

7.1 Introduction

World is in front of energy crisis due to extreme consumption of most depleting reserves of fossil fuels. As the human population increasing day by day the energy consumption is also increasing but the energy generated from non-renewable resources is limited. Depleting petroleum reserves as well as environmental issues with fossil fuels led for search of alternative fuels in replacing nonrenewable energy sources. Biodiesel as a fuel can replace fossil fuel and has shown that the use of biodiesel in diesel engines can reduce environmental pollution [Demirbas, 2007]. Biodiesel can be used directly in diesel engines without any modifications [Dorado et al., 2003b; Milan et al., 2013; Nabi et al., 2009]. Biodiesel decreases the emission of hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM). Synthesis of biodiesel from edible oils not only affects human food but also it increases the total cost of biodiesel production. Waste fish oil extracted from fish waste (waste parts of fish) has been used as feedstock for synthesis of biodiesel [Kusmiyati and Wulandari, 2006]. Huge quantity of waste is generated from fish processing industry [Rustad, 2007]. Waste fish oil extracted from waste parts of fish is used as raw oil for the production of biodiesel. Biodiesel from fish oil is not only reducing waste generating from fish processing industry but also it converts waste into a potential feedstock for the production of biodiesel. Synthesis of biodiesel through transesterification reaction using homogeneous acid/base or heterogeneous acid/ base or enzymes as catalysts. Separation and reusability is difficult in the case of homogeneous catalysts and enzymes are expensive materials for the synthesis of biodiesel. Biodiesel

can also be prepared through the process called supercritical methanolysis but in this process, huge amount of solvent (methanol) is needed so the entire process makes the synthesis of biodiesel more expensive. Heterogeneous catalysts have many advantages such as reusability, ease of separation (eliminate the separation step), and reduction in corrosion [Di Serio et al., 2007; Kulkarni and Dalai, 2006; Lopez et al., 2005]. In the present study, waste fish oil extracted from waste part of fish has been used as raw feedstock for the synthesis of biodiesel. Calcium oxide derived from waste crab shells has been used as heterogeneous base catalyst in the process since the calcium oxide has high catalytic activity. In the previous study, calcium oxide as catalyst gave high biodiesel yield (95 %) at optimum reaction conditions [Wei et al., 2009]. This chapter deals with the synthesis of biodiesel using calcium oxide as a solid base catalyst and effect of process has also been reported variables on biodiesel yield. Effect of co-solvent on biodiesel was studied and regenerated catalyst was reused up to five runs. Physical and chemical properties of synthesized biodiesel were determined according to ASTM standards.

7.2 Results and discussions

7.2.1 FT-IR analysis of biodiesel

Figure 7.1 represents the Fourier Transform Infrared Spectroscopy (FT-IR) of synthesized biodiesel. Sharp peak was observed at 720 cm^{-1} the existence of CH_2 group ($n > 4$ where n is number of CH_2 groups) in biodiesel. Absorption band at 1459 cm^{-1} was attributed to CH_2 and CH_3 groups in biodiesel. Sharp peak observed at 1741 cm^{-1} is ascribed to $\text{C}=\text{O}$ stretching frequency. The band occurred at 1168 cm^{-1} was due to $\text{C}-\text{O}$

stretching frequency of fatty acid methyl ester. Absorption bands were occurred at 2923 cm^{-1} and 2853 cm^{-1} indicated the existence of methylene group CH_2 (aliphatic hydrocarbons) in biodiesel.

