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Production of Biodiesel from Castor Oil using acid and Base catalysts

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Abstract

Biodiesel defined as the mono alkyl ester of vegetables oils or animal fats is an "alternative" diesel fuel that is becoming accepted in steadily growing numbers of countries around the world. As biodiesel comes from domestically produced renewable resources, it contributes to the domestic energy security. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. In this work, it is planned to produce methyl ester fuels based on non edible oils like castor oil by using different catalysts like NaOH and H_2SO_4. The effect of various parameters like temp, residence time, catalyst concentration investigated on yield of biodiesel and physical properties like Viscosity, Specific gravity, Acid value.

Keywords: Biodiesel, methyl ester, non edible oils, catalyst.

Introduction

The depleting reserves of fossil fuel and increasing demand for diesels and uncertainty in their availability is considered to be the important trigger for many initiatives to search for the alternative sources of energy, which can supplement or replace fossil fuels. One hundred years ago, Rudolf Diesel tested peanut oil as fuel for his engine for the first time on August 10, 1893 Biodiesel is the name of a clean burning alternative fuel, produced from domestic, renewable resources. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics[1]. Carmen Leonor Barajas Forero[2] studied biodiesel production by transesterification of castor oil with methanol using sodium hydroxide catalyst in batch reactor. They carried out run for two hours. There was no mention of reaction temperature but it appears he might have done at ambient temperature is reported small amount of soap formation since the feed castor oil containing 0.2 % moisture. The other advantage of castor oil biodiesel is cold flow properties because of its very low cloud and pour points. The authors reported the efficiency of the process in the range of 80-82 %. The authors tested this biodiesel and biodiesel mixture in internal combustion engines. The author concluded castor oil biodiesel can be used as petroleum diesel additive improving both environmental and flow behavior of the petroleum fuel. The authors were also concluded in large scale process preparation of biodiesel from castor oil would less than other vegetable oil. G. Perin et al[3] transesterified castor oil by microwave irradiation in presence of methanol / ethanol using mole ratio of oil to alcohol 1:6 and 10% w/w of acidic silica gel or basic alumina as catalyst and the acid catalysis. The authors reported more than 95% conversion at 3 hours reaction time, 60^0C temperature with 50 % sulphuric acid. Under similar conditions but with alumina using 50% KOH more than 95% conversions are obtained in 1 hour reaction time. Under above conditions of microwave irradiation greater than 95% conversions are obtained in 5 minutes with alumina in 50% KOH; whereas with SiO_2 in 50% H_2SO_4 catalyst. Microwave irradiated the conversion obtained is 95% in 30 minutes. The authors concluded in comparison with conventional heating the catalyzed alcoholysis assisted by microwaves is much faster and leads to higher yields of the desired fatty esters Adam Zieba[4] carried out transesterification of castor oil in a batch reactor with a oil to methanol ratio 1: 29, temperature 60^0C, stirring rate 500 rpm using sulphuric acid as catalyst. The catalyst concentration is varied from 0.5-3 weight %. He has reported a conversion more than 90% after 180 minutes reaction time when the catalyst concentration 1 and 3 weight % H_2SO_4 catalyst concentration the conversion is about 75%. He was also carried out experiments using sulfosalicylic acid and poly (4-styrene sulfonic acid), where conversions are reported as 90% at 270 minutes residence time and less than 10% conversion at 150 minutes respectively. Adam Zieba also performed experiment transesterification of castor oil by methanol using heterogeneous acid catalysts like o.6 gm $H_2SiW_{12}O_{40}/ZrO_2$, Polyaniline (PANI) prot. H_2SO_4 and 0.3 gm $H_2SiW_{12}O_{40}/ZrO_2$ where conversions are reported 75%, 55% and 20% respectively at residence time 500 minutes.

