CHAPTER 5

5.1 Introduction

Energy demand increased from the last century because of change in the lifestyle and population escalated. Fuel consumption has enlarged more than a few folds and is anticipated to further increase in the coming days [Bilgen, 2014]. Current energy requirements are delivered through diesel, coal, natural gas, and petrol but the present natural nonrenewable resources are finite and contemporary usage rates will indicate the fuel depletion [Höök and Tang, 2013], this depletion will lead to increase in fossil fuels price. Energy demand and inadequate availability of fossil fuels lead to search for alternative renewable energy resources which would be environmentally friendly and economically feasible and socially justifiable. Transportation sector and industry sectors are major energy consumption sectors. These sectors are major end users of liquefied petroleum gas, compressed petroleum gas, fuels like petrol, diesel and gasoline. This energy consumption will increase in future since rise in total number of vehicles which are responsible for toxic emissions but biodiesel controls emissions of toxic contaminants and carcinogens [Dorado et al., 2003a]. Pure and high quality biodiesel production is a major task not only for manufactures but also it’s a big challenge for researchers as well as scientists. Biodiesel synthesis via esterification followed by transesterification using homogeneous as well as heterogeneous catalysts. Synthesis of biodiesel without catalyst can also be possible such as by supercritical method [Demirbas, 2005] and subcritical method [Zexue et al., 2013]. In the absence of catalyst, soap formation does not occur in the process of synthesis of biodiesel but the supercritical alcoholysis takes huge quantity of alcohol than the conventional catalytic method i.e., solid base/acid transesterification [Kusdiana and Saka, 2001; Mansir et al., 2016; Sandesh et al., 2016]. Synthesis of biodiesel through the enzymatic reactions is environmentally safer and less side products are produced but the use of lipase or high cost of biocatalyst with alcohol may rise the total cost of biodiesel. In present work, biodiesel was synthesized from *Pongamia pinnata* **(**karanja) oil extracted from its seeds using calcium oxide as an efficient catalyst derived from waste crab shells. It is reported that [Kouzu et al., 2008] that the calcium oxide acts as a stable catalyst for the synthesis of biodiesel. Synthesis of biodiesel derived from vegetable oils or animal fats through the process called transesterification with alcohol is highly suggested to be used as alternative renewable resource for mineral diesel [Altın et al., 2001]. Biodiesel can reduce emissions of the prominent greenhouse gases. Biodiesel does not possess aromatic compounds, almost no sulfur and retains high cetane number than mineral diesel [Canakci and Van Gerpen, 2001; Peterson and Hustrulid, 1998].

5.2 Results and discussions

5.2.1 Effect of co-solvent on biodiesel synthesis

Effect of co-solvent on biodiesel yield was observed by taking different co-solvents such as toulene, diethyl ether, hexane, tetrahydrofuran (THF) and acetone (Figure 5.1). Co-solvent to methanol molar ratio was fixed at 1:1 while other factors such as methanol: oil (1:10), reaction temperature (65 °C), stirrer speed (650 rpm) and catalyst concentration (2.5 wt %) were kept constant. Reaction mixture exist as two phase system in which methanol exhibited hydrophilic nature and fish oil exhibited hydrophobic nature. This immiscibility between alcohol and oil can be reduced by using co-solvents [Encinar et al., 2016; Luu et al., 2014] to promote the reaction mixture towards the product side. Molar ratio (methanol: oil) of reaction mixture is more important factor for the production of biodiesel since transesterification is reversible [Hassan and Vinjamur, 2013], to shift the reaction to product side, more amount of methanol was used in reaction mixture. Among all the co-solvents, the biodiesel yield (95 %) was highest in the case of THF. Tetrahydrofuran (THF) facilitates the reaction mixture (oil phase and alcohol phase) to more homogeneous and also it reduced the energy consumption. So, THF was selected as co-solvent for the synthesis of biodiesel. Optimization of THF determined and was found maximum at 1:1 (co-solvent: alcohol) as shown in Figure 5.2.