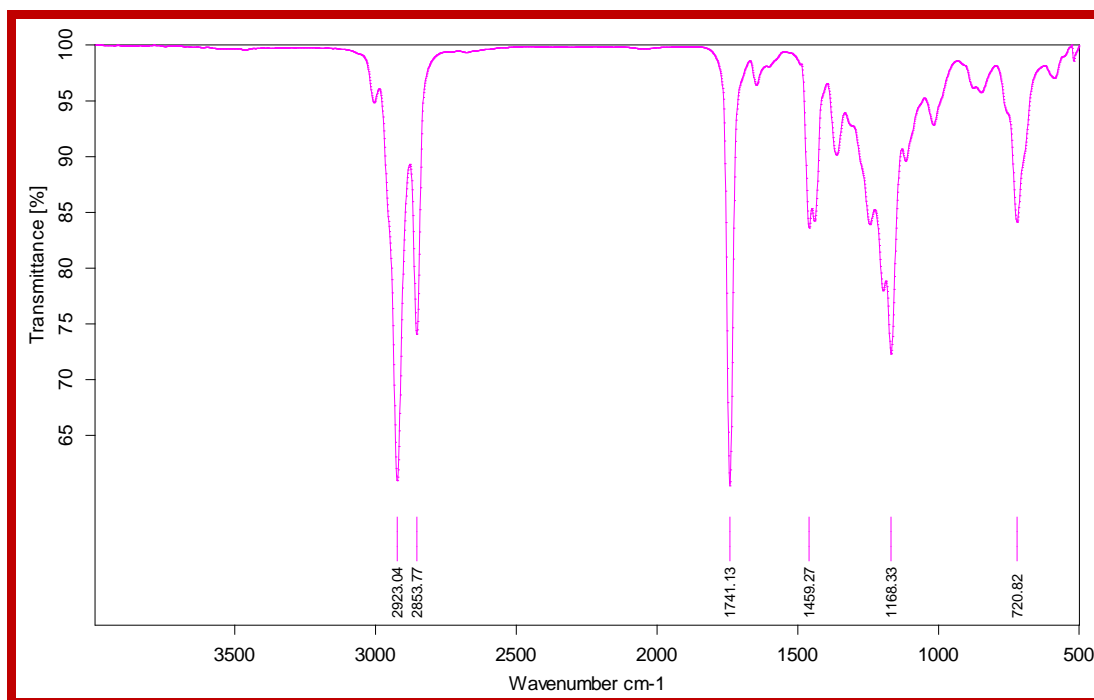


Figure 7.1 FT-IR spectrum of synthesized biodiesel.

7.2.2 Effect of reaction variables on biodiesel production

Acid value of waste fish oil was 11.80 mg KOH/g due to presence of FFA which inhibits the transesterification reaction. To prevail this limitation, acid esterification of fish oil was done, since it renders more conversion of biodiesel. The optimized conditions have been observed at 8:1 molar ratio (methanol to oil) with sulphuric acid (1.0 %) at 60 $^{\circ}\text{C}$ for 2 hours of reaction time, consequence in abating acid value from 11.80 to 0.42 mg

of KOH/g by acid esterification reaction where conversion of free fatty acid to fatty acid methyl ester and water.

7.2.2.1 Combined effect of catalyst concentration and methanol to oil molar ratio on biodiesel production

Combined effect of catalyst concentration and methanol: oil molar ratio on biodiesel yield with and without addition of co-solvent (tetrahydrofuran:methanol, 1:1) was studied. The quantity of catalyst is substantial part in biodiesel production. The potency of catalyst amount in transesterification reaction is demonstrated in the Figure 7.2. The impact of catalyst concentration ranging from 1.0 wt % to 3.0 wt % (w/w of oil) was examined under constant variables: stirring speed, 650 rpm; reaction time, 120 min at 65 °C, reaction temperature. As the catalyst concentration was enhanced from 1.0 wt % to 2.5 wt % a sharp increase in biodiesel yield from 71 % to 90 % without co-solvent and 76 % to 96 % with co-solvent was observed at 10:1, methanol to oil molar ratio. An effective catalyst quantity proffers higher prospect of its attachment with the reaction mixture (methanol to oil molar ratio). Maximum biodiesel yield 96 % was observed when the catalyst concentration raised up to 2.5 wt % and 10:1 methanol to oil molar ratio in the presence of co-solvent. Thereafter, the catalyst concentration was raised from 2.5 wt % to 3.0 wt % but there was no notable augmentation in biodiesel yield with addition of more catalyst concentration. Biodiesel yield slightly reduced when catalyst quantity was enhanced from 2.5 wt % to 3.0 wt % due to the formation of more viscous nature of the reaction mixture, which will create a strain in mixing of reaction mixture.

