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Transeterification of Castor oil

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Abstract

As supply of fossil fuel is limited whilst energy demand continues to rise, hence alternative renewable fuels have received increasing attention for future utilization. In this paper, it is planned to study transesterification reaction on castor oil in a batch reactor using potassium hydroxide as a catalyst. The variables chosen for the study were Residence time, Oil to methanol ratio, catalyst concentration; and reaction temperature. The effects of these variables on the viscosity of biodiesel were studied, since this is one of the important specifications in ASTM standard. Apart from viscosity other properties like sp.gr, acid value, and sap value were also determined for the biodiesel product

Keywords: Biodiesel, transesterification, castor oil.

Introduction

As supply of fossil fuel is limited whilst energy demand continues to rise, hence alternative renewable fuels have received increasing attention for future utilization. In this respect, fermentation, transesterification and pyrolysis of biomass, industrial and domestic wastes have been proposed as alternative solutions for the increasing of energy demand and environmental awareness[1]. In transestrification reaction, the vegetable oil or animal fat is reacted in the presence of a catalyst (usually a base) with an alcohol (usually methanol) to give the corresponding alkyl esters (or for methanol, the methyl esters) of the FA mixture that is found in the parent vegetable oil or animal fat[2]. Among the renewable resources for the production of alternative fuels, triglycerides have attracted much attention as alternative diesel engine fuels[3]

Mohammed H. Chakrabarti and Rafiq Ahmad[4] studied transesterification of castor oil with KOH dissolved in methanol. The operating conditions varied in the range; KOH catalyst concentration 2.1-3 gm for 250 ml feedstock; temperature 30-70^{0}C; reaction time 30-360 minutes. The authors have reported ester (biodiesel) content 48 % which is highest and glycerine 52%. When the reaction is carried out with 65 ml methanol and 2.4 gm KOH catalyst, reaction time 360 minutes at a temperature of 70^{0}C, converting 250 ml castor oil feedstock. They also performed parallel experiments involving two stage process viz esterification by acid followed by normal transesterification. This procedure was recommended by Marchetti et al. In this two stage esterification process, by Mohammed et al reported the ester content up to 85 %. The authors obtained castor biodiesel viscosity of 13.75 mm^2/sec and density 0.9279 at 15^{0}C. The castor oil used by the authors having viscosity 239.39 mm^2/sec.

Thermo analytical characterization of castor oil biodiesel is studied by Marta M. Conceicao et al[5]. The authors used thermo gravimetric and calorimetric techniques to analyze the thermal behavior of castor oil and biodiesel. They also reported the calorific capacity of castor oil biodiesel in the interval 55 to 125^{0}C which was reported 2.718 – 2680 and 1.855 – 2.179 j/gK respectively. They concluded that the transesterification reaction the castor oil can occur at lower temperatures that are at ambient temperatures due to its solubility in alcohol. They highlighted the advantage of castor oil feedstock compared to other oils.Volkhard Scholz[6] and coworkers the reviewed paper on prospects and risks of the use castor oil as fuel. The high viscosity and high water content complicates the use of straight castor oil as a fuel for internal combustion engines. The authors discussed the advantage and disadvantage of castor biodiesel like high calorific value, high cetane no. and low phosphorous and carbon residues. The disadvantages are higher viscosity and high compressibility, hygroscopicity causing filtration corrosion problems. Wiratni and coworkers[7] studied two step ethanolysis of castor oil using with sulphuric acid as a catalyst. In the one step process they reported 60% conversion at end of 120 minutes, and in the two steps process the conversion reported is 82% in 120 minutes. Very little information is available on Transesterification of castor oil in a flow reactor. Satoshi Furuta A, Hiromi Matsuhashi B, Kazushi Arata[8] has reported the transesterification reaction in packed bed reactor under atmospheric pressure. They have reported that reaction for the synthesis of fatty acid methyl ester from castor oil with Methanol was carried out in a flow reactor with 4.0 g of catalyst: molar ratio of methanol to oil 40 using sulfated zirconia as a catalyst (flow rate of methanol 4.4 g h^{-1};Castor oil 3.0 g h^{-1})

