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Optimization of Transesterification Process for Biodiesel Production from Linseed Oil

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ABSTRACT

Environmental degradation and fossil fuel depletion due to rapid use of fossil fuels promoted the interest in development of alternative fuels. The main aim of this work is to optimize the transesterification process for production of biodiesel from linseed oil, which has a better properties of Viscosity, Flash point, and Calorific value. Biodiesel production depends upon methanol quantity, potassium hydroxide quantity, reaction time, reaction temperature and stirrer speed. Efforts have been made to optimize transesterification process by considering some of the above parameters. In addition, some technical test procedures used to determine the properties of the biodiesel are described briefly.

KEY WORDS : Biodiesel, methanol, fuel, transesterification

INTRODUCTION

Alternative fuels, Energy Conservation and Management, Energy Efficiency and Environmental Protection have become important in recent years because of fossil fuel depletion and environmental degradation. The alternative fuels can be better tried for diesel engines as compared to petrol engines because of the construction of the diesel engine is very robust and can work at higher compression ratios along with a significant amount of excess air. Biodiesel obtained from vegetable oils has been considered a promising option [1].

The concept of using vegetable oil as an engine fuel dates back to 1885, when Rudolf Diesel (1858-1913) developed the first engine to run on peanut oil which he demonstrated at the World exhibition in Paris in 1900.he stated that ‘‘The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become in course of time as important as petroleum and the coal tar products of the present times’’. The major difficulties in using the crude vegetable oils in diesel engines are because of their high viscosity, low volatility and poor cold flow conditions. Vegetable oil when used as a fuel cause nozzle choking and coking, gumming, deposition on the piston top, sticking of piston rings and contamination of the lubricating oil. Injection difficulties and poor atomization due to its high viscosity are major problems. Apart from these, starting the engine may become difficult especially in cold weather; because of poor atomization and low volatility of the fuel [2]. There are four ways to use vegetable oil in a Diesel Engine.1. Direct use or blending in diesel fuel. 2. Micro emulsions in diesel fuel. 3. Thermal cracking (pyrolysis) of the vegetable oil. 4. Transesterification to produce biodiesel. Out of these, transesterification appears to be the most popular and the best way to use a vegetable oil.

Biodiesel is the name of a clean burning alternative fuel, produced from straight vegetable oil, animal oil/fats, tallow, waste cooking oil and, 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 engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. The process that is used to produce biodiesel is called transesterification. The largest possible source of suitable oil comes from both edible and non-edible vegetable oils such as rapeseed, palm or soybean, Mahua, Pongamia, Karanja, Linseed, Jatropha and Neem oil [3].

SELECTION OF NON-EDIBLE VEGETABLE OIL

The production of methyl esters from edible oils is currently much more expensive than hydrocarbon-based diesel fuels due to the relatively high costs of vegetable oils. The cost of biodiesel can be reduced if we consider non-edible oils, and used frying oils instead of edible oils. Non-edible oils such as Neem, Mahua, Karanja, Babassu, Jatropha and Linseed are easily available in many parts of the world including India, and are very cheap compared to edible oils. Vegetable oils offer an advantage of comparable fuel properties with diesel fuel,

and it was reported that diesel engine without any modification would run successfully on a blend of 20% vegetable oil and 80% diesel fuel without damage to engine parts.

Based on the literature survey the choice of oil for the present investigation is dependent upon the following criterion [3].

- It should be easily available.
- It should give the high heating value.
- It should be non-edible and preferably a crop oil.
- It should have low viscosity.

EXPERIMENTAL SETUP

A round bottom flask was used as laboratory scale reactor with a reflux condenser and it consists of motorized stirrer, straight coil electric heater, and stainless steel containers for the experimental purposes. The mixture was stirred at constant speed for all test runs and the temperature range of 60 deg C - 65 deg C was maintained during this experiment. Three trial runs were carried out for each combination of reactants and process conditions and average results are explained graphically in the Figures.1-10.

ESTERIFICATION PROCESS

Transesterification is the chemical reaction between triglycerides and alcohol in the presence of catalyst to produce monoesters. The long and branched chain triglyceride molecules are transformed to monoesters and glycerin. Transesterification process consists of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The Glycerides are converted into glycerol and yielding one ester molecule in each step. The properties of these esters are comparable to that of diesel. The overall transesterification reaction can be represented by the following reaction scheme [4].