Surplus amount of methanol will promote extreme conversion of biodiesel because of methanol will attach very likely with triglycerides and reaction continues to produce biodiesel [Ferrero et al., 2015]. To obtain high conversion of triglycerides, fatty acid into biodiesel (alkyl ester), a high molar ratio of oil to methanol is needed. Molar ratio of oil to methanol was raised from 4:1 to 14:1 at 65 °C, reaction temperature. Biodiesel yield got enriched from 59 % (at 1.0 wt %) to 78 % (at 3.0 wt %) with addition of co-solvent while the methanol to oil molar ratio was 4:1. As the methanol to oil molar ratio increased from 4:1 to 10:1, the biodiesel yield also increased from 59 % (at 1.0 wt %) to 96 % (at 2.5 wt %) in presence of co-solvent. In each experiment, with it was clearly observed that the addition of co-solvent (Tetrahydrofuran:Methanol, 1:1) to the reaction mixture greatly improved the biodiesel yield as shown in Figure 1. In mixture, methanol remains as emulsion droplets form which on attachment with catalyst molecule conducts to chain of reaction in biodiesel formation. Biodiesel yield was reduced when the methanol to oil molar ratio was enhanced from 10:1 to 14:1, this reduction in biodiesel yield can be ascribed to glycerol formation during biodiesel production that would diffuse in methanol and restrain the interface of methanol with calcium oxide [Boey et al., 2009].

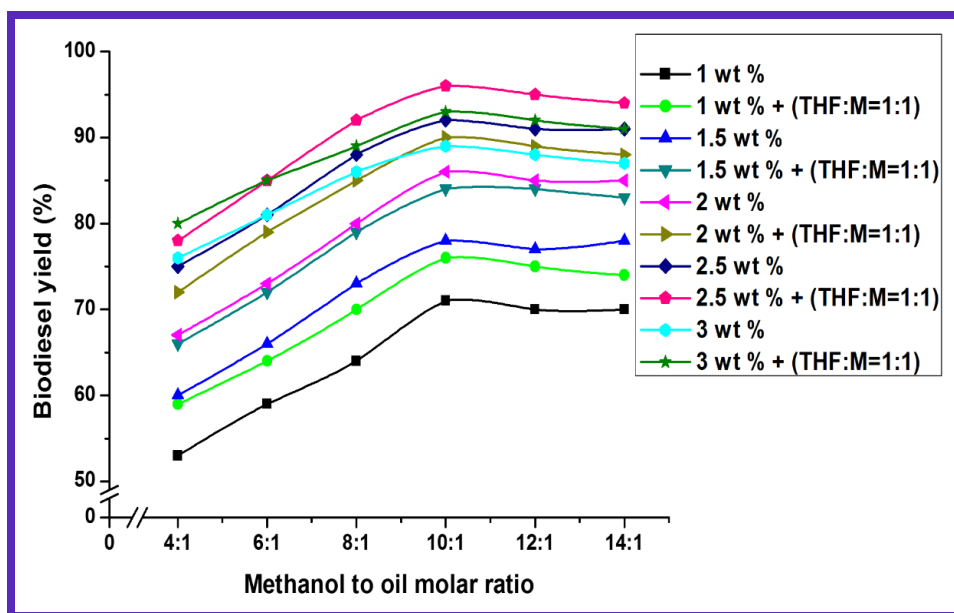


Figure 7.2 Represents the effect of catalyst concentration and methanol to oil molar ratio on biodiesel production.

7.2.2.2 Impact of reaction time on biodiesel production

Figure 7.3 represents the effect of reaction time on biodiesel yield using waste fish oil as a feedstock and calcium oxide (solid base) as catalyst derived from waste crab shell. Impact of reaction time on biodiesel yield was examined in 30 min to 180 min range, at 65 °C of reaction temperature, 10:1 methanol to oil molar ratio and 2.5 wt % catalyst concentration (calcium oxide). To infer the optimum reaction time, the stirrer speed was kept constant at 650 rpm. As we progressively increased the temperature of the reaction mixture, biodiesel yield was also increased. Biodiesel yield enriched up to 120 min with and without addition of co-solvent. Further, there was no significant increment in biodiesel production for the reason that soap formation via hydrolysis of ester is expected because of longer time [Leung and Guo, 2006]. Pure and high quality biodiesel yield 94%

was observed within 120 min of reaction time since co-solvent (Tetrahydrofuran) reduced the reaction time as well as energy of consumption for the production of biodiesel.