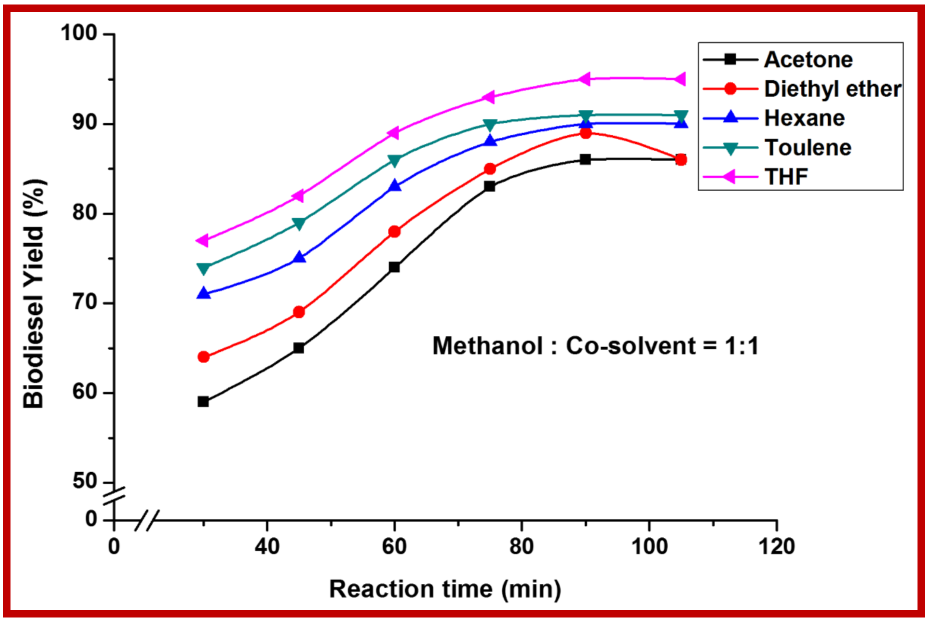

Figure 5.1 Effect of co-solvent on biodiesel yield using different co-solvents.

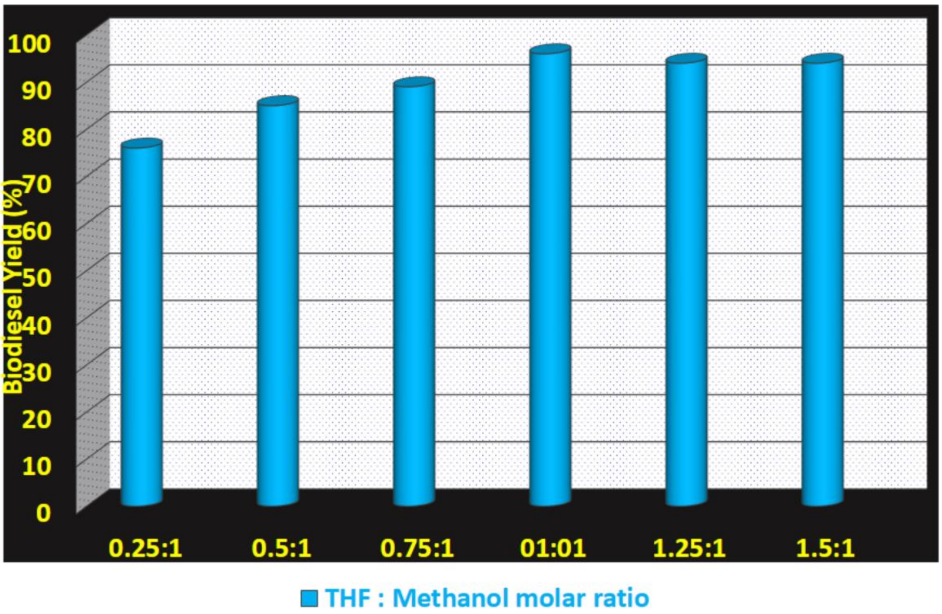

Figure 5.2 Represents the effect of tetrahydrofuran to methanol molar ratio on biodiesel.

5.2.2 FT-IR analysis of biodiesel

Fourier Transform Infrared Spectroscopy (FT-IR Spectroscopy) is analytical technique to determine functional groups present in the synthesized compound. Purified biodiesel was characterized with FT-IR spectroscopy as shown (Figure 5.3). Sharp and intense peaks were observed at 2923 cm^{-1} and 2854 cm^{-1} which ascribed the existence of methylene group (CH_2) which clearly designated the presence of aliphatic hydrocarbons in biodiesel [Hassen-Trabelsi et al., 2014; Lu et al., 2008]. Asymmetric vibrations occurring at 1459 cm^{-1} were assigned to CH_2 and CH_3 groups. Intense peak observed at 1742 cm^{-1} is attributed to C=O stretching frequency. Sharp absorption band occurred at 721 cm^{-1} was due the presence of more than four CH_2 groups in synthesized biodiesel

[Rohman and Man, 2010]. The band observed at 1160 cm^{-1} was due to C-O stretching frequency of fatty acid methyl of ester [Rohman et al., 2011].

