

8.1 Introduction

Inexpensive energy is need of each and every modern developing society [Holt, 1999] but in recent years, energy consumption is increasing day by day (IEA, 2015a. 2015 key world energy statistics) and energy resources are depleting [Brown et al., 2014] since they are limited. At present usage rate, one day they will be consumed. Use of fossil fuels may cause many environmental issues, such as acid rain, oil spills, air pollution and climate change. United Nations Environment Programme (UNEP) and World Meteorological Organization (WMO), were jointly set as a new body called Intergovernmental Panel on Climate Change (IPCC) in the year 1988 to assess the climate change related to science. This IPCC is providing scientific technology to the policymakers to mitigate the environmental risks [Hoffmann and Sgro, 2011] and preserve the pollution free climate for the generations to come. Alternative energy resource is needed in the place of fossil fuels due to their limited quantity and impact on environment. Therefore, the renewable energy sources are required to accomplish the world energy demand. There are many renewable energy sources which have potential to replace conventional fossil fuels but biodiesel has become more important for international fuel market because of its inherent advantages. Biodiesel is a green fuel which is derived from vegetable oils or fats (renewable resources) through transesterification reaction. Biodiesel can reduce the environmental risks, provide employment opportunity and arrange for energy independency. Biodiesel emits less CO, SO_x, unburnt hydrocarbons and particulate matter than the conventional mineral diesel. Biodiesel can be used directly with or without small

modification CI engine and biodiesel can be used directly as B 100 (100% biodiesel blended with 0% mineral diesel) or B 80 (80 % biodiesel blended with 20% mineral diesel), etc. In recent times, low cost feedstock such as animal fat obtained from meat market, waste frying oils and fish oil obtained from fish waste have been popular [Demirbaş, 2008] [Breucker et al., 1995; Yee et al., 2009]. According to Associated Chambers of Commerce and Industry of India (ASSOCHAM), an industry body anticipated that the fish production in India is set to cross 13 million tons (MT) in the year 2016.

The current chapter explained the synthesis of biodiesel using waste fish oil as a feedstock and β -tricalcium phosphate as solid base catalyst. Fish industry produces more waste (viscera, eyes, fins, tails and maw) in the form of discarded parts of fish. Fish oil was extracted from the discarded parts of fish (*Cirrhinus mrigala*, *Cirrhinus cirrhosa*, *Cirrhinus reba*) through the mechanical expeller followed by solvent extraction using petroleum ether as a solvent. Physical and chemical properties of waste fish oil were studied according ASTM standards. Waste fish bones along with residual portion left after extraction of waste fish oil from the discarded parts of fish. Waste fish bones along with residual portion was calcined at 800 °C to prepare β -tricalcium phosphate as solid base catalyst. Synthesized biodiesel was characterized with proton NMR and FT-IR and GCMS. Effect of co-solvent and reaction parameters such as reaction temperature, reaction time, stirrer speed and catalyst concentration on biodiesel yield were studied. Physical and chemical properties of biodiesel were measured according to ASTM standards.

Synthesized catalyst was washed with methanol and was reused up to five times with and without calcination.

8.2 Results and discussions

8.2.1 FT-IR analysis of biodiesel

Synthesized biodiesel was analysed with Fourier Transform Infrared Spectroscopy (FT-IR) as shown in Figure 8.1. Stretching vibrations occurred at 1742 cm^{-1} and 1164 cm^{-1} were corresponding to C=O and C-O respectively. Absorption band occurred at 721 cm^{-1} was corresponding to CH_2 groups ($n > 4$ where n is number of CH_2 groups). Absorption band at 1459 cm^{-1} was ascribed to CH_2 and CH_3 groups present in the synthesized biodiesel. Sharp peaks occurred at 2922 cm^{-1} and 2853 cm^{-1} corresponded to methylene group CH_2 (aliphatic hydrocarbons) in biodiesel.