Triglyceride + Alcohol $\xleftrightarrow{\text{catalyst}}$ Alkyl Ester + Glycerol

Stoichiometrically, three moles of alcohol are required for each mole of triglyceride, but in practice, a higher molar ratio is employed in order to displace the equilibrium for getting greater ester production. Though esters are the desired products of the transesterification reactions, glycerin recovery also is important due to its numerous applications in different industrial processes. Commonly used short chain alcohols are methanol, ethanol, propanol and butanol. The yield of esterification is independent of the type of alcohol used. Therefore, the eventual selection of one of these four alcohols will be based on cost and performance considerations. Methanol is used commercially because of its low price, its physical and chemical advantages (polar and shortest chain alcohol) and KOH is easily dissolved in it. Alkaline hydroxides are the most effective transesterification catalysts as compared to acid catalysts. Potassium hydroxide and sodium hydroxide are the commonly used alkaline catalysts. Alkaline catalyzed transesterification of vegetable oils is possible only if the acid value of oil is less than four. Higher percentage of FFA in the oil reduces the yield of the esterification process. However, methanol is toxic and its production depends on fossil fuels [5].

BIODIESEL PRODUCTION FROM LINSEED OIL:

In the transesterification process, alcohol reacts with oil to release three “ester chains” from the glycerin backbone of each triglyceride. Production of Biodiesel by transesterification process will consist of the following stages.

1. Removal of moisture from the oil.
2. Heating the oil to a required temperature.
3. Mixing of alcohol and catalyst in a required proportion.
4. Reaction of the alkoxide and vegetable oil in the reactor.
5. Separation of the glycerol.
6. Washing of the methyl ester.
7. Removal of the Moisture from the Biodiesel.

Optimization of transesterification process for biodiesel production depends upon various parameters such as

- Reaction temperature.
- Ratio of alcohol to oil.
- Catalyst type and concentration.
- Mixing intensity.
- Purity of reactants.
- Reaction temperature.

Efforts have been made to optimize transesterification process by considering some of the above parameters. The following sections give the details of the effects of the above parameters in producing biodiesel.

<u>Production of Biodiesel by Changing the Amount of Methanol used in the Reaction</u>

For this study, 200 ml of vegetable oil, 2 g of Potassium hydroxide as catalyst, reaction time of 3 hours in each sample were taken as standard quantity, and methanol was varied from 24 ml to 144 ml. Figures 1, and 2 represent the percentage yield of biodiesel and viscosity as a function of methanol quantity. It is seen that, there is no conversion with 24 ml of methanol.

The percentage of biodiesel yield increases with increase in methanol quantity; Fig.1 shows that when methanol quantity was varied from 72 ml to 144 ml, the percentage of biodiesel yield became nearly constant. Hence, one could conclude that the conversion of vegetable oil into biodiesel was almost completed with 72 ml of methanol.

It is clear from Fig.2 that if the methanol quantity in the sample is increased, the viscosity decreases up to a

certain quantity of methanol. The lowest viscosity is obtained for the sample using 120 ml of methanol and next highest value is at 96 ml. The highest viscosity was observed for the sample using 32 ml of methanol. Based on the consideration on the cost of methanol, it was decided that 96 ml of methanol was a suitable optimum quantity, which will gives a yield of 97% and a viscosity of 4.17mm2/s. Viscosity was very low (i.e. 4.10 mm^2/sec) at 120 ml of methanol but as yield was higher at 96 ml of methanol, therefore for cost of the methanol consideration we selected the optimum value of the methanol as 96 ml and viscosity as 4.17 mm^2/sec.

Production of Biodiesel by Changing the Quantity of the Base used

For this study, 200 ml of vegetable oil, 96 ml of methanol and a reaction time of 3 hours for each sample as standard quantity was taken and Potassium hydroxide as catalyst was varied from 1 g to 4 g. A plot of percentage biodiesel yield and viscosity versus quantity of potassium hydroxide is shown in Figures 3 and 4. It was found that the optimum quantity of catalyst works out to be about 1.5 g per 200 ml of oil to get the maximum percentage of biodiesel yield as shown in Fig. 3. It is clear from the Fig.4 that the viscosity is lowest (i.e. 3.9 mm^2/s) for the sample using 2 g potassium hydroxide and the highest viscosity (i.e. 4.58 mm^2/s) is observed for the sample using 1gm potassium hydroxide. Incidentally, the sample, which had the lowest viscosity, also had the lower calorific value.