Material and Methods

Castor (*Ricinus communis L.*) 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 unlimited industrial applications, castor oil enjoys tremendous demand world-wide. The current consumption of castor oil and its derivatives in the domestic market is estimated at about 300,000 tonnes. India is also the biggest exporter of castor oil and its derivatives at 87% share of the international trade in this commodity. Castor is an important non-edible oilseed crop and is grown especially in arid and semi arid region[6]

Experimental Setup: Reactor used for the transeterification reaction, consists of three necked flasks. In assembly of three necked flask central neck is used for stirrer, while other two necked used for thermometer and condenser as shown in above figure-1. Thermometer is used to record the temperature. The reactor was kept in constant temp bath, so as to maintain the temp, of reaction mixture constant over the complete length of experiment.

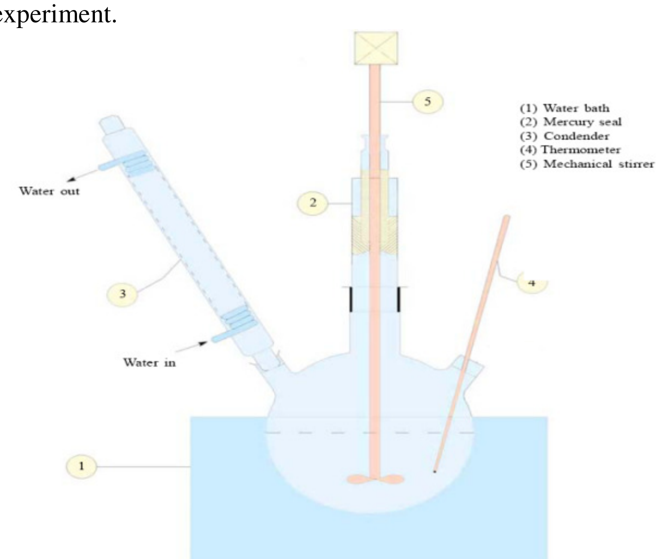


Figure-1
Experimental setup of Biodiesel production

Results and Discussion

Production of biodiesel by transesterification of castor oil with methanol containing sulfuric acid as a catalyst was studied in a batch reactor. The effects of variables chooses for study on biodiesel quality are: i. Residence time in batch reactor, ii. Oil to methanol ratio, iii. Catalyst concentration; and iv. Reaction Tamp.

The biodiesel is analyzed for specific gravity, viscosity, acid value and sap. value, specific gravity of biodiesel is determined at room temperature (37^{0}C). Kinematic viscosity is determined at 40^{0}C.The quality of biodiesel is 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$\pm$10 rpm as higher stirring speeds produces lot of vibrations.

The Effects of various parameters on biodiesel quality are discussed below

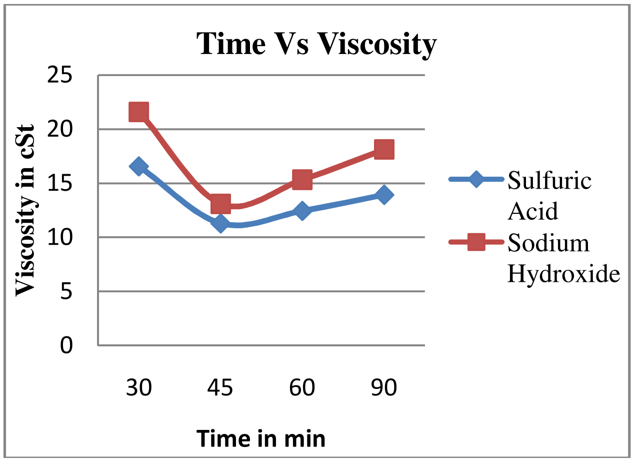
Catalysts used for the production of biodiesel are sulfuric acid and sodium hydroxide. Different runs were carried out for these catalysts varying the residence time, oil to methanol ratio, reaction temperature, catalyst concentration.