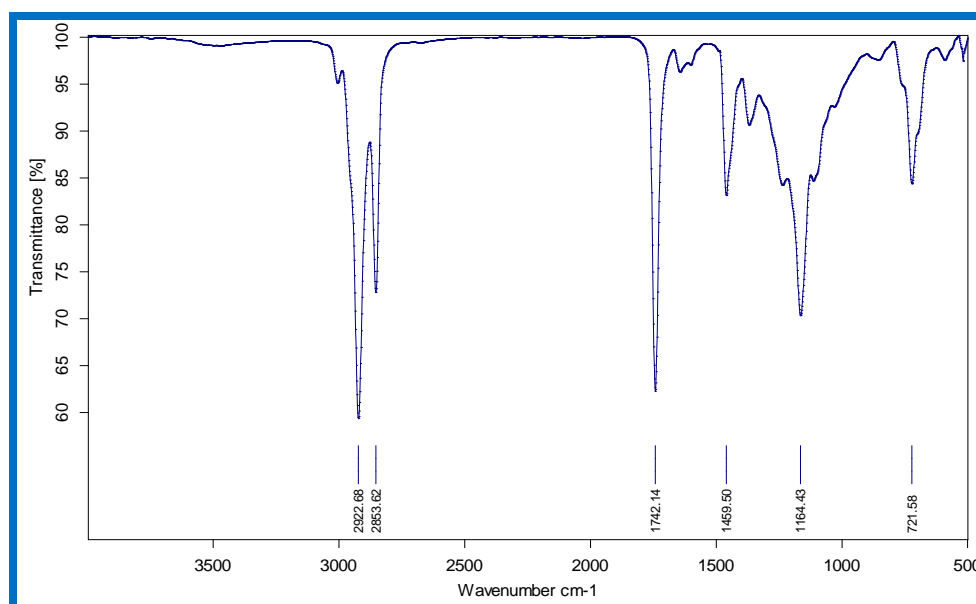


Figure 8.1 FT-IR spectrum of synthesized biodiesel.

8.2.2 Effect of reaction variables on biodiesel production

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

Catalyst concentration and methanol to oil molar ratio have significant roles in transesterification reactions for the synthesis of biodiesel. Combined effect of catalyst concentration as well as methanol to oil molar ratio was studied with and without co-solvent (tetrahydrofuran (THF): methanol (1:1)) as shown in Figure 8.2. Combined effect of catalyst concentration as well as methanol to oil molar ratio on biodiesel yield were observed, whereas the methanol to oil molar ratio was varied from 4:1 to 14:1 and other parameters (temperature (65 °C), reaction time (129 min), stirrer speed (650 rpm)) were kept constant. Catalyst concentration was increased from 1.0 wt % (w/w of oil) to 5.0 wt % (w/w of oil) but maximum biodiesel yield was observed at 4.0 wt % because sufficient amount of catalyst concentration is required to get higher biodiesel yield. Thereafter, catalyst concentration was increased beyond 4.0 wt %, there was no increment in biodiesel yield because reaction mixture became more viscous which led to trouble in mass transfer for the production of biodiesel. Methanol to oil molar ratio was increased from 4:1 to 10:1, the biodiesel yield also increased from 48 % to 90 % without co-solvent and 55 % to 94 % with co-solvent. Further, when increased methanol to oil molar ratio was increased from 10: 1 to 14:1, there was no improvement in the biodiesel yield because of reversible nature of the reaction mixture. High biodiesel yield (94 %) was found in the presence of co-solvent at 10: 1 methanol to oil molar ratio and 4.0 wt % (w/w of oil) catalyst concentration.