Material and Methods

In this experiment castor oil used as a raw material which was purchased from local market. Just like other vegetable oils, castor oil is a triglyceride of various fatty acids and about 10% glycerine. The fatty acids consist of approximately 80–90% ricinoleic acid, 3–6% linoleic acid, 2–4% oleic acid and 1–5% saturated fatty acids. The high content of ricinoleic acid is the reason for the versatile value of castor oil in technology (table 1). Compared with other vegetable oils, castor oil has a very high proportion of simply unsaturated fatty acids (18:1). A comparatively high proportion of those acids can be found only in the oil of the high oleic (HO) sunflower, appearing, however, as oleic acid. In castor oil it is ricinoleic acid, the only unsaturated fatty acid occurring in natural vegetable oils with a hydroxyl function of the carbon atom 12. The extraordinarily high viscosity of castor oil is attributed to the presence of this hydroxyl group[8].

Table-1
Composition of Castor Oil

Acid name	Average Percentage Range
Ricinoleic acid	85 to 95%
Oleic acid	6 to 2%
Linoleic acid	5 to 1%
Linolenic acid	1 to 0.5%
Stearic acid	1 to 0.5%
Palmitic acid	1 to 0.5%
Dihydroxystearic acid	0.5 to 0.3%
Others	0.5 to 0.2%

Experimental Set Up: Initially the range for operating condition was taken according to physical properties and stichiometric ratio. Methanol having boiling point 62^0C, therefore higher level for reaction temperature was taken 60^0C. As per stichiometry reaction carried out at 3:1 methanol to oil molar ratio. The reaction is a reversible one, so, an excess of methanol is necessary to drive the equilibrium towards methyl ester formation. Hence actual experimental tests had taken at higher molar ratio.

For each experiment, Castor oil of measured 100ml was added to a batch reactor and heated to specific temperature. Next, make dissolved solution of measured quantity of methanol and sodium hydroxide. By keeping required temperature constant add methanol, Potassium hydroxide solution in batch reactor where stirrer having speed 460 ±10 rpm. The reaction time is varied in the range of 30 to 60 min.

Results and Discussion

The product obtained during various runs was analyzed for specific gravity, viscosity, acid value and sap. Value. Specific gravity of biodiesel was determined at room temperature (37^0C). Kinematic viscosity was determined at 40^0C. The quality of biodiesel was measured mainly in terms of viscosity, since this one of the important specification in ASTM standards. Hence the quality of biodiesel is discussed in terms of change in viscosity with the variables like residence time, temperature, oil to alcohol ratio. The stirring speed selected for the all runs 460±10 rpm as higher stirring speeds produces lot of vibrations.

Effect of various parameters on biodiesel properties: Effect of residence time: Data are presented for changes of viscosity of biodiesel product for different reaction time are shown in table-1, and figure-1. Experiments work were carried out varying the residence time in the batch reactor from 30 minute to 90 minutes keeping other parameter like reaction temp 30^0C,oil to alcohol molar ratio 1:9 ,stirring speed 460±10. The data sows viscosity decreases with increasing time from 30min to 45 min. further value of viscosity increases with increasing time. Hence optimum reaction time may be taken as 45 min. with lowest viscosity 14.10cSt.

The variation of specific gravity with residence time appears as follow similar trend as that of viscosity. That is specific gravity decrease from 0.9096 to 0.882 as residence time is increased from 30 to 45 minutes, further increase in residence time from 60 to 90 minutes the specific gravity increases 0.882 to 0.9026 while acid value of biodiesel product decreases with increasing reaction time and saponification value decreases with increasing reaction time and further increases.