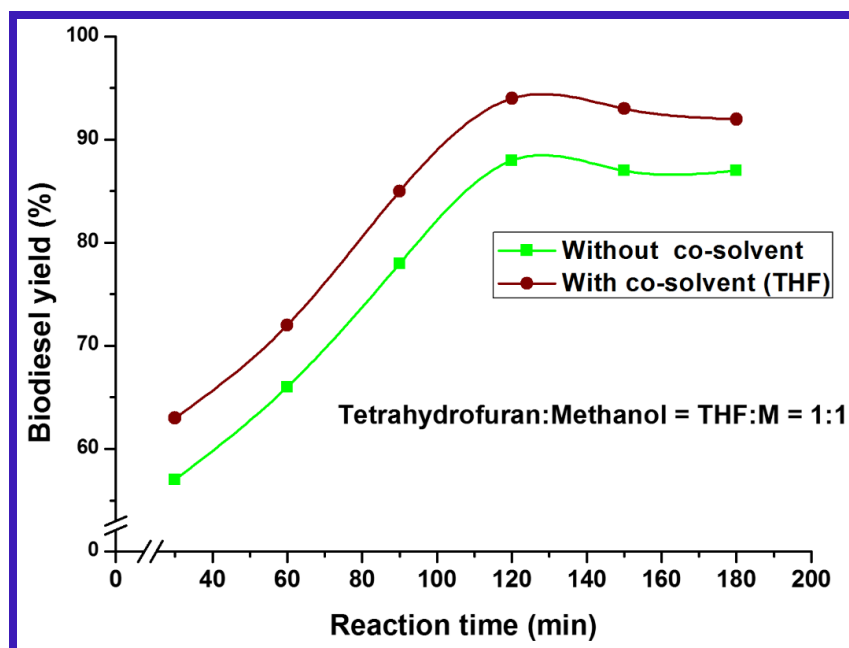


Figure 7.3 Represents the effect of reaction time on biodiesel production.

7.2.2.3 Impact of reaction temperature on biodiesel production

Figure 7.4 illustrates the effect of temperature on biodiesel yield. The reaction was carried out at different temperatures ranging from 35 °C to 85 °C and other parameters viz. (methanol to oil molar ratio, 10:1; reaction time, 120 min; stirrer speed, 650 rpm and catalyst concentration, 2.5 wt % were kept constant. Biodiesel yield increased from 58 % to 90 % without co-solvent and 65 % to 95 % with co-solvent as the reaction temperature increased from 35°C to 65°C. Higher temperature not only decreases the viscous nature of the reaction mixture [Clark et al., 1984] but also it facilitates the high mass transfer to get

high biodiesel production [Stamenković et al., 2008]. Maximum biodiesel yield 95 % was observed at 65 °C with the addition of co-solvent. Thereafter, when the reaction temperature was elevated from 65 °C to 85 °C, biodiesel yield diminished because of evaporation of methanol which reduced the methanol quantity to interact with reactants in biodiesel yield [Meher et al., 2006].

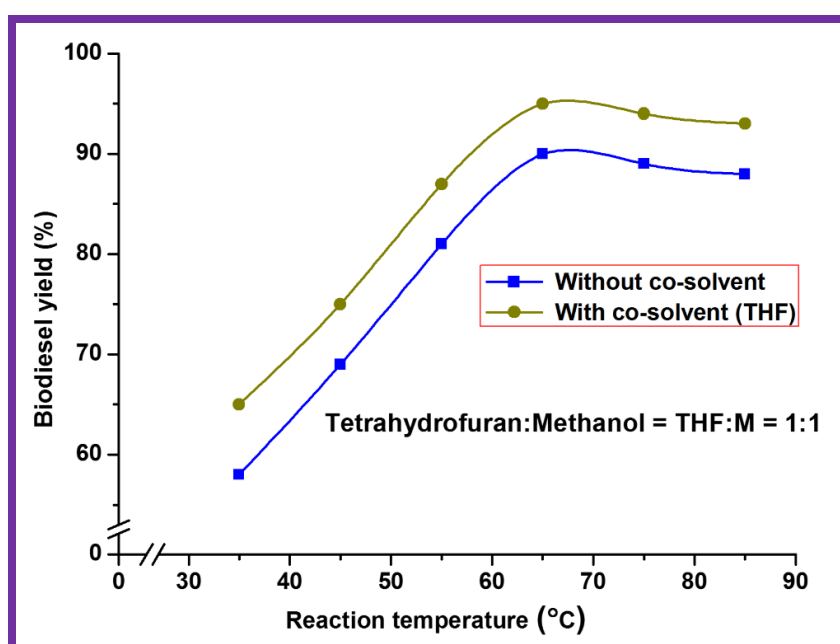


Figure 7.4 Represents the impact of reaction temperature on biodiesel.