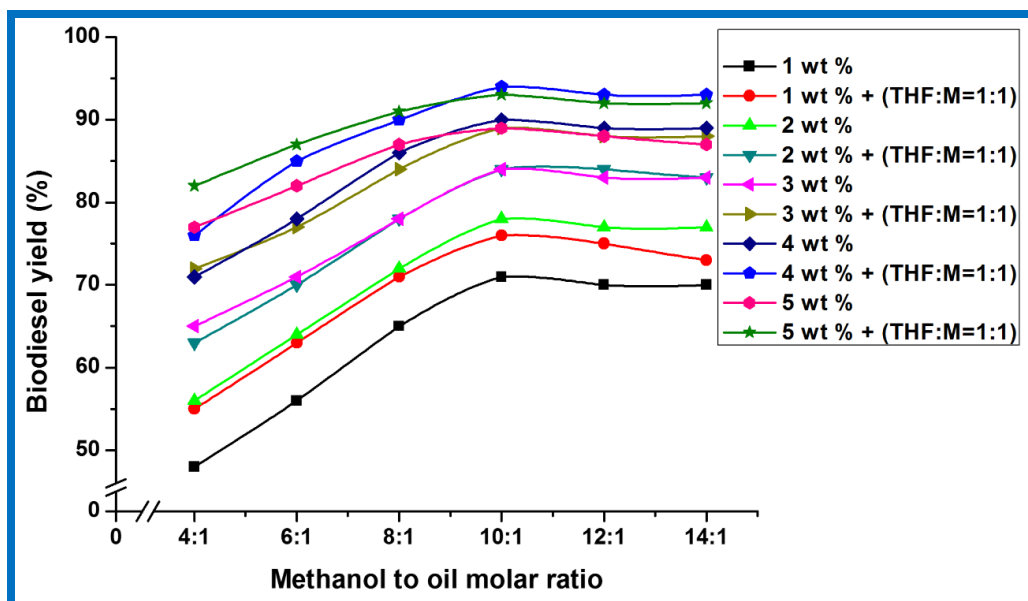


Figure 8.2 The effect of catalyst concentration and methanol to oil molar ratio on biodiesel yield.

8.2.2.2 Effect of reaction temperature on biodiesel yield

Figure 8.3 represents the effect of reaction temperature on biodiesel yield with and without addition of co-solvent (tetrahydrofuran (THF): methanol (1:1)) and the other parameters such as methanol to oil molar ratio (10:1), reaction time (129 min), stirrer speed (650 rpm) and catalyst concentration (4.0 wt %) were kept constant. Transesterification was carried out at different reaction temperatures ranging from 35 °C to 85 °C. As the reaction temperature increased from 35 °C to 65 °C, the biodiesel yield increased from 55 % to 88 % without co-solvent and 61 % to 93 % with co-solvent. Methanol evaporation has occurred as the temperature raised from 65 °C to 85 °C, consequently, there was no significant increment in biodiesel

yield. The optimum reaction temperature was 65 °C because at this reaction temperature high biodiesel yield 93 % was obtained in presence of co-solvent.

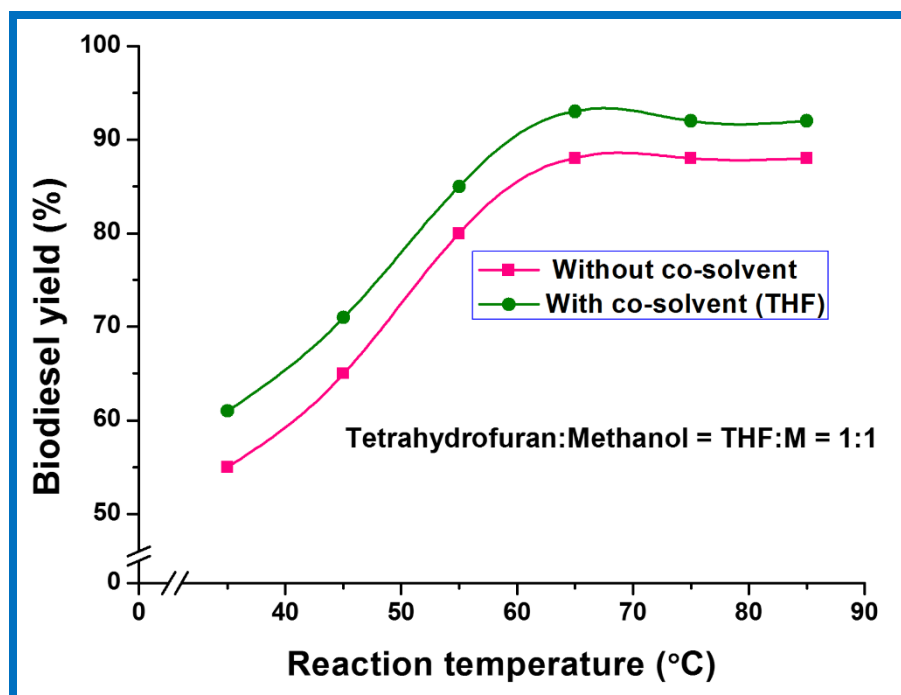


Figure 8.3 The effect of reaction temperature on biodiesel yield.