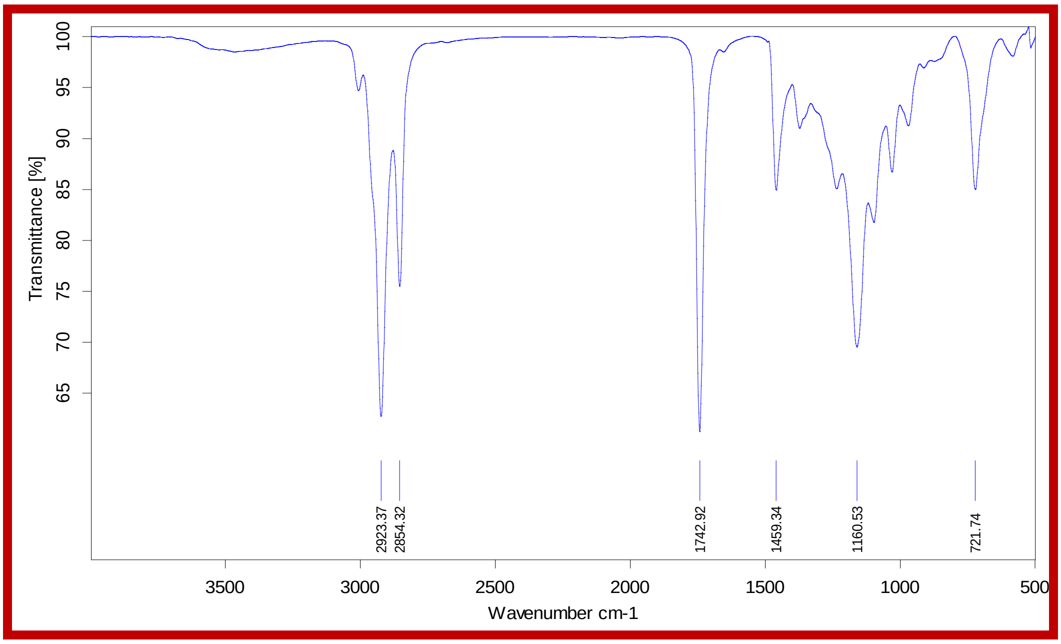

Figure 5.3 FI-IR spectrum of synthesized biodiesel.

5.2.3 Effect of reaction parameters on biodiesel yield

Acid value of feedstock plays a significant role in transesterification reaction for the synthesis of biodiesel. Acid value of oil having less than 1.0 % will facilitate direct transesterification [Hayyan et al., 2010] without conducting esterification step. However, high acid value 17. 68 mg KOH/g of *Pongamia pinnata* oil will undergo for two step reaction, i.e. esterification followed by transesterification. Esterification reaction of *Pongamia pinnata* oil using H_2SO_4 as homogeneous acid catalyst was done according to procedure mentioned in Section 3.5, Chapter 3. After esterification, acid value of

Pongamia pinnata oil was reduced to 0.44 mg KOH/g and transeserification reaction was performed. In transesterification reaction, biodiesel was synthesized from *Pongamia pinnata* oil using calcium oxide as solid base base catalyst.

5.2.3.1 Effect of catalyst concentration and methanol to oil molar ratio on biodiesel yield

Catalyst concentration has a significant role on biodiesel yield and has been demonstrated in Figure 5.4. The effect of catalyst concentration on biodiesel yield was observed by taking different catalyst concentrations ranging from 1.0 wt % (w/w of oil) to 3.0 wt % (w/w of oil) and this effect was studied under constant reaction conditions: temperature, 65 °C; stirrer speed, 650 rpm and reaction time, 105 min. A series of experiments was conducted to determine the combined effect of catalyst concentration as well as oil: methanol molar ratio and effect of co-solvent on biodiesel yield. Effect of catalyst concentration and methanol to oil molar ratio on biodiesel yield was studied with and without addition of co-solvent (Tetrahydrofuran: methanol (1:1) ratio). As the catalyst concentration was increased from 1.0 wt % to 2.5 wt %, there was an increment in biodiesel yield. Adequate catalyst concentration is required since it necessary the probability of catalyst contact with the reactants to get products but insufficient catalyst concentration will render higher chances of its contact with reactants [Wu et al., 2014]. As the catalyst concentration increased from 1.0 wt % to 2.5 wt %, the biodiesel yield also increased from 73 % (at 10:1, methanol to oil molar ratio) to 94 % (at 10:1, methanol to oil molar ratio) without co-solvent and 78 % (at 10:1, methanol to oil molar ratio) to 98 % (at 10:1, methanol to oil molar ratio) with co-solvent, thereafter the biodiesel yield got slightly decreased when the catalyst increased beyond the 2.5 wt %. It is attributed to increase the viscous nature of reaction mixture at high catalyst concentration loading to difficulty in mixing (mass transfer) [Tang et al., 2011]. A high biodiesel yield occurred at 2.5 wt % catalyst concentration with the addition of co-solvent. Methanol and oil form two phase system in the reaction mixture, so to contact alcohol molecule with triglycerides, excess of alcohol is needed since synthesis of biodiesel through transesterification reaction is reversible [Schuchardt et al., 1998]. Methanol: oil molar ratio was varied from 4:1 to 14:1 to study the effect of molar (oil: methanol) ratio on biodiesel, initially as the molar ratio increased the biodiesel yield also increased but high yield (96 %) was obtained at oil: methanol ratio of 1:10 with the addition of co-solvent, beyond which yield starts stagnating since motivating back the reversible reaction and slightly dropping the yield [Meher et al., 2006]. In addition, in each experiment, it was also observed that the addition of co-solvent contributes significantly to an increase in biodiesel yield.