Table-2
Variation of Viscosity with Time

Time of run (min)	30	45	60	90
Kinematic viscosity (cSt)	18.12	14.10	14.51	15.15
Specific gravity	0.9096	0.890	0.90	0.9026
Acid value	1.26	0.57	0.64	0.68
Sap value	177.6	173.4	174.3	174.9

Oil to methanol mole ratio: Variation of viscosity with oil to alcohol ratio as shown in table-2. Here oil to methanol ratio is change from 1:6 to 1:12, all the runs were carried at 30^0c with batch residence time a 45 minutes. This residence time chosen because optimum value as per earlier discussion. It observed that as oil to alcohol ratio is increases 1:6 to 1:9 mole ratio the product viscosity decreased from 18.18 to14.10 cSt. Further increase oil to alcohol ratio that is 1:12 two layers are not formed. Probably there may not be any reaction at this higher oil to alcohol ratio.

Specific gravity also follows a similar change at oil to alcohol ratio 1:9 the specific gravity of biodiesel layer is found to be lowest 0.882. Acid value and sap value also give similar trend and have lowest value of acid value 0.37 and 170.9 at this oil to alcohol ratio that is 1:9. From the above discussion it appears oil to alcohol ratio 1:9 and residence time of 45 minutes is optimum the parameters for biodiesel production. Viscosity decreases up to 1:9 mole ratios. Specific gravity initially decreases up to 1:9 mole ratio, and further increases up to 1:10 mole ratio and. Acid value shows similar trend as that of viscosity.

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Table-3
Variation of Viscosity with Oil to Alcohol Ratio

Oil to alcohol Mole ratio	**1:6**	**1:9**	**1:10**	**1:12**
Kinematic viscosity, (cSt)	18.18	14.10	19.84	Nil
Specific Gravity	0.9036	0.8820	0.9112	Nil
Acid value	0.97	0.57	0.84	Nil
Sap value	173.4	176.1	176.8	Nil

Effect of temperature: The effect of temperature on the properties of biodiesel like viscosity, specific gravity, acid value sap value and run time are shown in the table 4.3.3K. Runs were carried out at two temperatures 30 and 50^{0}C maintaining reaction time is 45 minutes. It was observed that at lower temperature that 30^{0}C the biodiesel product gave lower viscosity 14.1^{0}C St. Other properties like specific gravity, acid value and sap value are lower at 30^{0}C than 40^{0}C. The oil to alcohol ratio chosen for this runs is 1:9, since this is optimum (table-2).

Specific gravity increases with increasing temperature, the same changes are observed in acid value. It was observed that at lower temperature that 30^{0}C the biodiesel product gave lower Viscosity and further increases up to 50^{0}C. Acid value shows similar trend as that of viscosity. Sap value shows similar trend as that of specific gravity.

Table-4
Variation of Viscosity with Reaction Temperature

Reaction Temperature(^{0}C)	**30**	**40**	**50**
Kinematic viscosity, (cSt)	14.10	18.06	20.6
Specific gravity	0.890	0.9006	0.9010
Acid value	0.56	0.86	0.91
Sap value	173.4	176.1	176.8

Effect of catalyst concentration: The effect of catalyst concentration on various properties biodiesel is reported in the table 4.3.4K. In these runs catalyst concentration varied from 0.5 to 2 weight % based on amount of oil employed in the reaction. Other experimental conditions like oil to methanol mole ratio 1:9, reaction temperature 30^{0}C, stirrer speed 460$\pm$10 rpm and run time 45 minutes are kept constant, and catalyst concentration is varied. These variables are selected because they were at optimum, giving biodiesel product of viscosity 14.1^{0}C St, where 1 weight % catalyst concentration gave lowest value of viscosity 14.1^{0}C St.

The specific gravity of the product is lowest at 1 wt % catalyst concentration and increases with increasing catalyst concentration up to 2wt% . The specific gravity of product was increased and also at lowest concentration at 0. 5 wt%, specific gravity was higher. Probably lower catalyst concentration 0. 5 wt % conversions are very low. Therefore from above data, from table 4.4K, 1wt% catalyst concentration may be optimum in the range operating condition studied. Viscosity decreases with initially up to 1 wt. % catalyst concentration and then increases up to 2 wt. catalyst concentration. Specific gravity initially decreases up to 1 wt. % catalyst concentration and further increases. Acid value shows similar trend as that of viscosity. Sap value is practically constant after 1 wt. % catalyst concentration.