8.2.2.3 Effect of reaction time on biodiesel yield

Figure 8.4 represents influence of reaction time on biodiesel yield with and without co-solvent at different time intervals prolonging from 30 min to 195 min at 10:1 (methanol: oil) and other factors such as methanol to oil molar ratio, catalyst concentration, stirrer speed and reaction time were kept constant. Reaction time was increased in the presence of co-solvent from 30 min to 129 min, then biodiesel yield increased from 65 % to 94 %. As the reaction time increases biodiesel yield also increases

further when reaction time was outstretched from 129 min to 195 min, there was no increment in biodiesel yield, since longer time will facilitates the hydrolysis of methyl esters. High biodiesel yield (94 %) occurred at the end of 129 min with the addition of co-solvent.

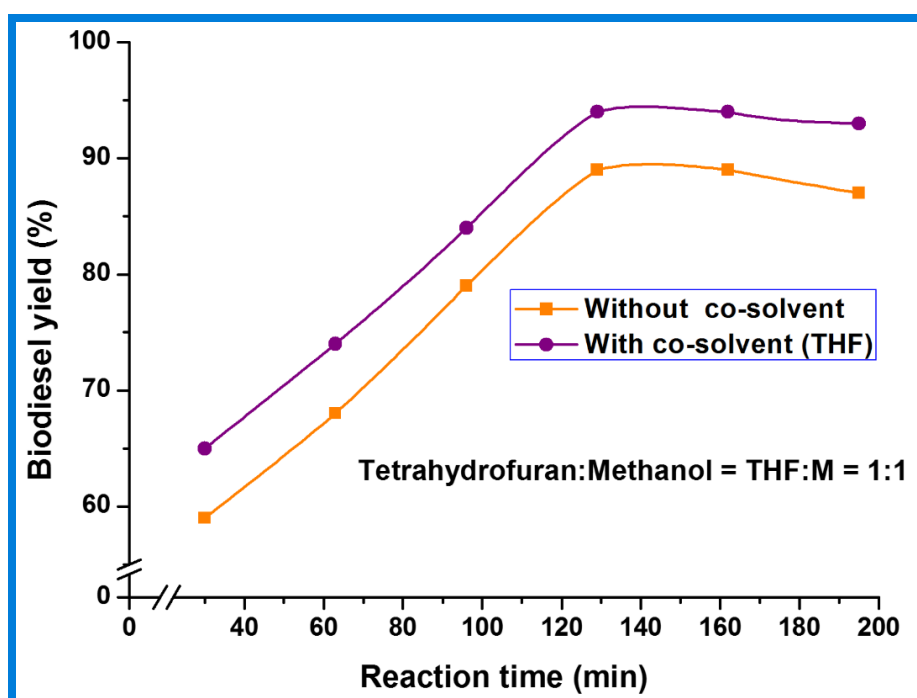


Figure 8.4 The effect of reaction time on biodiesel yield.

8.2.2.4 Effect of stirrer speed on biodiesel yield

Stirrer speed is one of the most significant parameter in the process of synthesizing biodiesel through transesterification reactions since feedstock for biodiesel synthesis such as oils and fats are immiscible or partially soluble in alcohol as well as in solid catalysts. A series of experiment were carried out to determine the effect of stirrer

speed on biodiesel with and without co-solvent (Figure 8.6). In each experiment, stirrer speed was varied from 350 rpm to 850 rpm, while other parameters biodiesel parameters were kept constant. Biodiesel yield was increased from 62 % to 91 % in the absence of co-solvent and 68 % to 95 % in the presence of co-solvent since the immiscibility of reaction mixture was reduced and is became more homogeneous as the stirrer speed increased from 350 rpm to 650 rpm, but beyond 650 rpm there was no increment in biodiesel yield since higher stirrer speed led to evaporation of methanol from the reaction mixture. High biodiesel yield (95 %) was obtained at optimum stirrer speed, 650 rpm in presence of co-solvent.

