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Experimental Investigation Of Effect Of Acid And Base Catalysts On Synthesis Of Castor (Ricinus Communis) Oil Biodiesel.

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Abstract: Due to increase in demand of petroleum products, the prices of petrol and diesel are increasing all over the world. As the available resources of fossil fuel are depleting at faster rate and by 2025 ,the world may face a severe crisis of petroleum fuels, hence an alternative sources of energy to replace fossil fuels are being explored worldwide. Biodiesel is one of the promising biofuels and an alternative for fossil fuels as a primary energy source for machineries and vehicles. It is defined as the mono alkyl ester of vegetables oils or animal fats. Due to its technical feasibility and nonpolluting characteristics, biodiesel is gaining acceptance in steadily growing numbers of countries around the world. Biodiesel is biodegradable, nontoxic, and essentially free of sulfur and aromatics. In this work, experimental investigation has been carried out to produce methyl ester fuels based on non-edible oils like castor oil by using different catalysts like NaOH and H_2SO_4.

The parameters such as temperature, residence time has significant effect on yield of biodiesel and physical properties like Viscosity, Specific gravity, Acid value. In this research the effect of acid and base catalysts was studied on yield of biodiesel and physical properties like viscosity, Specific gravity, Acid value

Keywords: Biodiesel, Methyl esters, catalyst

Introduction:

Since human civilization, the most fundamental requirement for human existence is the use of energy for various purposes which can easily be facilitated by solar energy, wind energy, hydropower, fossil fuels and so on, but the major source of energy is fossil fuels (petrol, diesel, kerosene, etc.) which are mostly used in different sectors. Fossil fuels are vastly used in industrial, agricultural, automobiles, commercial and household purpose. The consumption of fossil fuels has increased to a great level (Rafaat et al. 2008). The total consumption of fossil fuels globally is more than 10 million tons per day. The concerns over increasing fuel prices and scarcity of supply have promoted interest in the development of alternative source to petroleum fuels. Biodiesel extracted from vegetable oil is one such renewable alternative under consideration nowadays. The production of biodiesel would be cheap as it could be extracted from non-edible oil sources. Biodiesel has been defined as a mono-alkyl ester of vegetable oil or animal fats (Knothe, 2005). These resources of vegetable oil can be re-grown, and their supply can be considered infinite as compared to crude oil that is limited. Alternative oilseeds such as Jatropha oil, cottonseed oil, Karanja oil etc., are being investigated as biodiesel feedstocks. Castor (Ricinus communis L.) is one of the most promising non-edible oil crops, due to its high annual seed production and yield. Castor can be grown on marginal land and in semi-arid climate. Still, few studies are available regarding its fuel-related properties in its pure form or as a blend with petrodiesel, many of which are due to its extremely high content of ricinoleic acid.

Biodiesel is produced through a refinery process called transesterification reaction of vegetable oils and animal fat. This process is a reaction of the oil with an alcohol to remove the glycerin, which is a by-product of biodiesel production. In this study, the technical feasibility of Castor oil biodiesel was tested and the specifications in ASTM D6751 which are related to the fatty acid composition of pure castor methyl esters (B100) and its blend with petrodiesel in a 10% vol ratio (B10) were investigated. Distillation temperature and Kinematic viscosity of B100 (397 °C and 15.11 $mm^2\ s^{-1}$ respectively) were the only two properties which did not meet the desired standard limits. In contrast, B10 met all the specifications.

Most of the researchers use edible oils such as soybean oil and corn oil to produce biodiesel. But the prices of edible oils keep increasing due to demand for nutritional need. To overcome this issue, castor oil is the best option to make biodiesel because it is easier to plant and costs less than soybean, sunflower, or other seeds. Castor oil is a triglyceride of various fatty acids and about 10% glycerin. The fatty acids contains approximately 80–90% ricinoleic acid, 3–6% linoleic acid, 2–4% oleic acid and 1–5% saturated fatty acids (Pazir and Muhammad, 1991).

The catalyst plays an important role in production of biodiesel. Usually in transesterification of oils or fats homogeneous catalysts are used but it causes production of wastewater from washing process of catalyst residues and catalyst cannot be reused. Therefore, the development of heterogeneous solid catalyst has recently gained much attention on view of separation and does not produce soap. The solid catalyst is not dissolved in the reaction, and it can be easily separated from products and also can be regenerated and reused and it is environmentally friendly.