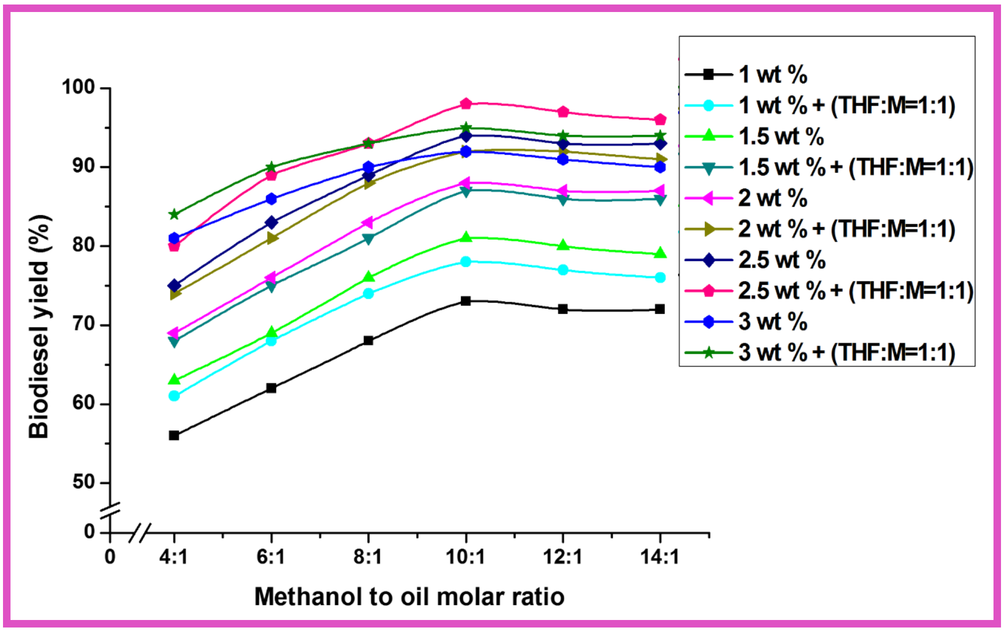

Figure 5.4 Effect of catalyst concentration and methanol to oil molar ratio on biodiesel yield.

5.2.3.2 Effect of reaction time on biodiesel yield

Effect of reaction time on biodiesel yield was studied with and without co-solvent at different time intervals extending from 30 min to 155 min and other factors such as methanol to oil molar ratio, 10:1; catalyst concentration, 2.5 wt % (w/w of oil); reaction time, 65 °C were kept constant (Figure 5.5). In order to determine the effective reaction time, the stirring rate was kept at 650 rpm. Sharp increase in biodiesel yield was observed when the reaction time was increased from 30 min to 105 min since biodiesel production increases with increase in reaction time [Freedman et al., 1984]. High biodiesel yield (96 %) was observed at the end of 105 min in presence of co-solvent. Further, reaction time was increased from 105 min to 155 min, but there was no significant increase in the biodiesel yield because longer time can be assumed to produce soap via hydrolysis of ester [Leung and Guo, 2006].