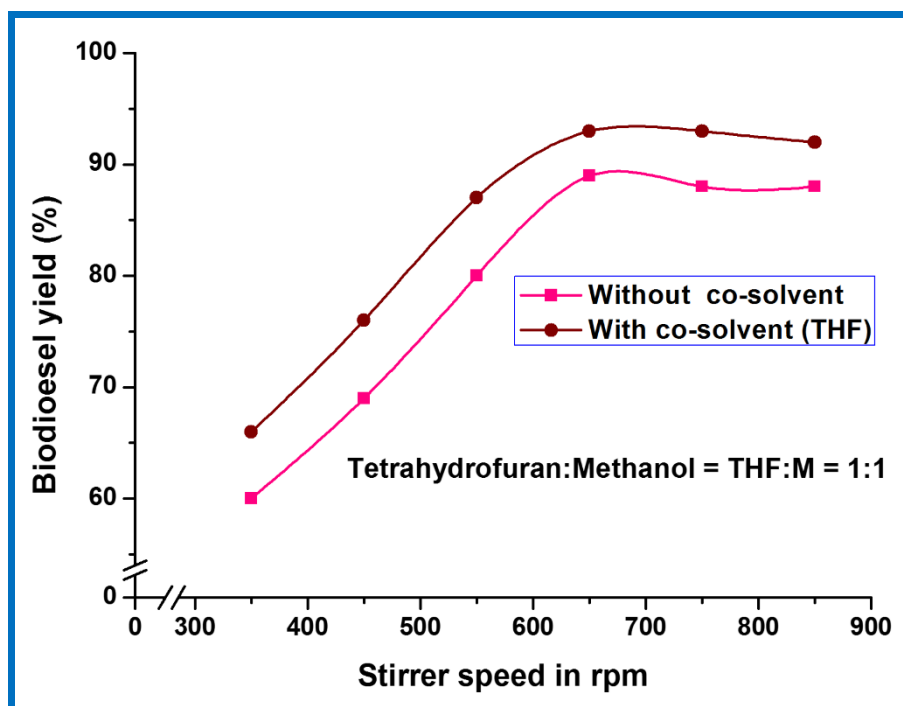


Figure 8.6 Represents the effect of stirrer speed on biodiesel yield.

8.2.3 NMR analysis of biodiesel

Biodiesel synthesized from waste fish oil was characterized by proton NMR as shown in Figure 8.5. The percentage conversion of waste fish oil to biodiesel was calculated by using the well-known equation (Eq. 8.1), which comprises 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 (98.03 %) from waste fish oil was obtained when the reaction parameters such as reaction time 129 min, stirrer speed 650 rpm, catalyst concentration 4.0 wt %, methanol to oil molar ratio 10:1, and reaction temperature 65 °C were used in transesterification reaction.