This research is about the production of biodiesel from castor oil using optimum catalyst concentration to get the maximum yield of biodiesel.

Materials and methods:

Basically, there are three basic routes to biodiesel production from oils and fats that is:

1. Base catalyzed transesterification of the oil,
2. Direct acid catalyzed transesterification of the oil, and
3. Conversion of the oil to its fatty acids and then to biodiesel.

Most of the biodiesel produced today is done with the base catalyzed reaction because it is low temperature and pressure; it yields high conversion (98%) with minimal side reactions and reaction time (Anonymous, 2007).

Literature survey on the topic reveals that different studies have been carried out using different alcohols such as methanol, ethanol, propanol, butanol, and amyl alcohol for biodiesel synthesis by transesterification reaction. Methanol and ethanol are used most frequently. Ethanol is a favored alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable, however methanol is the most commonly used alcohol because of its low cost and its physical and chemical advantages associated with being polar and the shortest chain alcohol. The reaction time is shorter in the methanolysis because of the physical and chemical properties of methanol.

Castor (Ricinus communis L.) is an important non-edible oilseed crop and is grown especially in arid and semi-arid region. It is cultivated around the world because of the commercial importance of its oil. India is the world's largest producer of castor seed and meets most of the global demand for castor oil[5] . India produces 8 to 8.5 lakh tonnes of castor seed annually, and accounting for more than 60% of the entire global production. Because of its limitless industrial applications, castor oil enjoys incredible demand world-wide. The current consumption of castor oil and its derivatives in the domestic market is estimated at about 300,000 tonnes.

Experimental Setup:

Reactor used for carrying out the transesterification reaction, consists of three necked flasks. In assembly of three necked flask central neck is used for stirrer, while other two necks were used for thermometer and condenser as shown in above figure 1. Thermometer was used to record the temperature. The temperature of reaction mixture was maintained constant throughout the complete length of experiment by placing reactor in constant temp bath.

Catalysts used for the production of biodiesel are sulfuric acid and sodium hydroxide. Different runs were carried out for these catalysts by varying the residence time , oil to methanol ratio and reaction temperature.

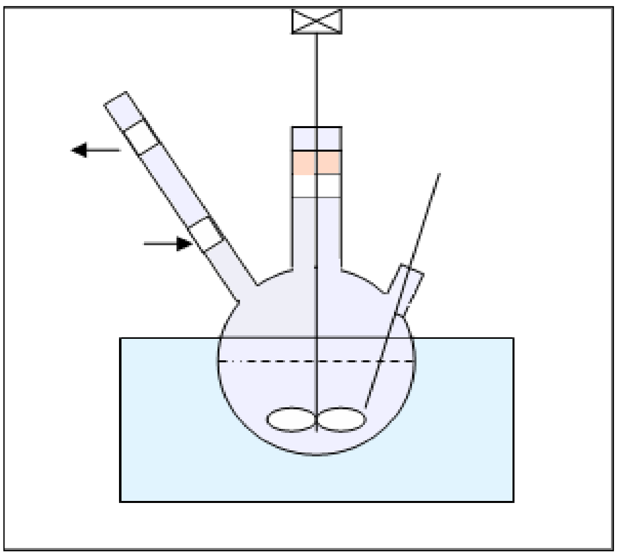

Figure1. Biodiesel synthesis-Experimental setup

Effect of residence time:

Various runs were carried out for acid and base catalysts in the batch reactor by varying the residence as shown in the table 1. The experimental runs were carried out at residence times of 30min,45 min,60min and 90 min. It was found that at the lowest residence time 30 minute the biodiesel viscosity was higher in both the catalysts. As the residence time in the batch reactor was increased further to 45 minute the viscosity decreased from 16.56 to 11.28cSt for sulfuric acid as catalyst. Further increase in residence time to 90 minutes the viscosity again increases from 11.28 to 13.93 cSt. Same trend of viscosity was followed by base catalysts i.e., sodium hydroxide that is from the above data one may conclude at 45 minutes residence time biodiesel gave lowest viscosity 11.28cSt, 13.10cSt, for sulfuric acid, sodium hydroxide, catalysts respectively as shown in figure 2. This seems to be the optimum time under the experimental condition studied. Runs for sulfuric acid catalyst are carried out at 55^0C with 3volume% as catalyst concentration. Whereas runs for sodium hydroxide catalysts were carried out at 30^0C with 1wt% of catalyst concentration. From the figure 3, it was observed that the specific gravity decrease from 0.9108 to 0.9009 as residence time is increased from 30 to 45 minutes, further increase in residence time from 60 to 90 minutes the specific gravity increases 0.9012 to 0.9052 for sulfuric acid as a catalyst. Specific gravity for sodium hydroxide catalyst decrease from 0.9106 to 0.8892 as residence time is increased from 30 to 45 minutes, further increase in residence time from 60to 90 minutes the specific gravity increases 0.9016 to 0.9039. Similar observations were made with regard to acid value at 45-minute residence time in both the catalysts gives lowest acid value as shown in figure-4.