Based on the yield of biodiesel and its viscosity considerations, the optimum quantity of KOH was taken to be 2 g. Viscosity of the biodiesel was minimum (i.e. 3.9 mm^2/s) at 2 g potassium hydroxide. Therefore, 2 g of KOH was selected as optimum amount of base required for the 98% yield of biodiesel.

Production of Biodiesel by Changing the Reaction Time

To study the effect of reaction time on the transesterification process, 200 ml of Vegetable Oil, 96 ml of Methanol and 2 g of Potassium hydroxide as a catalyst was taken; reaction time was varied from 30 min to 240 min. A plot of percentage yield and Viscosity of biodiesel versus reaction time is shown in Figures 5 and 6. The reaction with zero time was of course zero. As shown in Fig.5 the percentage yield increased drastically with time in the starting phase of 30-60 minutes; however, the quality of conversion was doubtful. After that, the yield became nearly constant, but the quality improved with time. The best time could be about 150 minutes. It is noticed from Fig.6 that the lowest viscosity was obtained for the sample whose reaction time is 180 minutes and highest viscosity is obtained for the sample whose reaction time was 60 minutes. Viscosity of the biodiesel is minimum (i.e. 4.0 mm^2/s) at 180 minutes. Therefore 180 minutes was selected as optimum reaction time required for the 97% yield of biodiesel.

Production of Biodiesel by Changing the Reaction Temperature

To study, the effect of reaction temperature on the transesterification process, 200 ml of vegetable oil, 96 ml of methanol and 2.0 g of potassium hydroxide as a catalyst was taken. Reaction temperature was varied from 35 deg C to 75 deg C for the reaction time of 180 minutes.

A plot of percentage yield of biodiesel and Viscosity versus reaction temperature is shown in Figures 7 and 8. It is noticed from Fig.7 that the percentage yield increased drastically with temperature in the starting phase of 35 deg C – 55 deg C however, the quality of conversion was doubtful. After that, the yield became nearly constant, and quality improved with temperature.

It may be observed from Fig. 8 that the lowest viscosity is obtained for the sample whose reaction temperature is 65 deg C and highest viscosity is obtained for the sample whose reaction temperature is 35 deg C. Viscosity of the biodiesel is minimum (i.e. 3.75 mm^2/s) at 65 deg C. Therefore 65 deg C was selected as optimum reaction temperature required for the 98% yield of biodiesel.

OPTIMIZATION OF TRANSESTERIFICATION PROCESS

The conclusion arrived from the effect of different variables was that the sample which consists of 200 ml of vegetable oil, 96 ml of methanol, 2 g of potassium hydroxide and a reaction time of 180 minutes, had properties fairly close to diesel fuel. It was necessary to see the effect of reaction time on the transesterification process on the optimized sample as mentioned above. Figures 9 and 10 give the plot of percentage yield of biodiesel and viscosity versus reaction time for the optimized sample.

It is observed from Fig.9 that the maximum biodiesel yield is obtained for the sample whose reaction time is 150 minutes and lowest yield for a reaction time of 30 minutes, another peak occurs at a reaction time of about 120 minutes, third peak occurs at a reaction time of 180 minutes. For other reaction times, the yield of biodiesel is more or less the same. Based on the above graph one can conclude that 180 minutes of reaction time is sufficient to produce biodiesel. As shown in Fig.10 that the lowest viscosity is observed for the sample whose reaction time is 180 minutes and the highest viscosity is observed for the sample whose reaction time is 30 minutes. Samples whose reaction times are 150, 180, 210 and 240 minutes had nearly the same viscosity. Therefore, one could select the sample whose reaction time is 180 minutes as a standard sample for biodiesel production in the laboratory and optimal values are given in Table 1.