$$C = 100(2A_{CH_3}) / (3A_{\alpha-CH_2}) \quad (8.1)$$

$$C = 100(2 \times 3) / (3 \times 2.07)$$

$$C = 96.61 \%$$

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

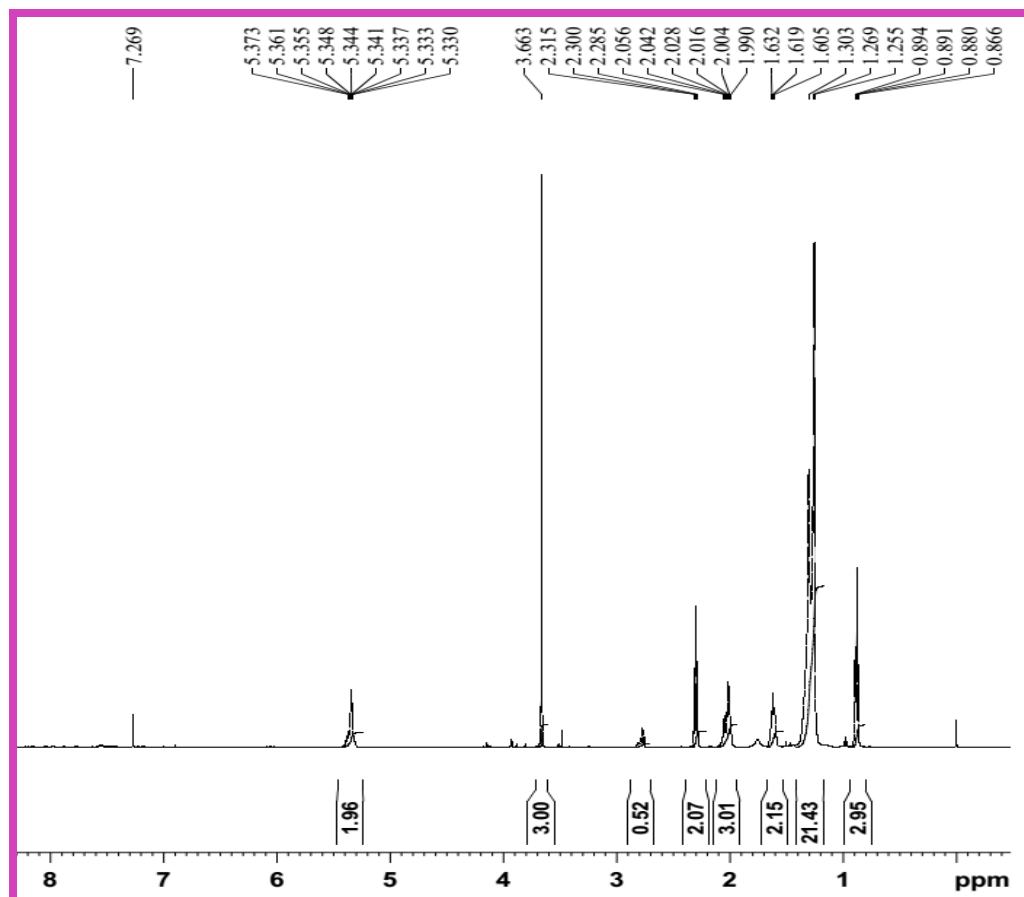


Figure 8.5 Represents the proton NMR spectrum of synthesized biodiesel.

8.2.4 Separation and purification of biodiesel

After completion of transesterification reaction, the reaction mixture was poured into separating funnel in which reaction mixture got separated into two different layer. Biodiesel was taken out and washed with hot distilled water. Water content was removed with rotavapor and this whole separation and purification of biodiesel method was done as mentioned in Section 5.2.5, Chapter 5. Physical and chemical properties of synthesized biodiesel were studied according to ASTM standards and were found that the synthesized

biodiesel completely attained the specifications of biodiesel standards as shown in Table 8.1.

Table 8.1 Physical and chemical properties of biodiesel synthesized from waste fish oil using β - tricalcium phosphate as a catalyst.

Property	Unit	ASTM Standards	Value	ASTM D 6751 Biodiesel specifications	
				Min	Max
Color	-		Yellowish red	-	-
Acid value	mg KOH/g	ASTM D 664	0.383	-	0.5
Density @15.5 °C	g/cm ³	ASTM D 1298	0.873	0.875	0.90
Boiling point	°C	-	356	-	-
Cloud point	°C	ASTM D 1510	1	Report	Report
Pour point	°C	ASTM D 97	-1	-	-
Kinematic viscosity, at 40 °C	mm ² /s	ASTM D 445	5.07	1.9	6.0
Flash point	°C	ASTM D 93	161	120	-
Cetane number		ASTM D613	49.3	47	-
Calorific value	cal/g	ASTM D 4809	3981	-	-
Water content	in%	ASTM D 2709	0.001%	-	0.05
Copper strip corrosion	3h/50 °C	ASTM D 130	No Corrosion observed	-	3