Table-5
Variation of Viscosity with Catalyst Concentration

Catalyst concentration Weight %	**0.5**	**1**	**1.5**	**2.0**
Kinematic viscosity, (cSt)	16.48	14.10	16.91	18.36
Specific gravity	0.9028	0.882	0.9017	0.9136
Acid value	0.98	0.57	0.59	0.59
Sap value	175.2	174.6	173.4	173.5

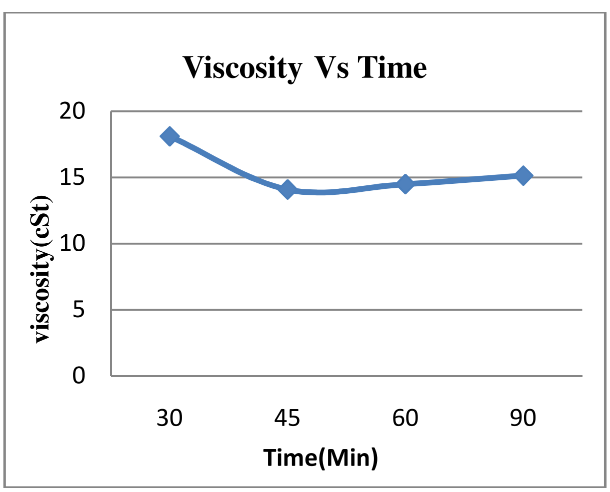

Figure-1
Variation of Viscosity Vs Reaction Time