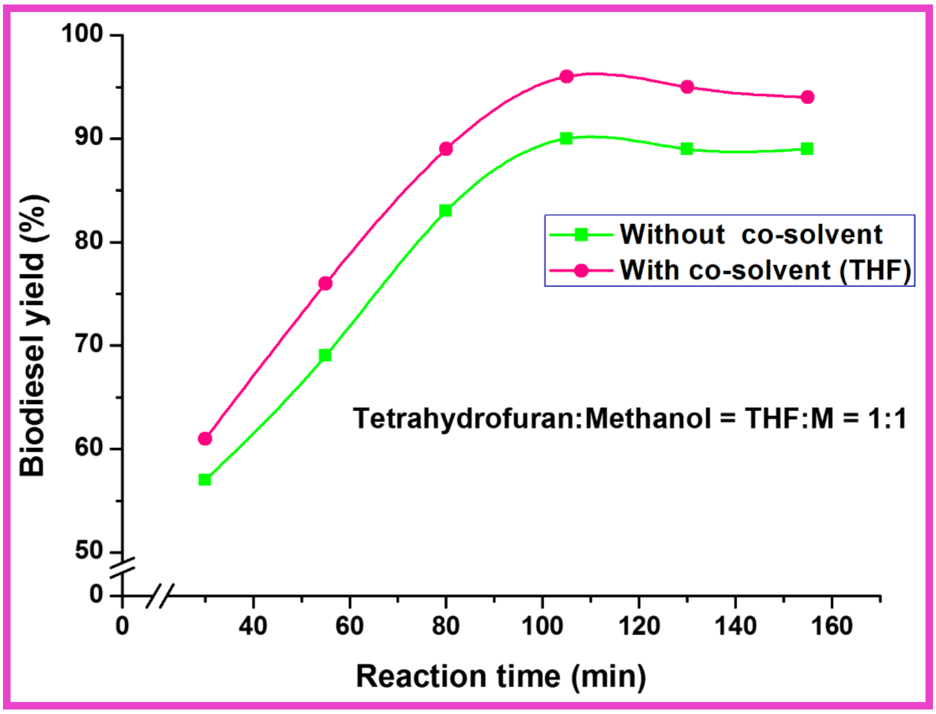

Figure 5.5 Effect of reaction time on biodiesel yield.

5.2.3.3 Effect of reaction temperature on biodiesel yield

Figure 5.6 represents the effect of temperature on biodiesel yield with and without co-solvent. The transesterification of *Pongamia pinnata* oil using 2.5 wt % (w/w of oil) of CaO catalyst was carried out at different temperature ranging from 35 °C to 85°C and other parameters such as methanol to oil 10:1, reaction time, 120 min, stirrer speed, 650 rpm were kept constant. Biodiesel yield gradually increased with increase in temperature from 35 °C to 65 °C but the sharp increase in the biodiesel production was observed when the temperature rose from 35 °C to 55 °C, since transesterification reaction has been reported to be affected with the rise of temperature [Okitsu et al., 2013; Patil et al., 2011]. A high biodiesel production (96%) was achieved at a moderate reaction temperature of 65 °C in the presence of co-solvent because co-solvent facilitates the two phase reaction mixture into more homogeneous mixture. As temperature of the reaction increases, biodiesel yield also increases [Helwani et al., 2009]. Temperature of reaction mixture was increased from 65 °C to 85 °C, the biodiesel yield decreased due to evaporation of methanol which reduced the amount of methanol in contact with reactants in transesterification reaction [Meher et al., 2006].

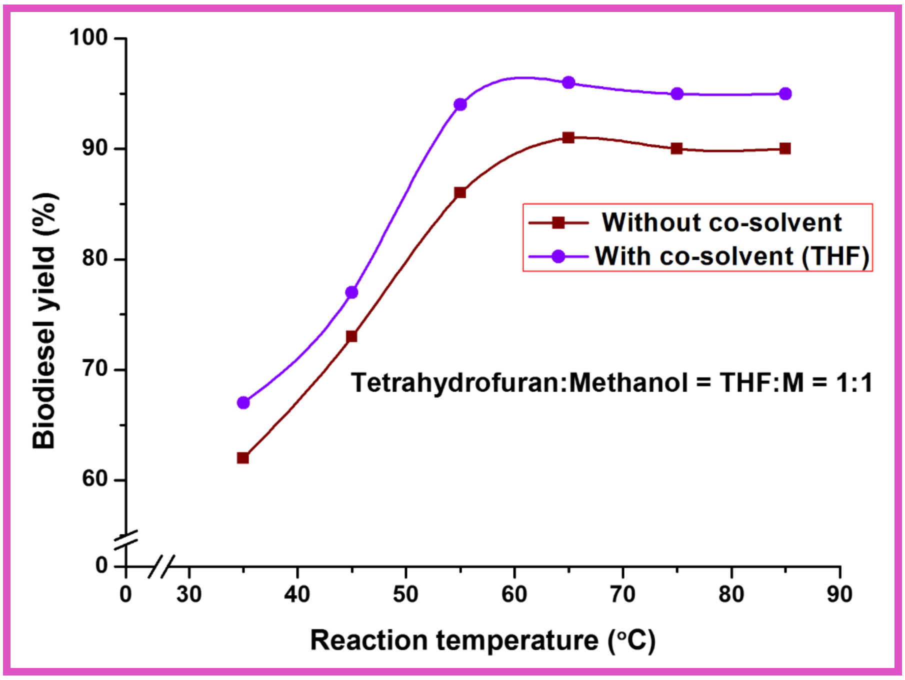

Figure 5.6 Effect of reaction temperature on biodiesel yield.