Effect of residence time: Various runs were carried out for acid and base catalysts in the batch reactor by varying residence time from 30 minute to 90 minutes as shown in the table-1.At the lowest residence time 30 minute the biodiesel viscosity is found to be higher in all the catalysts. As the residence in the batch reactor increased further to 45 minute the viscosity decrease from 16.56 to 11.28cSt for sulfuric acid as catalyst. Further increase in residence time to 90 minutes the viscosity again increase from 11.28 to 13.93 cSt. Same trend of viscosity was followed by base catalysts i.e sodium hydroide 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. This seems to be the optimum time under the experimental condition studied. Runs for sulfuric acid catalyst are carried out at 55^{0}C with 3volume% as catalyst concentration. Whereas runs for sodium hydroxide catalysts were carried out at 30^{0}C with 1wt% of catalyst concentration.

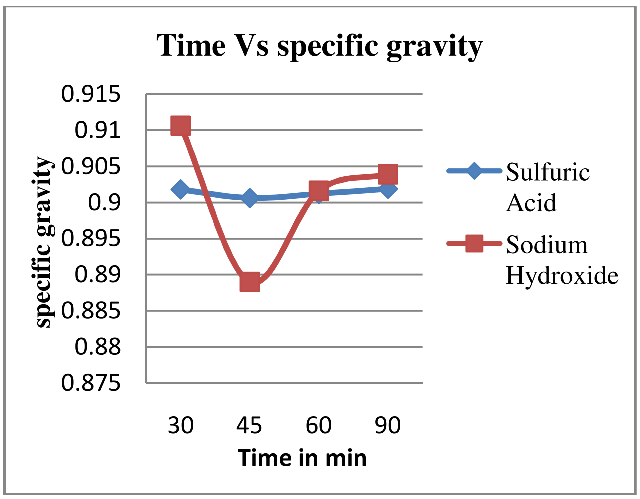
The variation of density with residence time appears a follow similar trend as that of viscosity for all the catalysts. That is specific gravity decrease from 0.9108 to 0.9009 as residence time is increased from 30 to 45 minutes, further increase in residence time from 60 to 90 minutes the specific gravity 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 60 to 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.

Table-1
Variation of viscosity, specific gravity, acid value with time

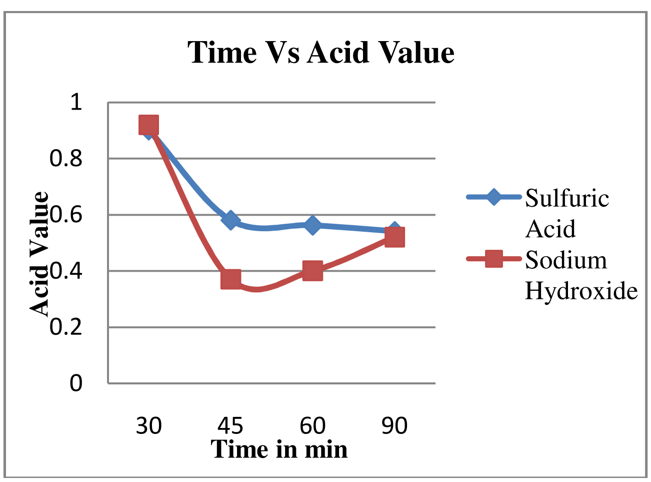
Time of Run (min)	30	45	60	90
Kinematic viscosity, (cSt) for Sulfuric Acid As Catalyst	16.56	11.28	12.44	13.93
Kinematic viscosity, (cSt) for Sodium Hydroxide As Catalyst	21.57	13.10	15.33	18.11
Specific gravity for Sulfuric Acid As Catalyst	0.9018	0.9006	0.9012	0.9019
Specific gravity for Sodium Hydroxide As Catalyst	0.9106	0.889	0.9016	0.9039
Acid value for Sulfuric Acid As Catalyst	0.90	0.58	0.562	0.541
Acid value for Sodium Hydroxide As Catalyst	0.92	0.37	0.40	0.52