Table-1 Effect of residence time on parameters such as viscosity, specific gravity, and acid value.

Time of experimental run (minute)	**30**	**45**	**60**	**90**
Kinematic Viscosity (cSt) for Sulfuric acid as a Catalyst	15.50	11.10	11.44	13.55
Kinematic Viscosity (cSt) for Sodium hydroxide as a Catalyst	20.88	12.80	13.90	18.00
Specific gravity for Sulfuric acid as a Catalyst	0.9018	0.9001	0.9040	0.9022
Specific gravity for Sodium hydroxide as a Catalyst	0.911	0.890	0.9050	0.9048
Acid value for Sulfuric acid as a Catalyst	0.89	0.56	0.57	0.56
Acid value for Sodium hydroxide as a Catalyst	0.94	0.35	0.44	0.55

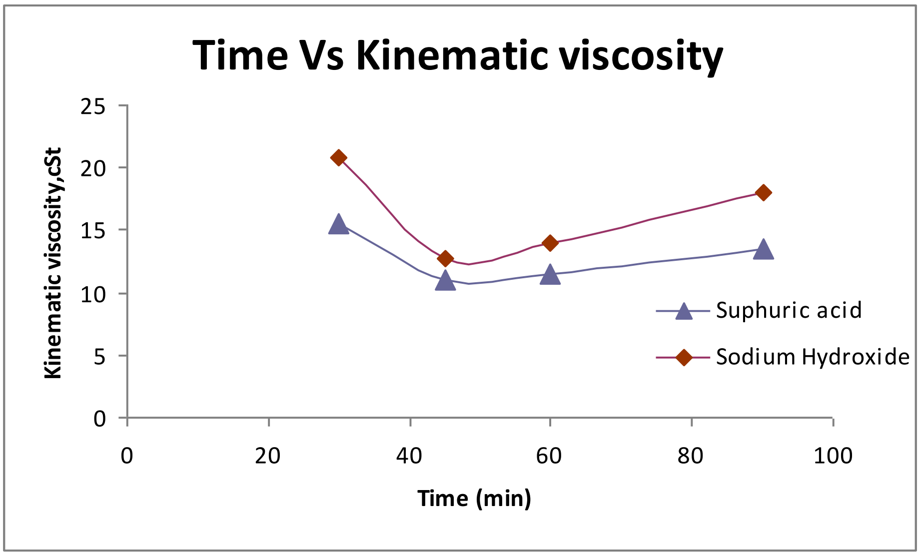

Figure-2: Kinematic Viscosity V/s Time

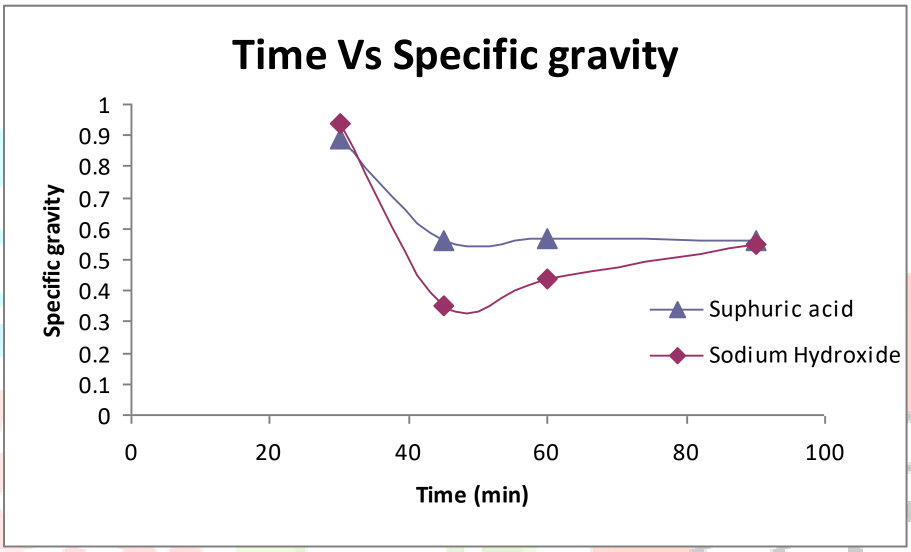

Figure-3: Specific gravity vs Time

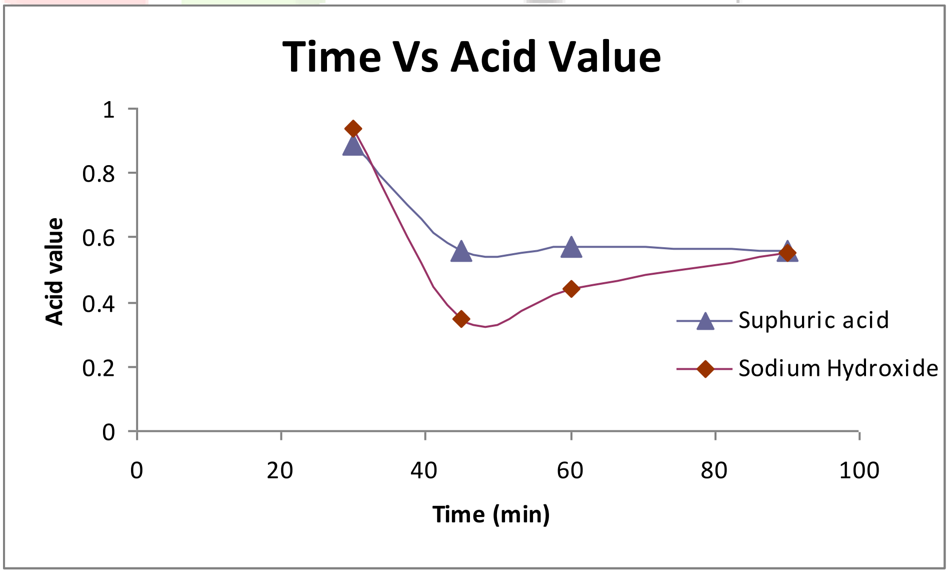

Figure-4: Acid value vs Time

Oil to methanol mole ratio:

It was observed that for the sulfuric acid catalyst with increasing oil to methanol molar ratio from 1:6 to 1:15, biodiesel product viscosity decreases from 19.96 cSt to 6.63cSt. And that for sodium hydroxide catalysts, oil to alcohol ratio is increases 1:6 to 1:9 mole ratios the product viscosity decreased from 15.68 to 13.10 cSt, as shown in figure 5. 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 in both catalysts. While Sp. gravity for sulfuric acid catalyst decreases from 0.9023 to 0.9006 when oil to methanol molar ratio increases from 1:6 to 1:12 (oil to methanol) and then increases further from 0.9009 to 0.9015 as oil to methanol molar ratio increases to 1:15 as shown in figure 6. The specific gravity for sodium hydroxide also follows a similar change at oil to alcohol ratio 1:9 the specific gravity of biodiesel layer is found to be lowest 0.8892 for sodium hydroxide as shown in figure 7. 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 using sodium hydroxide as catalysts. Whereas 1:10 molar ratio is optimum for biodiesel production using sulfuric acid as a catalyst.

Table-2-Effect of oil to methanol mole ratio on viscosity, specific gravity, acid vale.