5.2.3.4 Effect of stirrer speed on biodiesel yield

Figure 5.7 represents the effect of stirrer speed ranging from 350 rpm to 850 rpm on biodiesel yield. Effect of stirrer speed on biodiesel production was investigated using 2.5 wt % (w/w of oil) of catalyst and 10:1 methanol to oil molar ratio in 105 min at 65 °C. Stirrer speed is effective in all transesterification reactions for the synthesis of biodiesel [Mjalli and Hussain, 2009]. A high biodiesel yield (97 %) was obtained when the stirrer speed was 650 rpm with the addition of co-solvent, with further increase in stirrer speed from 650 rpm to 850 rpm, there was no significant increase in biodiesel yield but small reduction was observed in the yield. This reduction in biodiesel yield may be attributed to vaporization of methanol when stirrer speed increases. It seems that higher stirrer speed inhibited the interaction between the reactants and methanol.

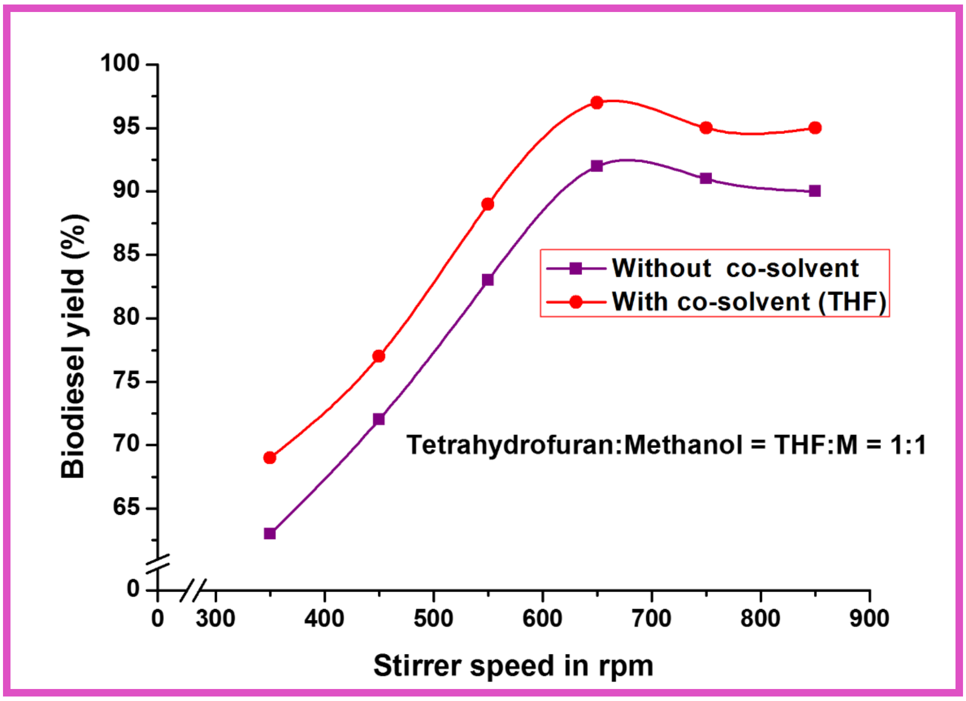

Figure 5.7 Effect of stirrer speed on biodiesel yield.

5.2.4 Characterization of biodiesel by proton NMR analysis

The conversion of triglycerides (oil) to fatty acid methyl ester (biodiesel) was analysed using proton NMR spectroscopy. The ^{1}H NMR spectrum of biodiesel product is shown in Figure 5.8. The percentage conversion of *Pongamia pinnata* oil to biodiesel was calculated by using the ratio of integrated signals (area under the signal obtained by integration) at 3.69 ppm (A_{ME}) and 2.30 ppm (A_{CH2}) in the following equation (Eq. 5.1). Maximum biodiesel conversion (99. 55 %) was obtained at the methanol to oil molar ratio 10:1, catalyst concentration 2.5 wt %, reaction time 105 min and stirrer speed 650 rpm at 65 °C.

$C = 100(2A_{CH3})/(3A\alpha\text{-}_{CH2})$ (5.1)

$C = 100(2*2.24)/(3*1.5)$

$C= 99.55\ \%$

C denotes the conversion (%) of triglycerides to fatty acid methyl esters; the factors 2 and 3 in numerator and denominator are ascribed to the number of protons on methylene and number of protons on methyl ester.