7.2.2.4 Impact of agitation on biodiesel production

Effect of agitation speed on biodiesel production was studied ranging from 350 rpm to 850 rpm. Impact of stirrer speed on biodiesel production was examined with 2.5 wt % (catalyst concentration), 10:1 (methanol to oil molar ratio), and 120 min (reaction time) at 65 °C (reaction temperature). A notable increment in biodiesel yield was

observed when the agitation rate was raised from 350 rpm to 650 rpm. In each experiment it was found that the addition of co-solvent (Tetrahydrofuran) gave high yield as shown in Figure 7.5. High yield (94 %) and pure biodiesel was achieved at 650 rpm in presence of co-solvent. Furthermore, escalation in agitation rate from 650 rpm to 850 rpm provided no considerable increment in biodiesel. This abatement in biodiesel yield may be ascribed to evaporation of methanol when agitation rate increases impeding the interface between the methanol and reactants [Roy et al., 2014].

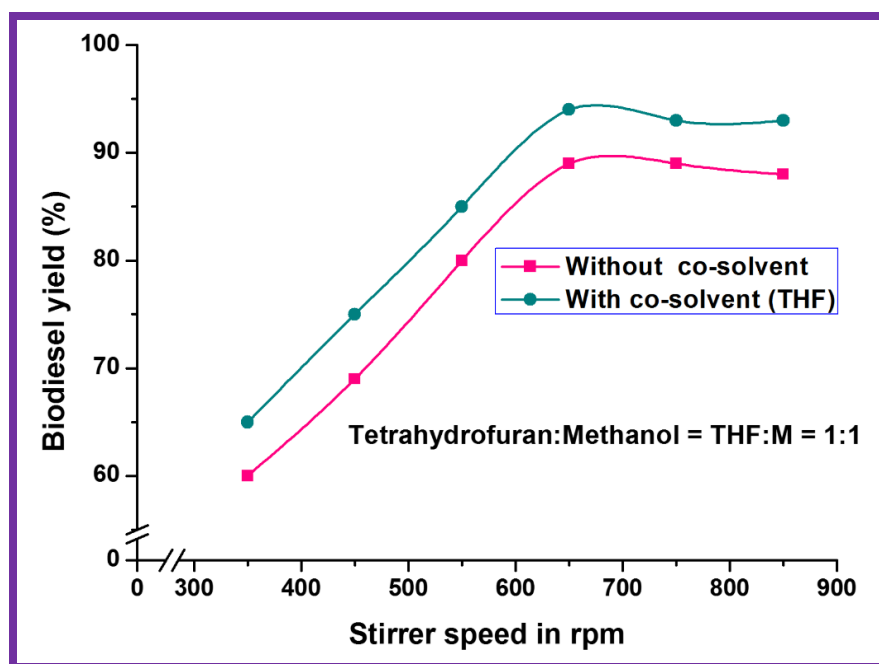


Figure 7.5 Represents the impact of agitation rate on biodiesel production.

7.2.3 NMR of biodiesel

Figure 7.6 represents the proton NMR spectroscopy of synthesized biodiesel. The percentage conversion of fish oil to biodiesel was calculated by using the well-known

equation (Eq. 7.1) 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_{CH_2}). High biodiesel conversion (98.52 %) from fish oil was obtained when the reaction variables such as catalyst concentration 2.5 wt %, methanol to oil molar ratio 10:1, reaction time 120 min, stirrer speed 650 rpm and reaction temperature 65 °C were used in transesterification reaction.