8.2.5 Reusability of catalyst

Figure 8.7 represents the reusability of β -tricalcium phosphate catalyst in transesterification reactions. Reusability of catalyst was done in two ways: first method and second method discussed in Section 5.2.6, Chapter 5. In the first and second methods, catalyst (β -tricalcium phosphate) derived from solid matter was reused up to five times. In the first run, according to first method catalyst gave 86 % biodiesel yield. With the addition of co-solvent and in the fifth run catalyst (β -tricalcium phosphate) gave 71 %

biodiesel yield which got slightly decreased from first run to fifth run. In the second method: in the first run catalyst (β -tricalcium phosphate) gave 91 % biodiesel yield and in the fifth run calcined catalyst (β -tricalcium phosphate) gave 80 % biodiesel yield which was 9 % more than the fifth run in the first method.

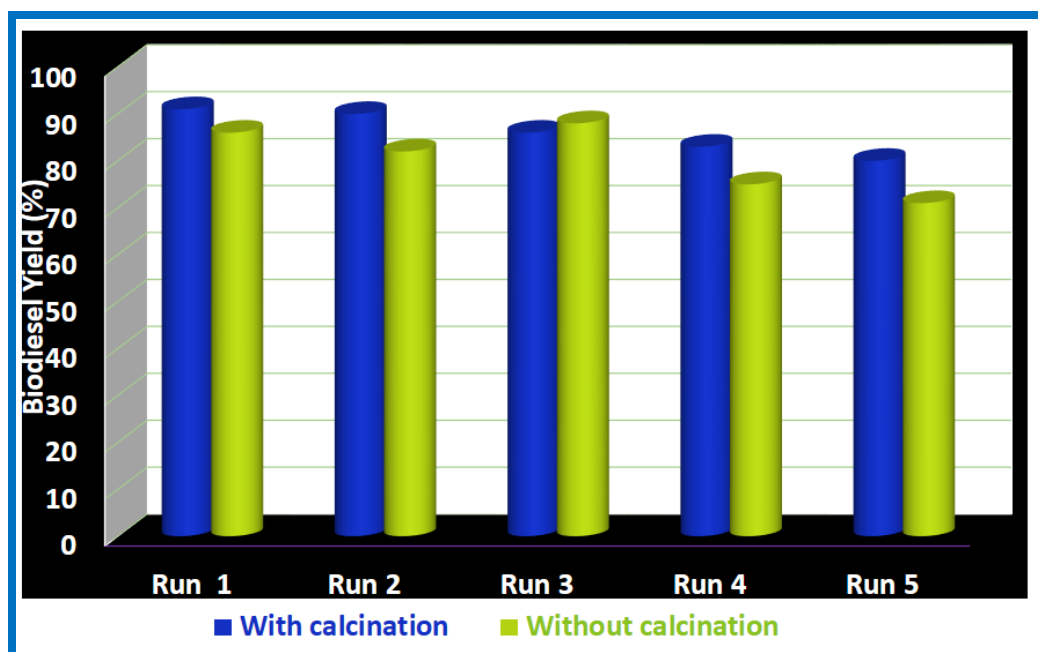


Figure 8.7 Represents the reusability of β -tricalcium phosphate catalyst.

8.3 Conclusions

Waste fish oil was extracted from the waste parts of the fish and was used as raw feedstock for the synthesis of biodiesel using β -tricalcium phosphate as a solid base catalyst. Esterification followed by transesterification reactions were carried out for the synthesis of biodiesel. Biodiesel was characterized with proton NMR,

FT-IR and the conversion was calculated with help of proton NMR by using well known formula. Effect of parameters such as reaction temperature, reaction time, stirrer speed, and catalyst concentration were studied with and without co-solvent. High biodiesel yield (94 %) was obtained when 4.0 wt % of catalyst concentration, methanol to oil 10: 1 (tetrahydrofuran (THF): methanol (1:1)) molar ratio, stirrer speed 650 rpm, at 65 °C for 129 min. Maximum biodiesel conversion from waste fish oil was found to be 96.61 %. Physical and chemical properties of produced biodiesel were analyzed according to ASTM standards. Catalyst reusability was detected up to five runs and in fifth run, the yield got decreased.