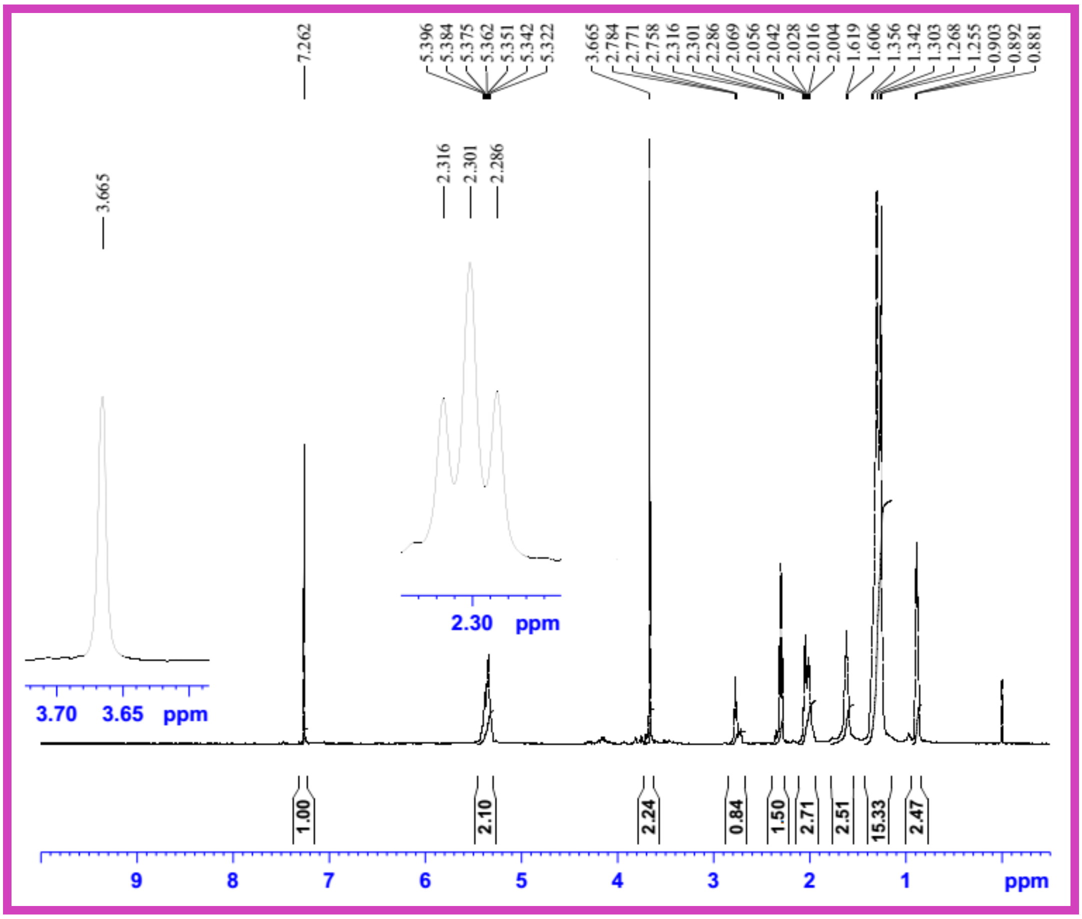

Figure 5.8 Represents the proton NMR spectra of synthesized biodiesel.

5.2.5 Separation and purification of biodiesel

As the transeserification reaction completed, the reaction mixture was transferred into separating funnel to separate biodiesel from other products through the gravitational force. Biodiesel was separated from the reaction mixture since reaction mixture formed two clear layers. Further crude biodiesel was washed with 10 % acid water (ortho-phosphoric acid) with constant stirring for 5 min at 55 °C. Thereafter, biodiesel was washed three times with hot distilled water. Insignificant amount of suspended catalyst was removed with centrifuge and water content as well as unreacted methanol remained in biodiesel were removed with rotavapour to get pure biodiesel. Physical and chemical properties of pure biodiesel were studied according to ASTM standards. Density of synthesized biodiesel was reduced from 0.934 (*Pongamia pinnata* oil) to 0.849 (biodiesel) and the flash point, pour point were reduced from 214 °C to 162 °C and from 4 °C to -1 °C respectively. Kinematic viscosity at 40 °C was reduced from 39.3 (mm^2/s) to 5.4 (mm^2/s), for the reason that density is directly proportional to viscosity. This synthesized biodiesel completely complied with the ASTM standards as shown in Table 5.1.