PROPERTIES OF BIODIESEL

Since biodiesel is produced in quite differently scaled plants from vegetable oils of varying origin and quality, it is necessary to standardize fuel quality so as to guarantee engine performance. In order to evaluate various physical, chemical, and thermal properties several tests were conducted to characterize biodiesel in relation to diesel oil. The properties of biodiesel and diesel fuels, as given in Table 2, show many similarities, and therefore, biodiesel is rated as a strong candidate as an alternative to diesel. Most of the fuel properties of linseed oil methyl ester are quite comparable to those of diesel.

The transesterification process reduces the molecular weight of the oil to one-third, viscosity by about one-eighth, and increases the volatility marginally [7].The present results obtained show that, the transesterification process improved the fuel properties of the oil with respect to specific gravity, viscosity, flash point and acid value. The comparison of these properties with diesel shows that the methyl ester has a relatively closer fuel property values to that of diesel (than that of oil). Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection from the diesel injector. The viscosity of fatty acid methyl-esters can go to very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. The viscosity of biodiesel is closer to that of diesel. Hence, no hardware modifications are required for handling this fuel (Biodiesel) in the existing engine [8]. Viscosity index is an arbitrary number indicating the effect of change of temperature on the Kinematic viscosity of an oil. A high viscosity index signifies relatively small change of Kinematic viscosity with temperature.

Benzoic acid was used as a reference fuel to determine the calorific value of biodiesel and linseed oil. The results of the tests conducted on various fuels using Bomb calorimeter are given in Table 2.The residue left after combustion of diesel oil in the crucible was in the form of black carbon ash pellets (charcoal like foamy substance). The quantity of such a foamy charcoal like ash substance was very low in case of Linseed oil methyl ester combustion. This typical observation points out lesser ash content and cleaner combustion characteristics of linseed oil methyl ester [9].

The calorific values of methyl esters are lower than that of diesel because of their oxygen content. Biodiesel contains 10 – 11% oxygen (w/w), thereby enhancing the combustion process in an engine [10]. Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flash point of biodiesel is higher than petrodiesel, which is safer for transport purpose. The flash point of linseed oil is lowered by transesterification process but it is still higher than that of diesel. A small percentage addition of biodiesel with diesel increases the flash point of diesel. Hence, it is safer to store biodiesel–diesel blends as compared to diesel.

Pour point analysis shows that performance of biodiesel is as good as diesel oil in cold conditions. It has also been reported that the use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the biodiesel without having any negative effect on its cold flow properties. Copper strip corrosion test serves as a measure of possible difficulties with copper, brass or bronze parts of the fuel system. The presence of acids or Sulphur containing compounds can tarnish the copper strip, thus indicating the possibilities for the corrosion. Acid number is used to determine the level of free fatty acids that may be present in the biodiesel. Higher acid number biodiesel may increase the fuelling system deposits and corrosion.

CONCLUSION

Based on the above tests one can conclude that transesterification is one of the best methods to improve the fuel properties of the triglycerides. Optimization of transesterification process for biodiesel production depends upon several parameters such as methanol quantity, potassium hydroxide quantity, reaction time, reaction temperature and stirrer speed.

The yield of biodiesel decreases with the increase of moisture content and free fatty acids present in the oil and temperature of the reaction should be maintained below the boiling point of the alcohol.

The present results obtained shows that, the transesterification process improved the fuel properties of the oil with respect to specific gravity, viscosity, flash point and acid value. A comparison of these properties with diesel shows that methyl ester has relatively closer fuel property values to those of diesel than those of pure vegetable oil. Hence, no hardware modifications are required for handling this fuel (biodiesel) in the existing engine. Biodiesel is proved to be a potential candidate for partial substitute of mineral diesel oil.

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Table 1.Optimised values for Biodiesel Production.

Oil (ml)	Methanol(ml)	KOH (g)	Tempr. (^{O}C)	Time (min)	Yield (%)	Viscosity (mm^2/s)
200	96	2	65	180	97	3.75

Table 2. Various Properties of different Fuels.

