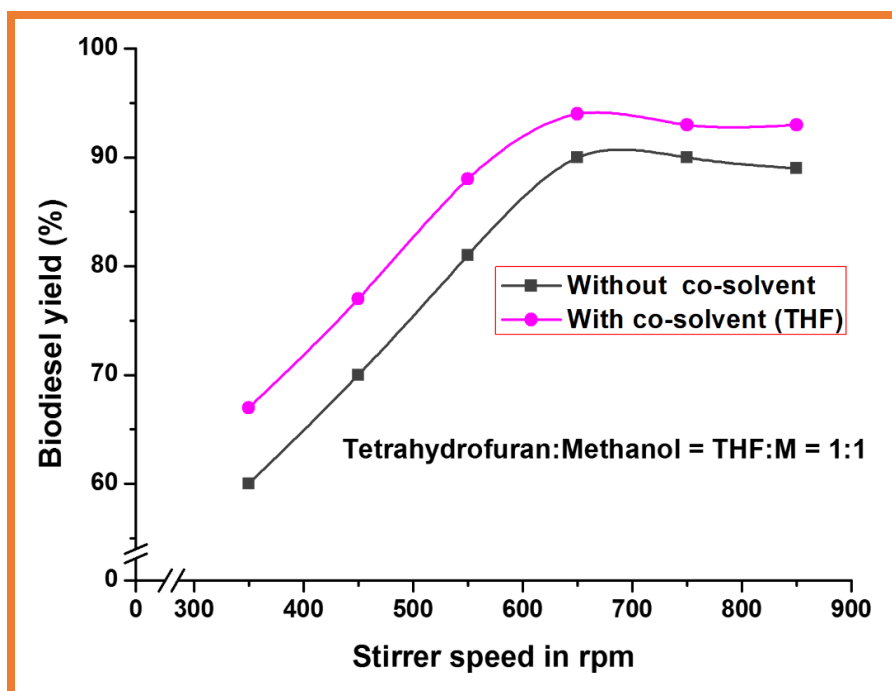
Figure 6.4 Effect of mixing rate on biodiesel yield.

6.2.2.4 Effect of reaction time on biodiesel yield

Effect of reaction time on biodiesel yield was studied using *Pongamia pinnata* oil as feedstock and β-tricalcium phosphate as a solid base catalyst with and without co-solvent. In all the experiments, reaction time was varied 30 min to 170 min and other factors were kept constant. Reaction time increased from 30 to 114 min, the biodiesel yield also increased from 58 % to 90 % without addition of co-solvent and 65 % to 95 % with addition of co-solvent since increase in reaction time will increase the biodiesel yield [Freedman et al., 1984]. Maximum biodiesel yield (95 %) occurred at optimum reaction time (114 min) as shown in Figure 6.5. Biodiesel yield was obviously effected by the presence of co-solvent since all the reactions were observed at shorter reaction time. Reaction time was increased from

114 min to 170 min, but there was no significant increase in biodiesel yield since long period of time will convert biodiesel into soap through hydrolysis of ester [Leung and Guo, 2006].
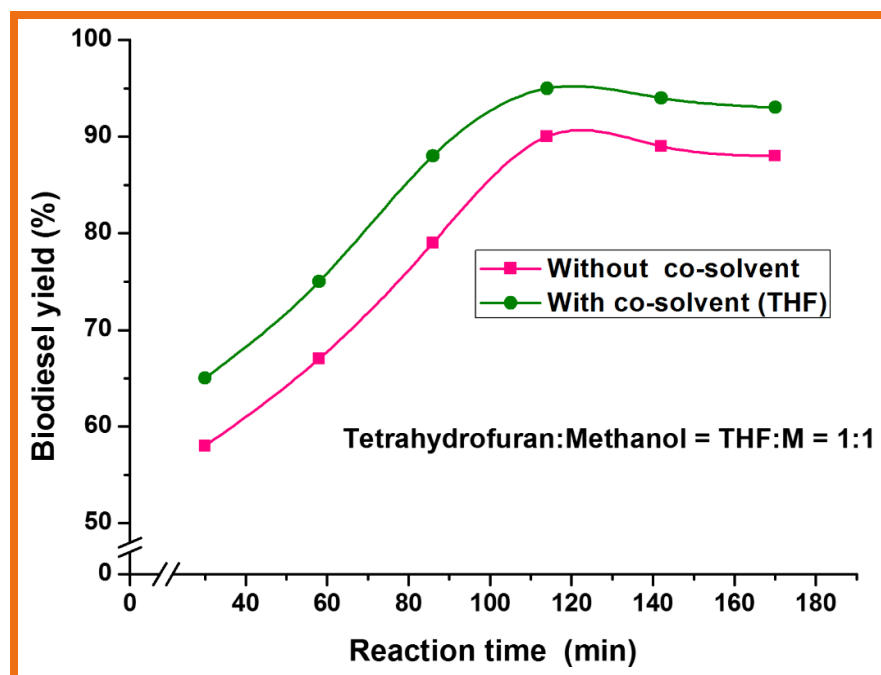

Figure 6.5 Represents the effect of reaction time on biodiesel yield.