Oil to alcohol mole ratio	1:06	1:09	1:10	1:12	1:15
Kinematic viscosity,(cSt)for sulfuric acid as catalyst	19.96	11.28	10.56	9.7	6.63
Kinematic viscosity,(Cst)for sodium hydroxide as catalyst	21.57	13.1	15.51	16.56	Nil
Specific gravity for sulfuric acid as catalyst	0.9023	0.9006	0.9006	0.9009	0.9015
Specific gravity for sodium hydroxide as catalyst	0.9145	0.8892	0.9047	0.9092	Nil
Acid value for sulfuric acid as catalyst	0.61	0.58	0.56	0.52	0.49
Acid value for sodium hydroxide as catalyst	0.576	0.37	0.426	0.48	0.48

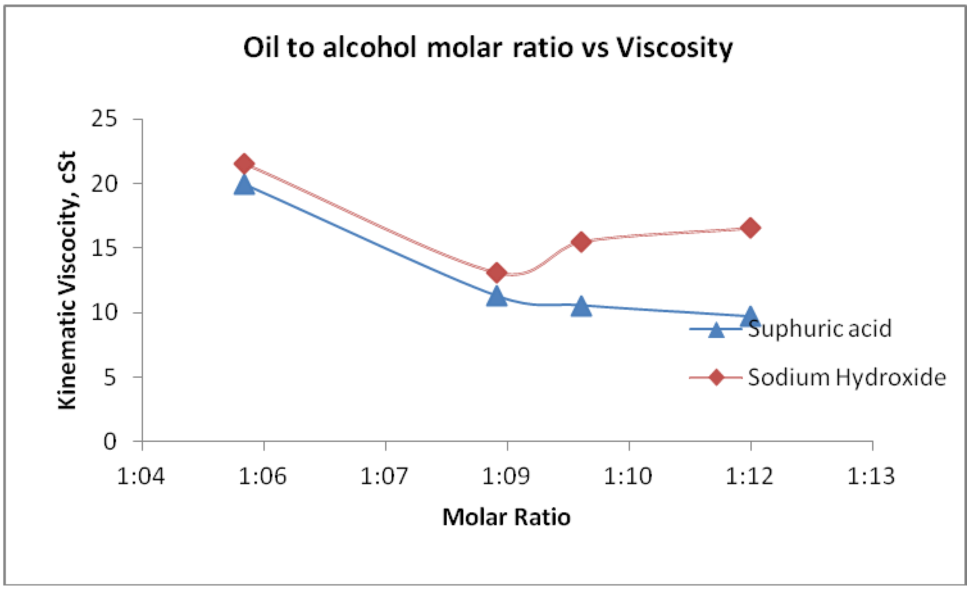

Figure-5: Viscosity V/s Molar ratio

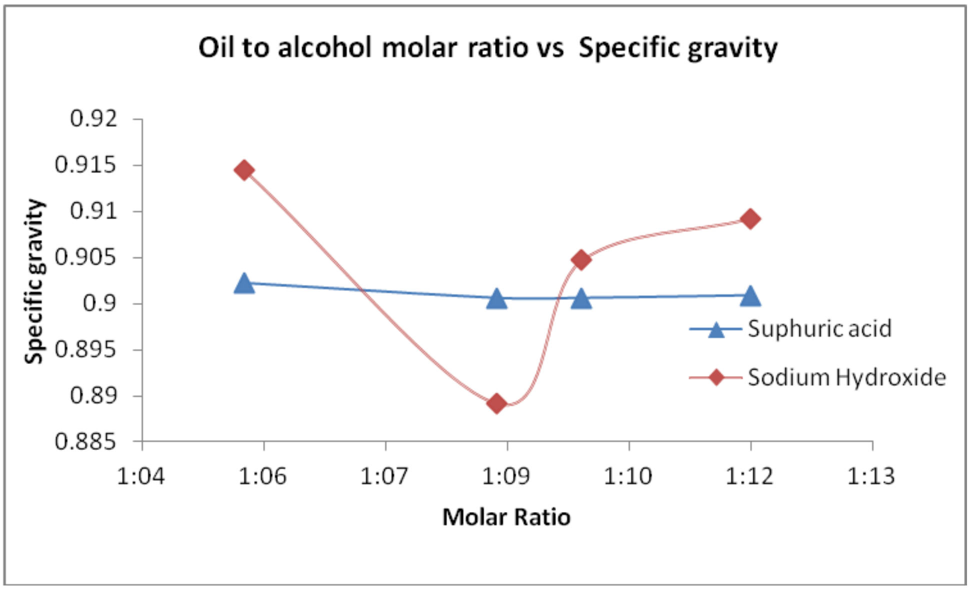

Figure-6: Specific gravity V/s Molar ratio

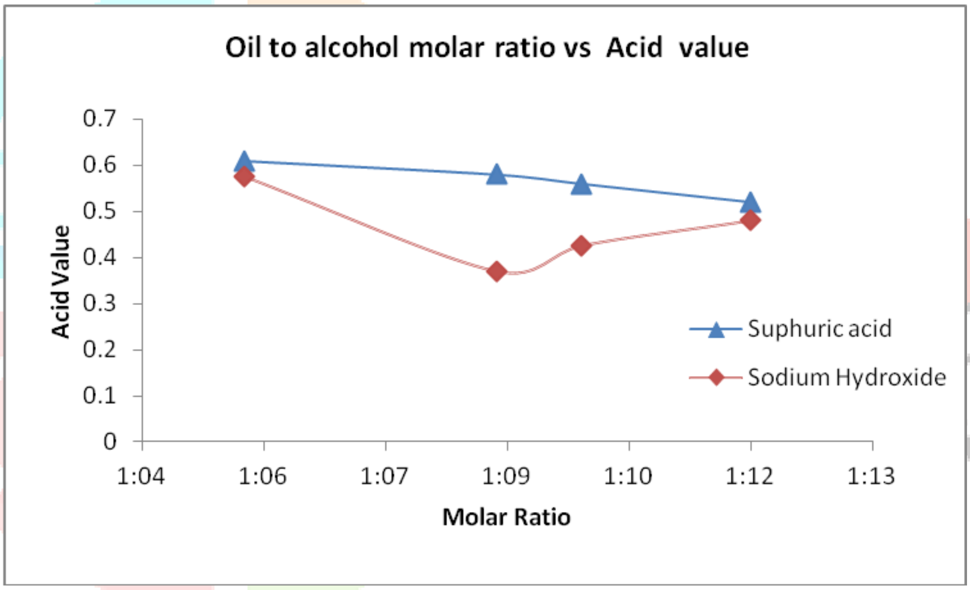

Figure-7: Acid Value V/s Molar ratio

Conclusion:

Production of biodiesel by transesterification of castor oil has been studied in a batch reactor using different catalysts namely sulfuric acid, sodium hydroxide. The variables chosen for the studies are:

1. Residence time,
2. Oil to methanol ratio,
3. 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, were also determined for the biodiesel product.

The following conclusions were drawn from the study using Sulfuric Acid as catalyst:

As the reaction time increases from 30 min to 45 min it was found that viscosity decreased from 16.56cSt to 11.28cSt and, then viscosity increases, further with increasing time. Hence optimum reaction time was found to be 45 min. Oil to methanol ratio was varied from 1:6 to 1:18 molar ratio. It was found that viscosity of biodiesel decreases with increasing molar ratio in above range of oil to methanol ratio. At 1:15 oil to methanol ratio biodiesel viscosity