Graph-1
Variation of viscosity Vs Time



Graph-2
Variation of Specific Gravity Vs Time



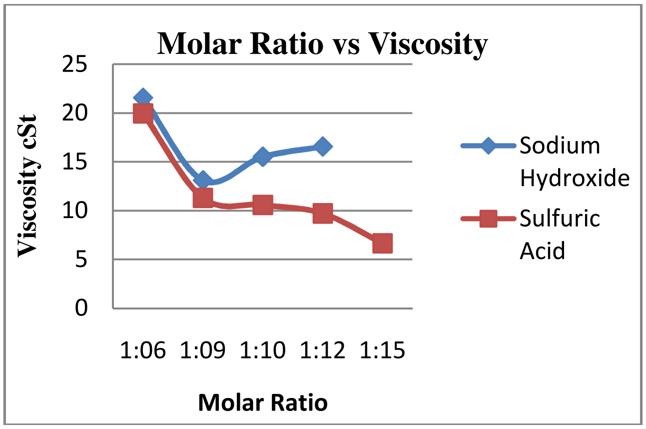
Graph-3
Variation of Acid Value Vs Time

Oil to methanol mole ratio: It is observed that for 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,. 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.

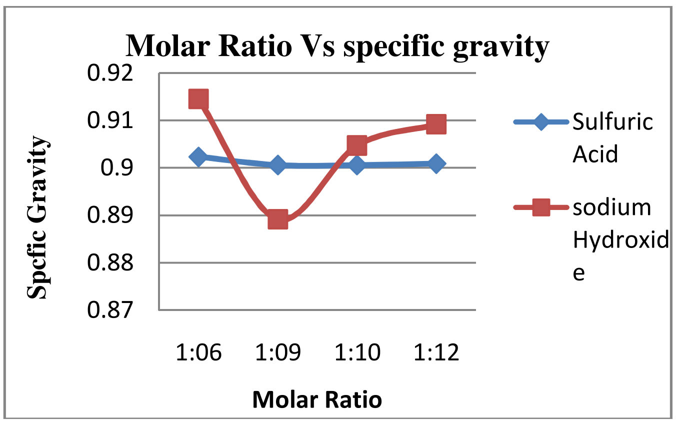
While Sp. gravity for sulfuric acid catalyst decreases from 0.9023 to 0.9006 when oil to methanol molar ratio increases from 1:6 to 1:12 (oil to methanol) and then increases further from 0.9009 to 0.9015 as oil to methanol molar ratio increases to 1:15. Specific gravity for sodium hydroxide also follows 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. 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
Variation of viscosity, specific gravity, acid value and sap value with oil to methanol mole ratio

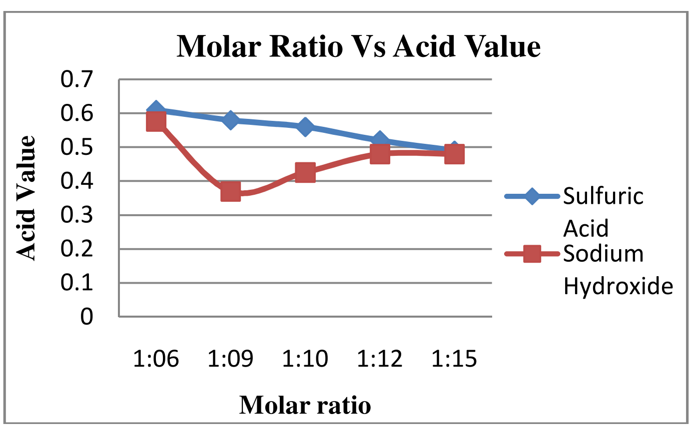
Oil to alcohol mole ratio	1:06	1:09	1:10	1:12	1:15
Kinematic viscosity, (cSt) for sulfuric acid as catalyst	19.96	11.28	10.56	9.7	6.63
Kinematic viscosity, (cSt) for sodium hydroxide as catalyst	21.57	13.1	15.51	16.56	Nil
Specific gravity for for sulfuric acid as catalyst	0.9023	0.9006	0.9006	0.9009	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