5.2.6 Catalyst reusability

Figure 5.9 represents the reusability of calcium oxide catalyst in transesterification. Reusability of catalyst was done in two ways: in the first method (i) calcium oxide catalyst was washed with methanol and reused; in the second method, (ii) calcium oxide catalyst washed with methanol and re calcined at 700 °C for 3 h. In the first case the calcium oxide derived from waste crab shells was reused up to five times. In the first run, according to first method catalyst gave 90 % biodiesel yield with the addition of co-solvent and in the fifth run calcium oxide catalyst gave 77 % biodiesel yield which got slightly decreased from first run to fifth run, thus the catalyst activity of reused CaO was decreased in the fifth run due to the adsorption of atmospheric O_2 or CO_2 or H_2O [Kaur and Ali, 2014] and the formation of $Ca(OH)_2$ [Roschat et al., 2016]. In the second method: in the first run after calcination at 700 °C for 3 h, catalyst gave 95 % biodiesel yield while in the fifth run calcined catalyst gave 84 % biodiesel yield which was 7%

Table 5.1 Physical and chemical properties of biodiesel from *Pongamia pinnata* oil as a feedstock 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	0.42	-	0.5
Density	g/cm^3	ASTM D 1298	0.849	0.875	0.90
Cloud point	°C	ASTM D 1510	1	Report	Report
Pour point	°C	ASTM D 97	-1	-	-
Kinematic viscosity(mm^2/s), at 40 °C	mm^2/s	ASTM D 445	5.4	1.9	6.0
Cetane number		ASTM D613	48.5	47	-
Flash point	°C	ASTM D 93	162	120	-
Calorific value	kcal/kg	ASTM D 4809	3802	-	-
Water content	in %	ASTM D 2709	0.002%	-	0.05
Copper strip corrosion	3h/50 °C	ASTM D 130	No Corrosion observed	-	3

more than the fifth run in the first method since after calcination, $Ca(OH)_2$ will convert into CaO and adsorbed atmospheric O_2 or CO_2 or H_2O will not be able to stay on the surface of catalyst. Hence, it can be concluded that the second method was chosen for calcium oxide catalyst derived from waste crab shells reusability.

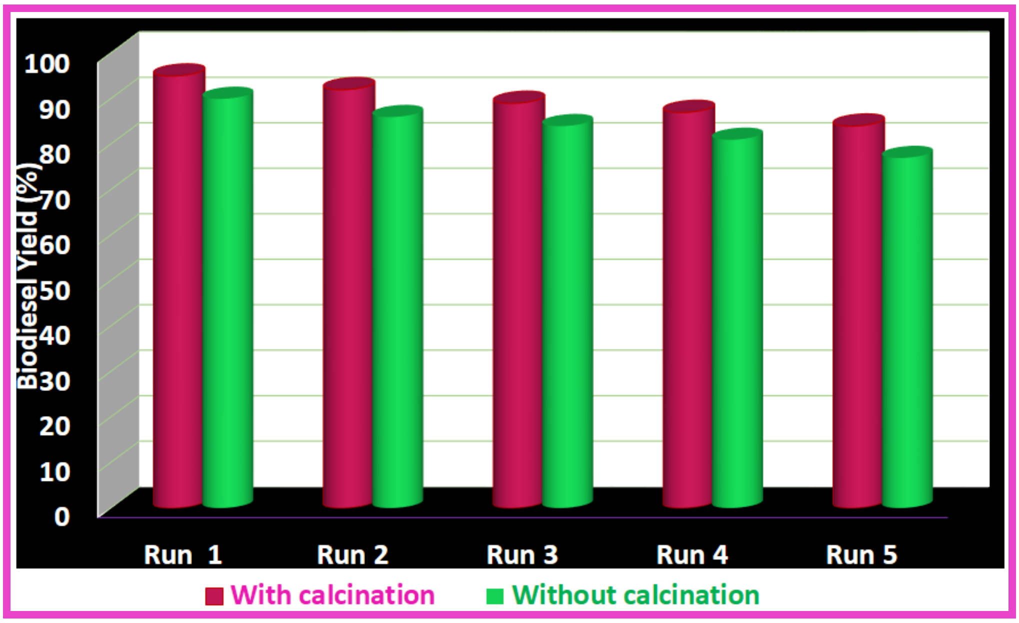

Figure 5.9 Reusability of calcium oxide catalyst in transesterification.

5.3 Conclusions

High quality and pure biodiesel was synthesized from *Pongamia pinnata* oil using solid base calcium oxide catalyst. *Pongamia pinnata* oil was extracted from its seeds through the solvent extraction using different solvents. Synthesized biodiesel was characterized with proton NMR as well as FT-IR. Calcium oxide was prepared from waste crab shells and prepared catalyst was characterized using SEM, XRD, FT-IR and TG/DTA/DTG. Effect of various parameters such as catalyst concentration, reaction time, molar ratio (methanol to oil), reaction temperature and stirrer speed on biodiesel yield were optimized. Maximum biodiesel yield was obtained at optimized reaction conditions were, oil: methanol molar ratio, 10:1; reaction time 105 min; catalyst concentration 2.5 wt % and stirrer speed 650 rpm at 65 °C. High biodiesel conversion (99.55 %) was obtained at optimum reaction conditions. The fuel properties of the biodiesel such as kinematic viscosity, density, and cloud point were determined as per the ASTM biodiesel standards and found to adhere to the specifications.