Properties	ASTM Test	Diesel	Linseed Oil	LOME	B20
Viscosity at 40 ^{0}C (mm^2/s)	D445	2.246	24.36	3.75	2.57
Viscosity at 100 ^{0}C (mm^2/s)	D445	1.10	15.73	1.98	1.35
Viscosity index	D445	359.3	184.31	262.3	338
Calorific value in (MJ/Kg)	D240	43.68	39.20	40.13	41.9
Specific gravity	D4052	0.850	0.903	0.860	0.87
API gravity (^{O}C)	D4052	34.97	25.19	30.97	32.8
Flash point (^{O}C)	D93	70	238	163	156
Cloud point ^{O}C	D2500	-6	2	-3.5	-4
Pour point (^{O}C)	D97	-16	-4	-14	-15
Aniline point (^{O}C)	-----	72		30 - 100	40 - 100
Copper strip corrosion	D130	---	---	1a	1a
Raid vapour pressure (kPa)	D323	---	---	13.79	13.9
Acid value (mg KOH/g)	D974	<1	3.71	0.78	0.76
Carbon residue (wt %)	D524	0.015	0.28	0.032	0.03

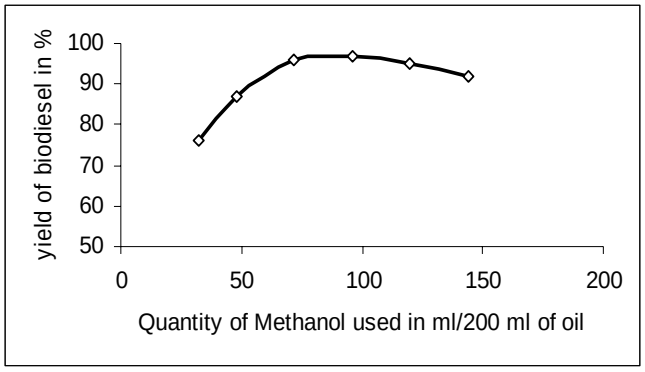

Figure1 Effect of Amount of Methanol on Biodiesel Yield

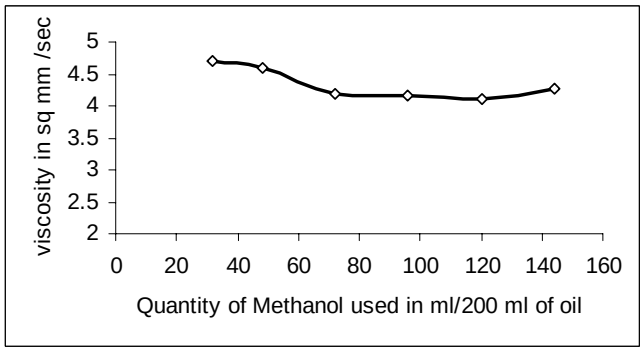

Figure 2 Effect of Amount of Methanol on Viscosity

Figure 3 Effect of Amount of Base on Biodiesel Yield.