was found to be lowest 6.63cSt, whereas according to ASTM specifications the viscosity of the biodiesel should be in the range from 1.9cSt to 6cSt.Thus the viscosity obtained experiments is slightly higher than ASTM range. The reaction temperature in batch reactor was varied from 30-55 ^oC keeping other operating conditions constant such as reaction time 45min, cat conc. 3 volume % of H_2SO_4, and oil to methanol mole ratio 1:9.it was observed that viscosity decreases with increasing temp. The optimum temperature was found to be 55 ^oC which gave lowest viscosity of biodiesel as 11.28 cSt. But at 1:15 molar ratio, viscosity was 6.63cSt.

The following conclusions were drawn from the study using Sodium Hydroxide as a catalyst:

As the reaction time increases from 30min to 45 min using sodium hydroxide as a catalyst, it was found that viscosity decreased from 21.57cSt to 13.10cSt and further, viscosity increases with increasing time. Hence optimum reaction time was found to be 45min. Oil to methanol ratio was varied from 1:6 to 1:12 molar ratio for sodium hydroxide as a catalyst. It was found that viscosity decreases in the above range of oil to methanol ratio. At 1:9 oil to methanol ratio biodiesel viscosity was found to be 13.10cSt. The reaction temperature in a batch reactor was varied from 30-50 ^oC keeping other operating conditions constant such as reaction time 45 min, cat conc. 1wt% sodium hydroxide and oil to methanol mole ratio 1:9. It was observed that viscosity increases with increasing temp. The optimum temperature was found to be 30 ^oC which gave lowest viscosity of biodiesel as 13.10 cSt.

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