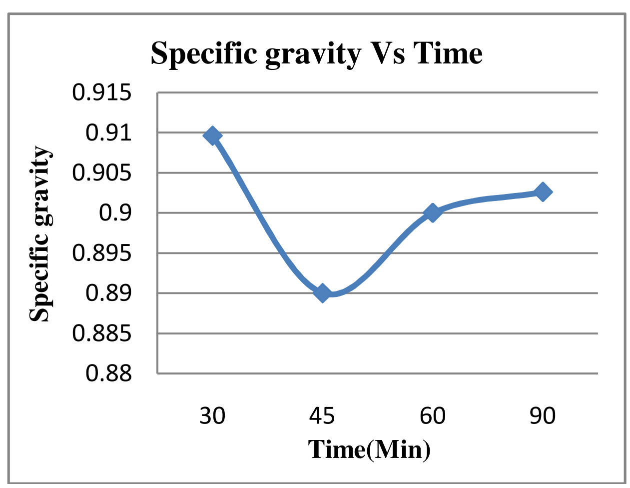

Figure-2
Variation of Specific Gravity Vs Reaction Time

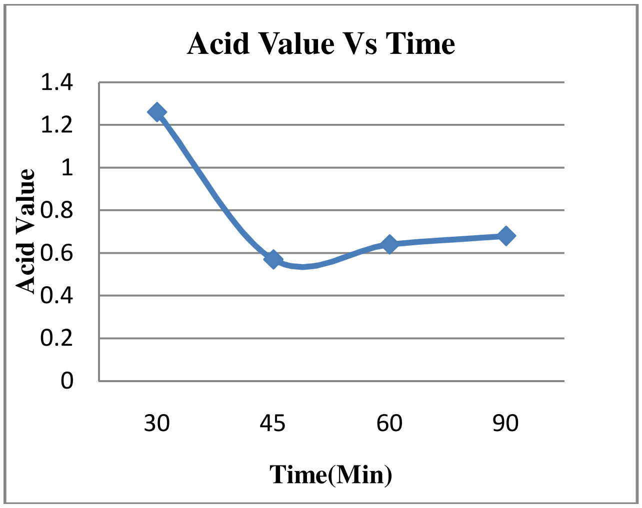

Figure-3
Variation of Acid value Vs Reaction Time

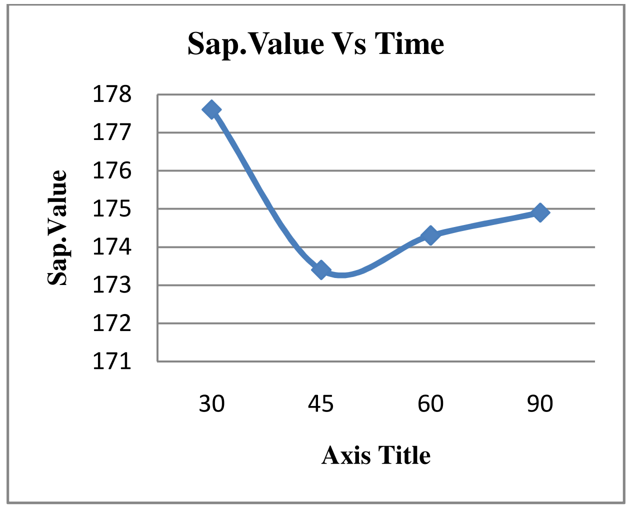

Figure-4
Variation of Sap value Vs Reaction Time

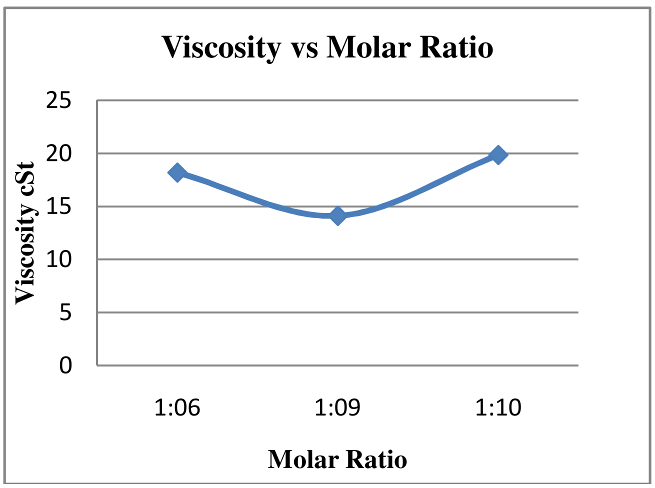

Figure-5
Variation of Viscosity Vs Molar Ratio