Graph-4
Variation of viscosity Vs Molar Ratio



Graph-5
Variation of Acid Value Vs Molar Ratio

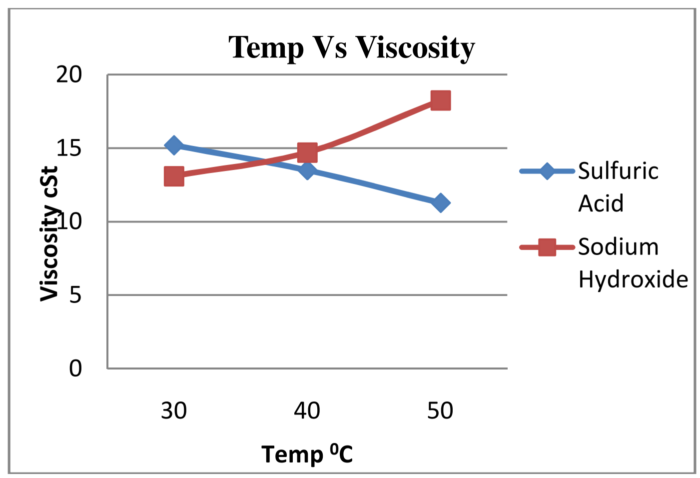


Graph-6
Variation of Specific Gravity Vs Molar Ratio

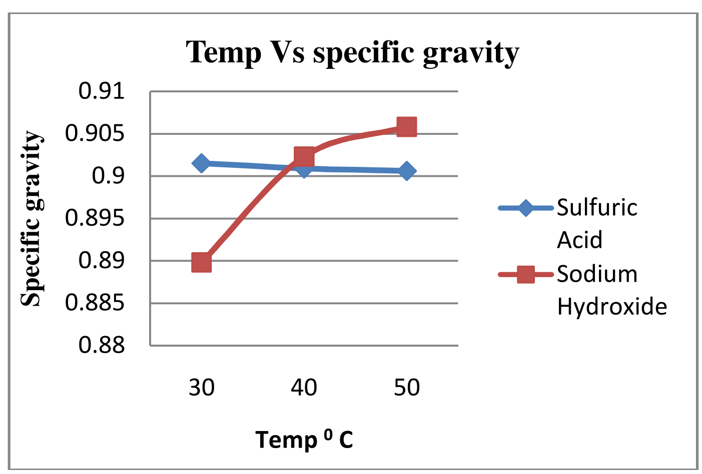
Effect of temperature: For sulfuric acid as a catalyst, reaction temp increased from 30°C to 50°C it is observed that, viscosity of biodiesel product decreases from 15.22 to 11.28cSt. Specific gravity, Acid value follows same trends as that of viscosity .Where as for Sodium Hydroxide as a catalyst viscosity is increases from13.10 to 18.25cSt, with increasing reaction temperature from 30^{0}c to 50^{0}c. Specific gravity, acid value follows same trends as that of viscosity for sodium hydroxide as a catalysts.

Table-3
Variation of viscosity, specific gravity, acid value and sap value with temperature