$$C = 100(2A_{CH_3}) / (3A_{\alpha-CH_2}) \quad (7.1)$$

$$C = 100(2 \times 3) / (3 \times 2.03)$$

$$C = 98.52 \%$$

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

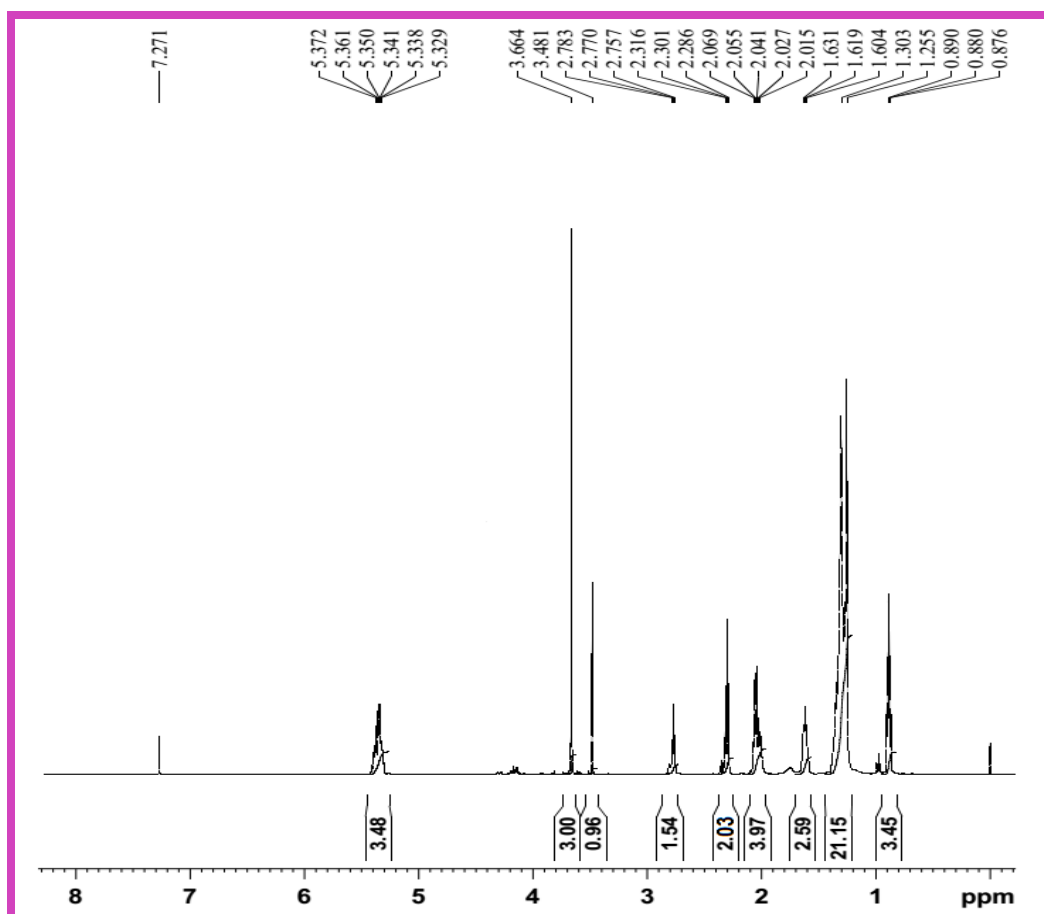


Figure 7.6 The proton NMR of synthesized biodiesel.

7.2.4 Separation and purification of biodiesel

The reaction mixture was kept in separating funnel for overnight to separate biodiesel from its byproducts. Filtration and centrifugation methods were used to expel solid suspended matter from synthesized biodiesel. After separation, biodiesel was washed with hot distilled water to remove impurities, then rotavapor was used to eliminate residual water and methanol in synthesized biodiesel as mentioned in Section 5.2.5, Chapter 5. Biodiesel qualities were defined using ASTM standards. The

synthesized biodiesel entirely satisfied the ASTM biodiesel standards as shown in Table 7.1.

Table 7.1 Physical and chemical properties of biodiesel from waste fish oil as a feedstock and calcium oxide as a solid base catalyst.