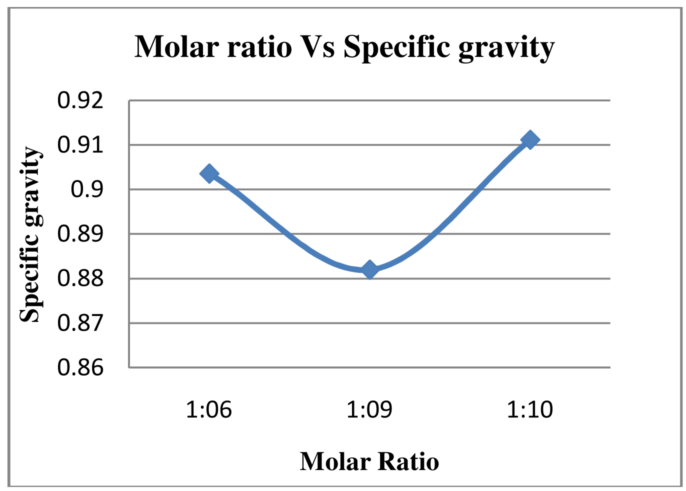

Figure-6
Variation of Molar ratio Vs Specific gravity

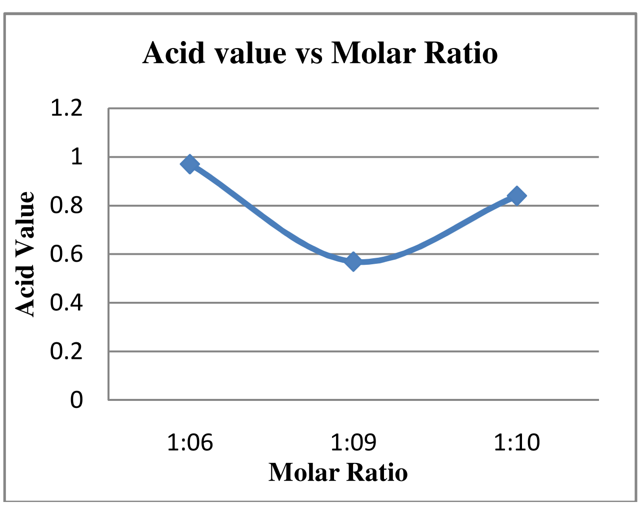

Figure-7
Variation of Acid value Vs Molar Ratio

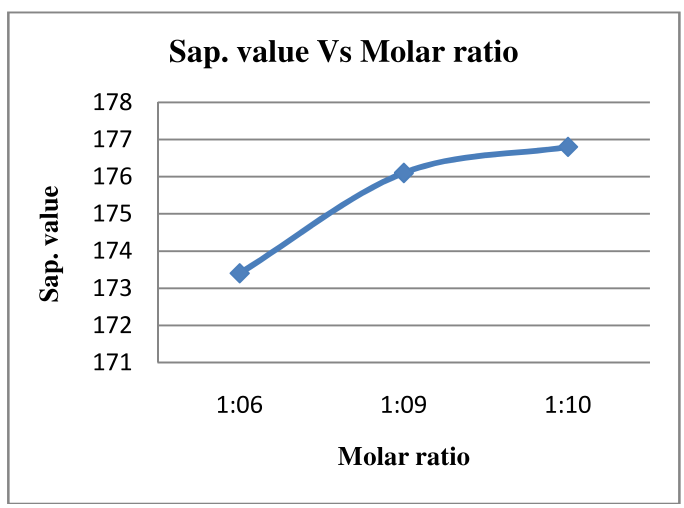

Figure-8
Variation of Sap.value Vs Molar Ratio

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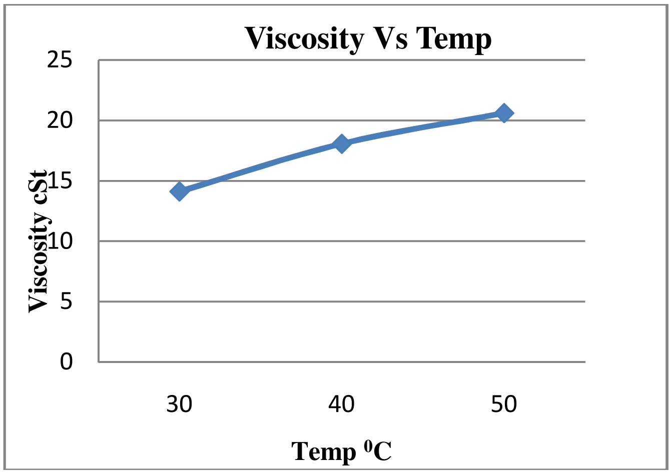