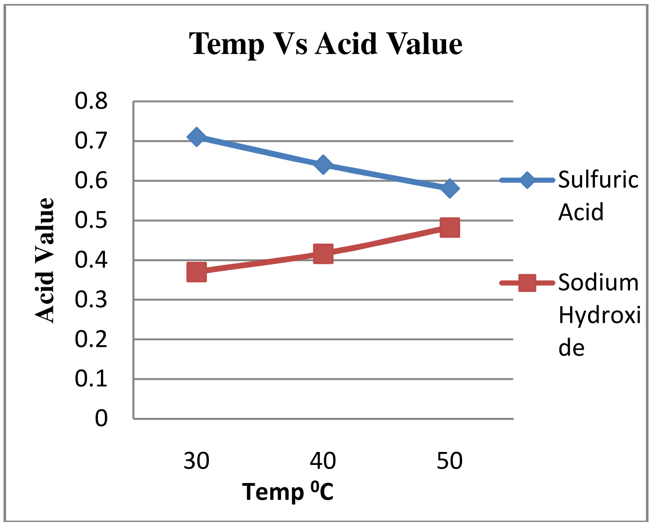
Reaction Temperature(^{0}c)	**30**	**40**	**50**
Kinematic viscosity, (cSt) for Sulfuric Acid As Catalyst	15.2	13.5	11.28
Kinematic viscosity, (cSt) for Sodium Hydroxide As Catalyst	13.1	14.71	18.25
Specific gravity for for Sulfuric Acid As Catalyst	0.9015	0.9009	0.9006
Specific gravity for Sodium Hydroxide As Catalyst	0.8898	0.9023	0.9058
Acid value for Sulfuric Acid As Catalyst	0.71	0.64	0.58
Acid value for Sodium Hydroxide As Catalyst	0.37	0.416	0.482



Graph-7
Variation of Viscosity Vs Temp



Graph-8
Variation of Viscosity Vs Temp



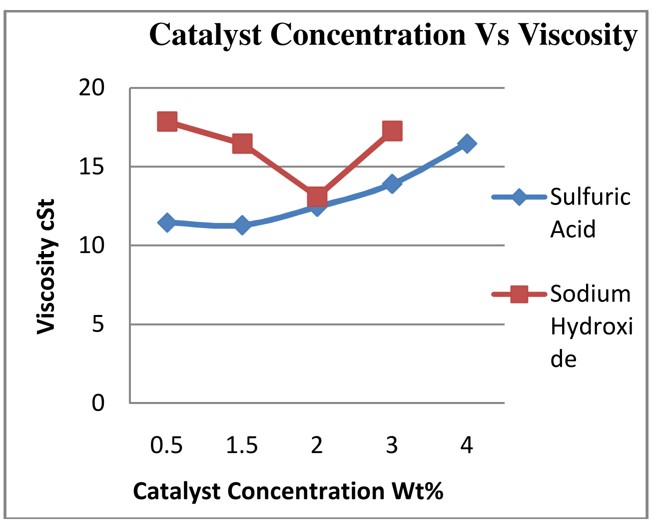
Graph-9
Variation of Acid Value Vs Temp

Effect of catalyst concentration: Here it observed that viscosity is first decreases from catalyst concentration 0.5wt% of sulfuric acid to 3 volume % of sulfuric and then increases further with increasing catalyst concentration, lowest value of kinematics viscosity 11.28 cSt is obtain at 3 volume % of sulfuric acid as catalyst. Similar observations are made with regards to specific gravity of biodiesel product. But acid value is increases as catalyst concentration increased from 1 volume % of sulfuric acid to 8 volume % of sulfuric acid.

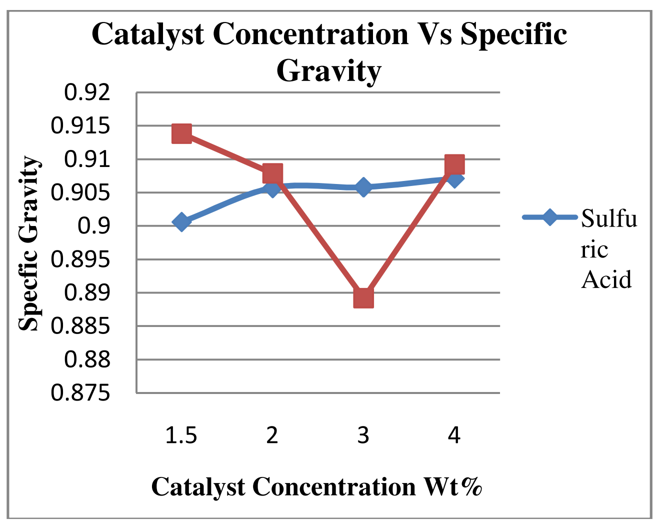
Here it observed that for sodium hydroxide catalysts viscosity are first decreases from catalyst concentration 0.5 wt and of sodium hydroxide as a catalyst and then increases further with increasing catalyst concentration, lowest value of kinematics viscosity 13.10 cSt for sodium hydroxide catalysts. Similar observations are made with regards to specific gravity, acid value of biodiesel product.