6.2.3 NMR analysis of synthesized biodiesel

Synthesized biodiesel was analysed by using proton NMR since it is more sensitive and accurate analytical technique to determine the conversion of biodiesel from *Ponmgamia pinnata* oil. The percentage conversion of *Pongamia pinnata* oil to biodiesel was calculated by using the well-known equation (Eq. 6.1) which contains the ratio of integrated signals (area under the signal obtained by integration) at 3.69 ppm (A_{ME}) and 2.30 ppm (A_{CH2}). Maximum biodiesel conversion (98. 03 %) from *Pongamia pinnata* oil

was obtained when the reaction parameters, such as reaction time 114 min, methanol to oil molar ratio 10:1, catalyst concentration 4.0 wt %, stirrer speed 650 rpm and reaction temperature 65 °C were used in transesterification reaction.

$C = 100(2A_{CH3})/(3A\alpha\text{-}_{CH2})$ (6.1)

$C = 100(2*3)/(3*2.04)$

C= 98.03 %

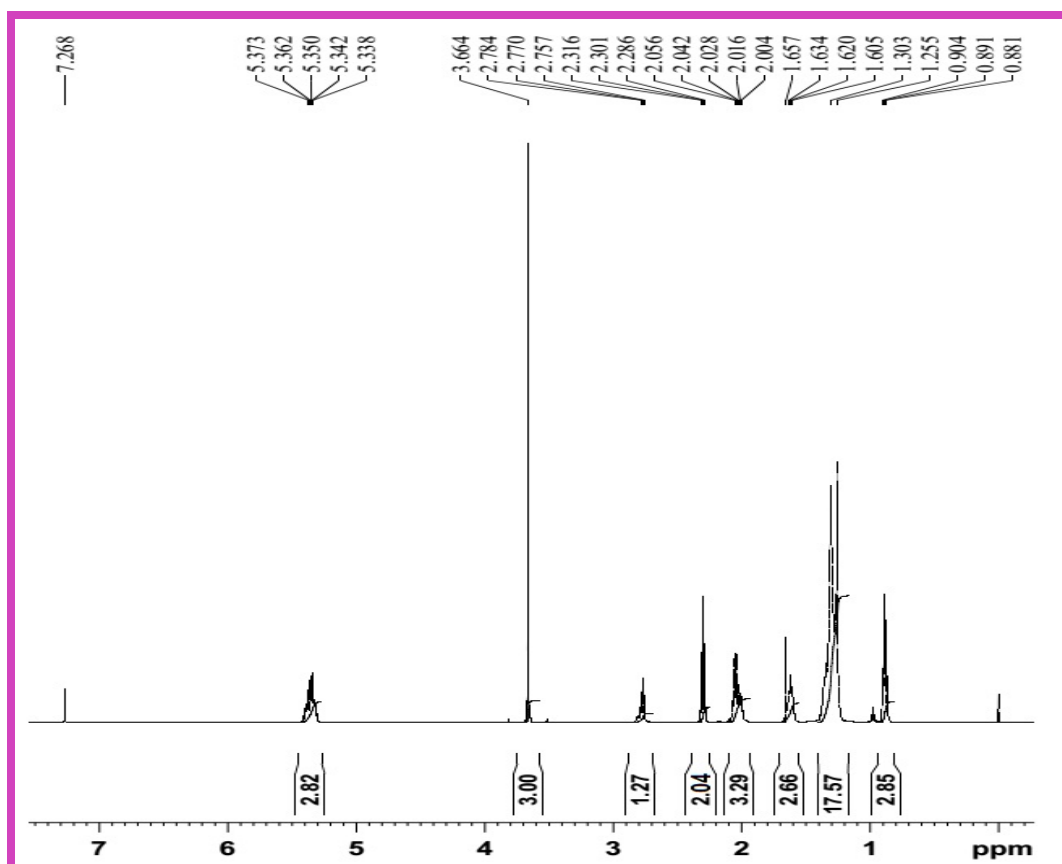C denotes the conversion (%) of triglycerides to fatty acid methyl esters.

Figure 6.6 Represents the proton NMR analysis of synthesized biodiesel.

6.2.4 Separation and purification of biodiesel

Biodiesel was separated from its by-products by using separating funnel and washed with hot distilled water. Water content was removed with rotavapor and further purification process was conducted as reported in Section 5.2.5, chapter 5. After purification process high quality and pure biodiesel was obtained. Physical and chemical properties of biodiesel were determined according to ASTM standards. Physical and chemical properties of synthesized biodiesel conform to the specifications of ASTM biodiesel standards as shown in Table 6.1.

Table 6.1 Physical and chemical properties of biodiesel synthesized from *Pongamia pinnata* oil and calcium oxide as catalyst.