Figure-9
Variation of Viscosity with Temperature

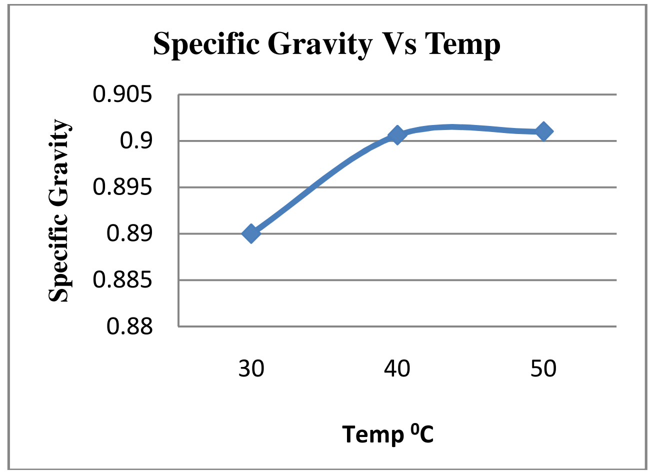

Figure-10
Variation of Specific Gravity with Temperature

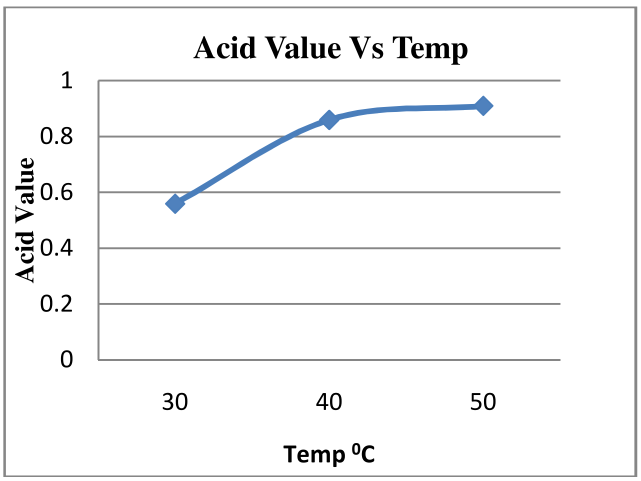

Figure-11
Variation of Acid Value with Temperature

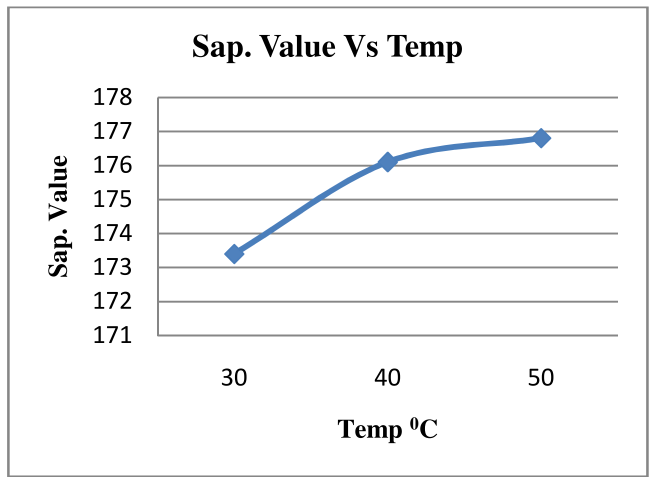

Figure-12
Variation of Sap. Value with Temperature

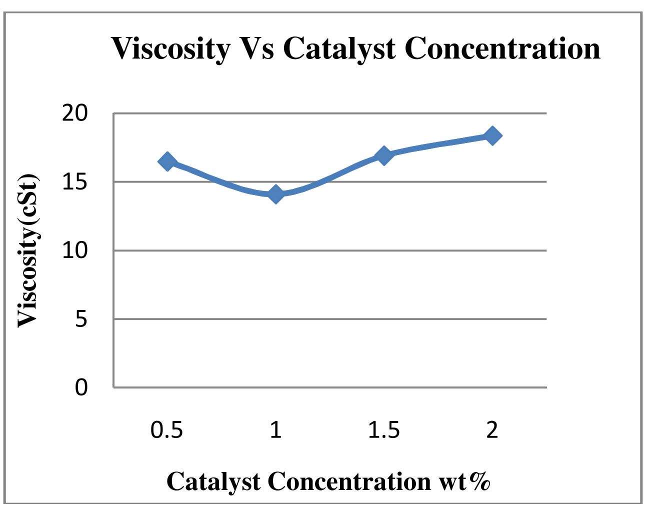

Figure-13
Variation of Viscosity with Cat.Conc.