Table-4
Variation of viscosity, specific gravity, acid value and sap value with Catalyst Concentration

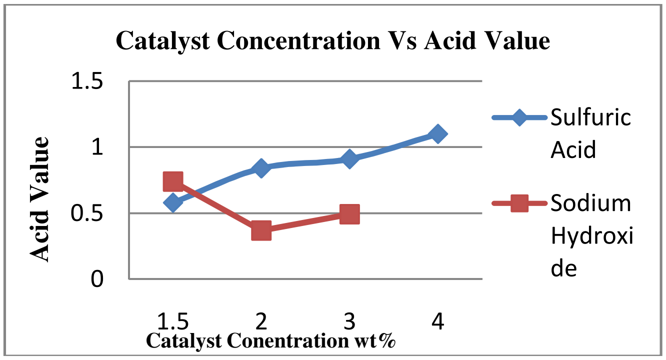
Catalyst concentration	0.5	0.75	1	1.25	1.5	2	3	4
Kinematic viscosity, (cSt) for Sulfuric Acid As Catalyst	11.44	Nil	Nil	Nil	11.28	12.44	13.90	16.46
Kinematic viscosity, (cSt) for Sodium Hydroxide As Catalyst	17.85	16.46	13.10	17.26	Nil	Nil	Nil	Nil
Specific gravity for for Sulfuric Acid As Catalyst	0.91	Nil	Nil	Nil	0.9006	0.9057	0.9058	0.9071
Specific gravity for Sodium Hydroxide As Catalyst	0.9138	0.90787	0.8892	0.9092	Nil	Nil	Nil	Nil
Acid value for Sulfuric Acid As Catalyst	0.525	Nil	Nil	Nil	0.58	0.84	0.91	1.1
Acid value for Sodium Hydroxide As Catalyst	0.842	0.740	0.37	0.493	Nil	Nil	Nil	Nil



Graph-10
Variation of Catalyst Concentration Vs Viscosity



Graph-10
Variation of Catalyst Concentration Vs Sp.Gravity



Graph-12
Variation of Catalyst Concentration Vs Acid value

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 study are: i. Residence time, ii. Oil to methanol ratio, iii. Catalyst concentration; and iv. 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 30min 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 45min. As the catalyst concentration in a batch reactor was varied from 1 volume % to 8 volume % of sulfuric acid keeping other operating conditions constant, such as reaction temperature 55^0C, oil to methanol mole ratio 1:9, reaction time 45min. Increasing catalyst concentration from 1 volume % to 3 volume % . It was found that viscosity was decreasing from 11.44cSt to 11.28cSt and further, it was increasing with increasing catalyst concentration. The optimum catalyst concentration was found to be 3 volume %, which gave lowest viscosity 11.28cSt of biodiesel. 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 30-55^0C keeping other operating conditions constant such as reaction time 45 min, 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 55^0C 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. The catalyst concentration in a batch reactor was varied from 0.5 to 1.5wt% sodium hydroxide of oil keeping other operating conditions constant, such as reaction temperature 30^0C, oil to methanol mole ratio 1:9, reaction time 45min. Increasing in catalyst concentration from 0.5 wt % to 1 wt% sodium hydroxide, it was found that viscosity was decreasing from 17.85cSt to 13.10cSt and further it was increasing with catalyst concentration. The optimum catalyst concentration was found to be 1wt% sodium hydroxide which gave lowest viscosity 13.10cSt. 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 30-50^0C 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 30^0C which gave lowest viscosity of biodiesel as 13.10 cSt.

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