Property	Unit	ASTM Standards	*Pongamia pinnata* oil biodiesel	ASTM D 6751 Biodiesel specifications	
				Min	Max
Color	-		Yellowish red	-	-
Acid value	mg KOH/g	ASTM D 664	0.41	-	0.5
Density	g/cm^3	ASTM D 1298	0.856	0.875	0.90
Cloud point	°C	ASTM D 1510	1	Report	Report
Pour point	°C	ASTM D 97	0	-	-
Kinematic viscosity(mm^2/s), at 40 °C	mm^2/s	ASTM D 445	5.6	1.9	6.0
Cetane number		ASTM D613	49.6	47	-
Flash point	°C	ASTM D 93	174	120	-
Calorific value	kcal/kg	ASTM D 4809	3986	-	-
Water content	in %	ASTM D 2709	0.003%	-	0.05
Copper strip corrosion	3h/50 °C	ASTM D 130	No Corrosion observed	-	3

6.2.5 Reusability of catalyst

Catalyst reusability was investigated through a series of transesterification reactions as shown in Figure 6.7. Reusability of β-tricalcium phosphate catalyst was studied with two different methods: (i) catalyst was washed with methanol reused and (ii) catalyst was washed with methanol and recalcined at 700 °C and

reused. Reusability of catalyst was explained in details in Section 5.2.6, Chapter 5. In the first method (in the first run), synthesized catalyst gave 88 % (biodiesel yield) and in the fifth run catalyst gave 70 % biodiesel yield in the presence of co-solvent. In the second method (in the first run), calcined catalyst gave 93 % biodiesel yield which was 5 % higher than the first method in the first run. In the second method catalyst loses adsorbed water molecules when we conducted recalcination at 700 °C.
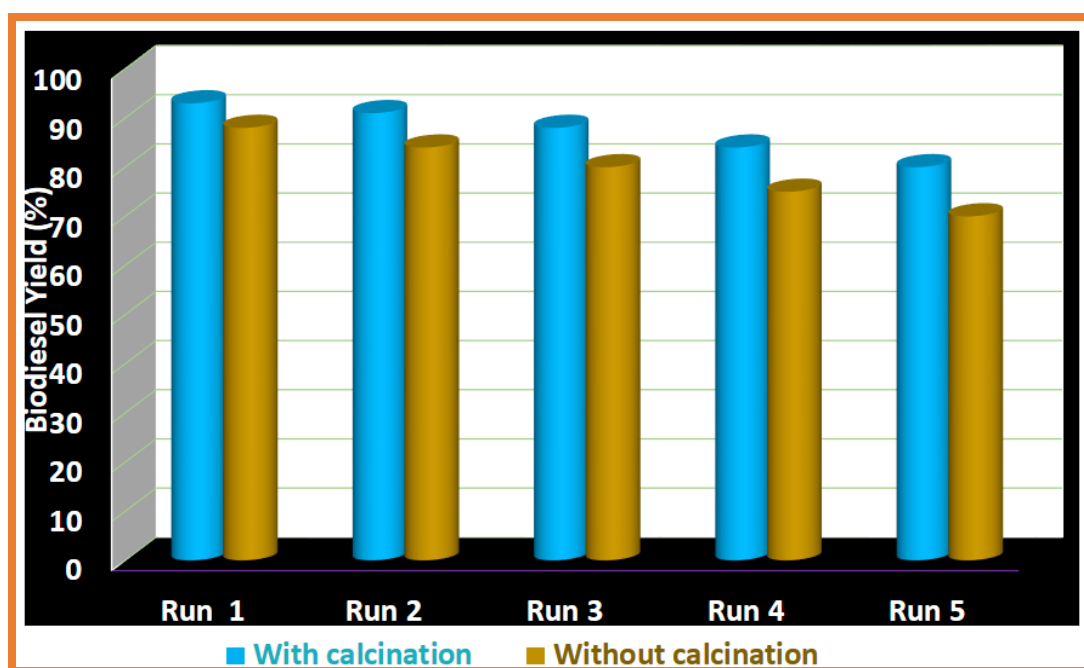

Figure 6.7 Represents the reusability of β-tricalcium phosphate catalyst.

6.3 Conclusions

Synthesis of biodiesel using *pongamia pinnata* oil as a feedstock and β-tricalcium phosphate catalyst as solid base catalyst. *Pongamia pinnata* oil was extracted from

its seeds by using different solvents and β-tricalcium phosphate catalyst derived from solid matter. Esterification followed by transesterification reactions were conducted for the synthesis of biodiesel. Prepared catalyst was characterized with TG/DTA/DTG and FT-IR, SEM/EDS and XRD. Biodiesel was characterized with proton NMR, GC-MS, FT-IR. Biodiesel parameters such as reaction time, reaction temperature, catalyst concentration, and stirrer speed were studied with and without co-solvent. Maximum biodiesel yield (96 %) was obtained when 4.0 wt % of synthesized catalyst, methanol: oil 10: 1 (and hexane: methanol 1:1) molar ratio, stirrer speed was 650 rpm, at 65 °C for 114 min. Pure and high quality biodiesel conversion (98.03 %) was obtained from *Pongamia pinnata* oil. Physical and chemical properties of synthesized biodiesel were determined according to ASTM standards. Reusability of catalyst was observed up to five times where the catalyst was reusable up to five times without much loss of catalytic activity.