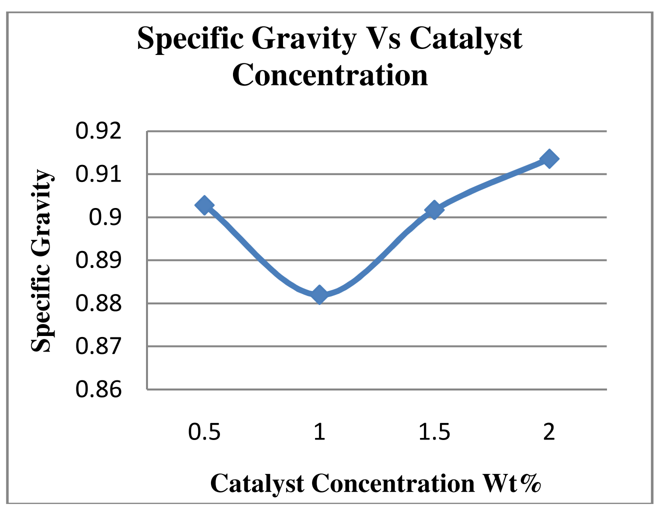

Figure-14
Variation of Sp. Gravity with Cat Conc

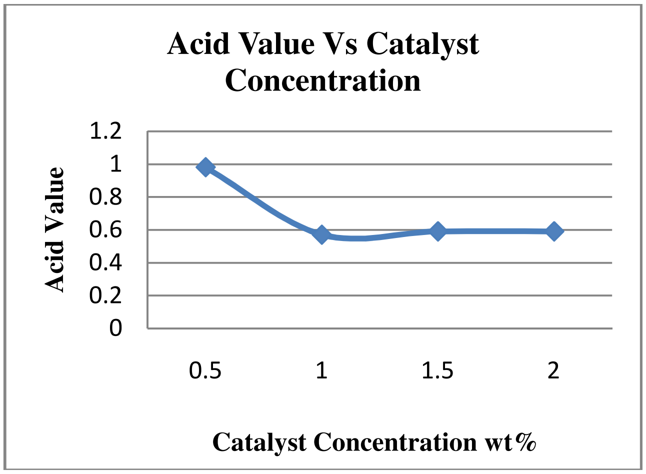

Figure-15
Variation of Acid value with Cat Conc

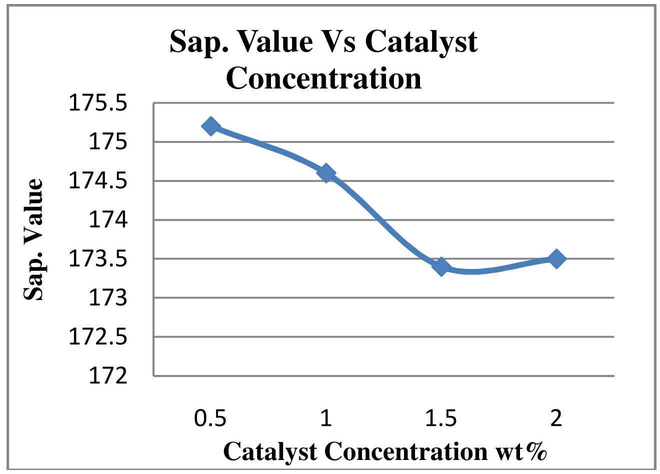

Figure-16
Variation of Acid value with Cat Conc

Conclusion

Production of biodiesel by transeterification of castor oil has been studied in a batch reactor using potassium hydroxideas a catalyst. The variables chosen for the study were residence time, oil to methanol ratio, catalyst concentration; and reaction temperature. The effects of these variables on the viscosity of biodiesel were studied, since this is one of the important specifications in ASTM standard. Apart from viscosity other properties like sp.gr, acid value, and sap value were also determined for the biodiesel product. From the above discussion it may be concluded that the optimum operating condition studied in the present work, oil to methanol mole ratio 1:9, temperature =30^{o}C, catalyst concentration 1 wt % and run time 45 min.

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