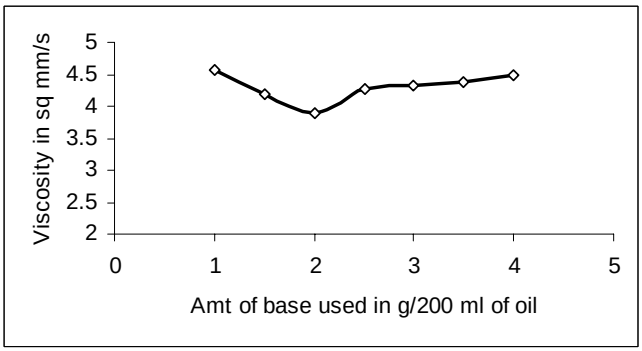

Figure 4 Effect of Amount of Base on Viscosity

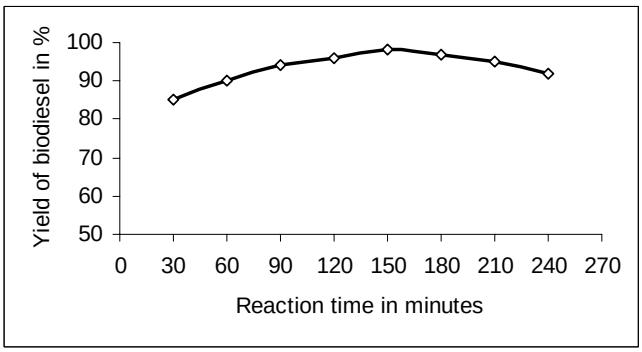

Figure 5 Effect of Reaction Time on Biodiesel Yield

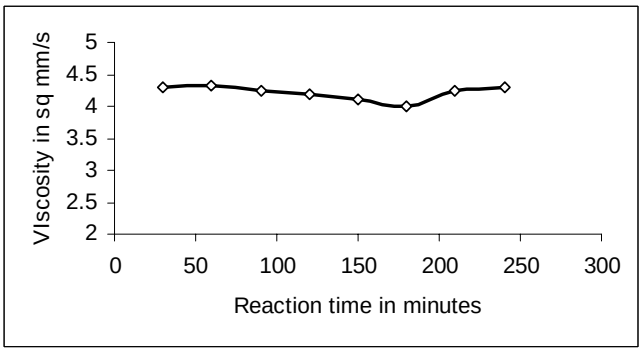

Figure 6 Effect of Reaction Time on Viscosity

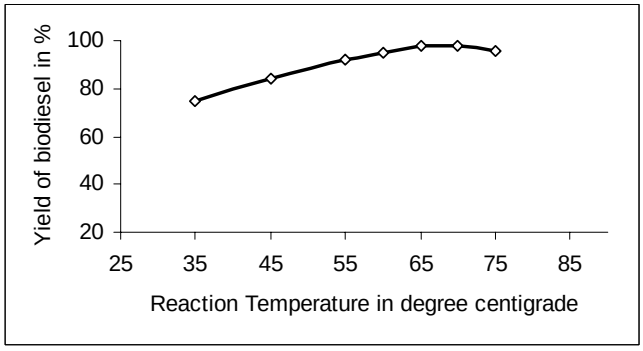

Figure 7 Effect of Reaction Temperature on Yield

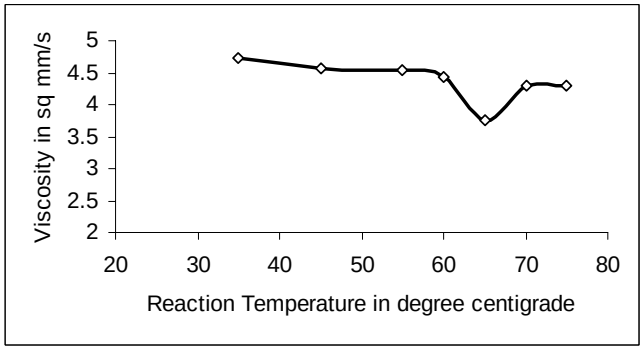

Figure 8 Effect of Reaction Temperature on Viscosity

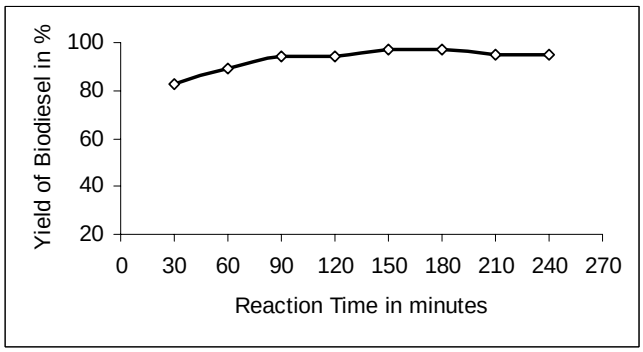

Figure 9 Effect of Reaction Time on Yield

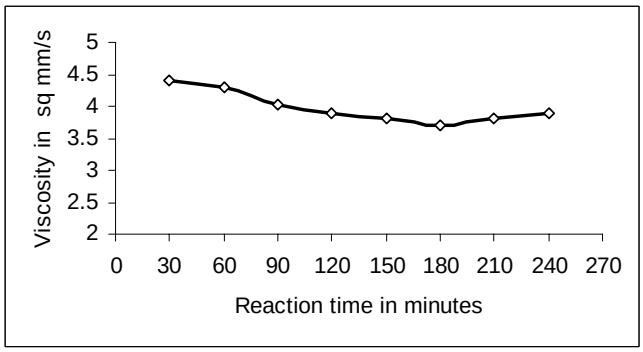

Figure 10 Effect of Reaction Time on Viscosity