Property	Unit	ASTM Standards	Value	ASTM D 6751 Biodiesel specifications	
				Min	Max
Color	-		Yellowish red	-	-
Acid value	mg KOH/g	ASTM D 664	0.37	-	0.5
Density @15.5 °C	g/cm ³	ASTM D 1298	0.861	0.875	0.90
Boiling point	°C	-	353	-	-
Cloud point	°C	ASTM D 1510	0	Report	Report
Pour point	°C	ASTM D 97	-2	-	-
Kinematic viscosity, at 40 °C	mm ² /s	ASTM D 445	4.99	1.9	6.0
Flash point	°C	ASTM D 93	154	120	-
Cetane number		ASTM D613	48.76	47	-
Calorific value	cal/g	ASTM D 4809	3896	-	-
Water content	in%	ASTM D 2709	0.001%	-	0.05
Copper strip corrosion	3h/50 °C	ASTM D 130	No Corrosion observed	-	3

7.2.5 Reusability of catalyst

After washing with, methanol catalyst was reused in two methods. In first method, the used catalyst was washed with methanol and reused, and in the second method catalyst was washed with methanol, further calcined at 700 °C and reused up to 5 runs for the synthesis of biodiesel as shown in Figure 7.7. Reusability of catalyst in the second method gave more biodiesel yield (93 % in the first run, and 79 % in the fifth run) than in

the first method (88 % in the first run and 68 % in the fifth run) since calcinations provide to initiate the activity site of catalyst and amends the biodiesel yield.

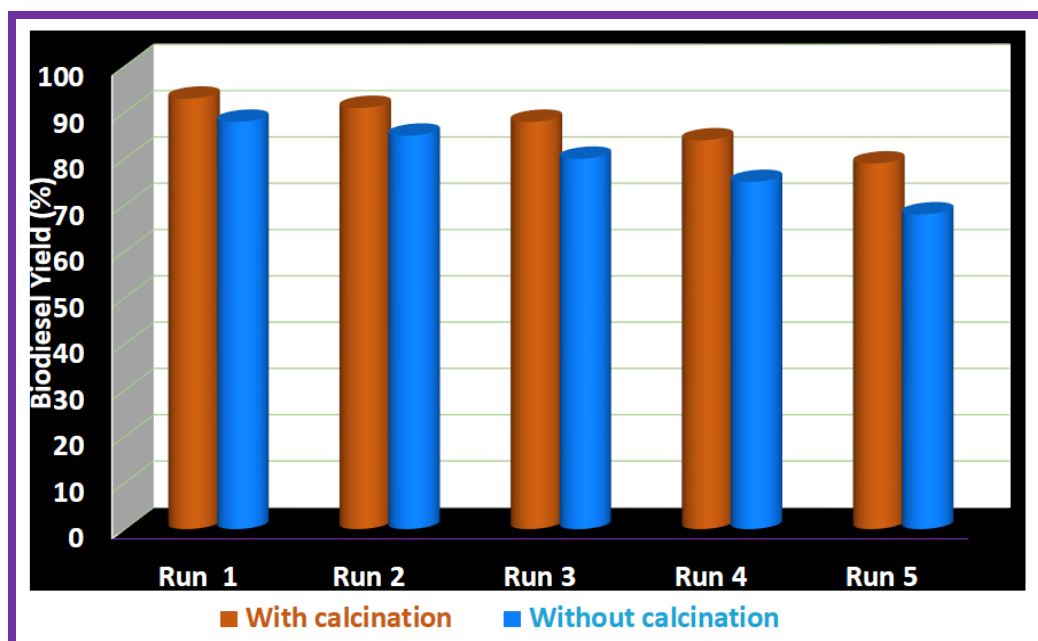


Figure 7.7 Represents the reusability of calcium oxide catalyst.

7.3 Conclusions

Heterogeneous solid base catalyst CaO was prepared by calcinations of crab shell for transesterification of waste fish oil. The catalyst was characterized by TG/DTA/DTG, XRD, SEM/EDS, and FT-IR techniques. High biodiesel yield, 96 % was obtained when methanol to oil molar ratio, 14:1; catalyst concentration, 2.5 wt %; reaction time, 120 min; stirrer speed, 650 rpm; and reaction temperature 65 °C were taken. Effect of co-solvent on biodiesel yield was studied. High biodiesel conversion (98.52 %) was obtained

from waste fish oil. Reusability of catalyst was examined up to five runs. The qualities of biodiesel were ascertained as per ASTM biodiesel standards which were to specification.