

The Viscosity Method for Monitoring Transesterification of Vegetable Oils for Biodiesel

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Abstract

The transesterification of vegetable oils such as canola oil, soybean oil and corn oil with the changes of catalyst and molar ratio of methanol to oil was performed at 60°C and 1000s⁻¹ of shear rate on the rotary viscometer. The viscosity of fatty acid methyl esters was calculated by experimental shear stress. The viscosity of fatty acid methyl ester at different temperature was estimated by Orrick and Erbar's model. The overall yield was predicted through monitoring the viscosity of fatty acid methyl esters. The overall yield at the 1:6 molar ratio and 0.6wt% NaOH for vegetable oils showed 85 - 95% for 5.1 – 7.1 x10⁻³ Pa s of viscosity in 25 minutes and was predicted well by the relation of viscosity(η_{mix}) monitored.

Keywords: rotary viscometer, Orrick and Erbar's model, unsaturated bonds, functional groups, relation of viscosity (η_{mix})

1. Introduction

Fossil fuel combustion releases a large amount of CO₂ blocked away from the atmosphere and contributes to a global warming. So the most significant impact of the emitting CO₂ level is the world climate change – green house gas effect (Shay, 1993). At the same time, due to the shortage of global petroleum supply and political issues, the price of crude oil has been climbing to a historic high point.

The discussion on these matters leads to an enforced search for production of fuels

from renewable sources, and a lot of interests are being placed on biodiesel (fatty acid methyl esters, FAME) from biological sources such as vegetable and animal oils. Biodiesel called as an alternative diesel fuel is produced from the transesterification of triglyceride with short - chained alcohol using a base or acid catalyst (Lotero et al., 2005; Schwab et al., 1987).

During transesterification, mono and diglyceride are present and mono glyceride acts as an emulsifier to dissolve a little amount of glycerine in biodiesel. Therefore, the separation of biodiesel and glycerin mixture is difficult, and the increased turbidity from the high cloud point as well as pour point makes the quality of it go worse for winter (Srivastava et al., 2000). In this respects, the viscosity of biodiesel mixture is one of important parameters that characterize the quality of biodiesel because of its concern on the application to ensure proper fuel flow in diesel engines (Ali et al., 1995b; Canakci et al., 2001). As the transesterification proceeds, the viscosity of biodiesel mixture is going down with time (Allen et al., 1999). When the transesterification reaches the equilibrium, the minimum viscosity of biodiesel mixture is attained. The degree of transesterification of triglyceride to reach the equilibrium can be judged by the changes of viscosity.

Up to now, many analytical methods using chromatographic analysis are being used to evaluate the degree of conversion of triglyceride into biodiesel (Liu et al., 1994). Knoke (2000) has applied ¹H nuclear magnetic resonance spectroscopy to monitor the transesterification. However, the disadvantages of chromatographic methods are the high costs and no real time indication due to the treatment of sample. De Filippis et al. (1995) have studied the correlation between the fatty acid methyl ester concentration and its viscosity. There is a possibility that the viscosity change could be used in the on-line process monitoring of transesterification. The on-line process monitoring system process is applied to find out the condition of minimum viscosity of biodiesel mixture. And the viscosity changes have an effect on an overall yield of biodiesel. Therefore, a process monitoring methods based on viscosity measurement will control the desirable quality of the biodiesel.

In my research, the transesterification of vegetable oils using alkaline catalysts was performed in rotary viscometer. This paper aims to find out the relation of the viscosity of biodiesel mixture and the overall yield of it on the equilibrium of transesterification from monitoring the viscosity changes in the experimental ranges.

2. Materials and Methods

2.1. Chemical

Canola, peanut and corn oils were purchased from Sigma Aldrich Chemical Co. (St. Louse, MO). Also NaOH, KOH and NaOCH₃ were purchased from Cole Parmer (Vernon Hill, IN).

Methods

The rotary viscometer (LV DV-11+PRO, Brookfield, Co. U.S.) consists of inner mixer (volume: 9ml) and NV Sensor. The temperature was controlled by steam - jacket. The vegetable oils preheated to 60°C were put into the mixer. The alkaline catalysts, which were dissolved into 200ml of methanol, were fed to the bottom of the mixer using the syringe. The transesterification was done with the changes (1:4, 1:6, 1:8) of molar ratio and the changes (0.4wt%, 0.6wt%, 0.8wt %) of catalyst amount. The shear stress was read under 1000s⁻¹ of shear rate by the sensor. The sample was taken at the intervals of 5min, 15min, 20min and 25min. And the methanol was removed by the vacuum distillation. The mixed solvent (n – hexane and chloroform; 2:1 of mixing ratio (v/v)) extracted biodiesel mixture. After the extraction, the extracted mixture was separated as the upper portion (biodiesel) and the bottom portion (glycerine) by the centrifugation. The mixed solvents of upper portion were removed by the vacuum distillation. 1ml of sample was injected to the column of HPLC (US, ISCO 2350). The compositions and amounts of fatty acid methyl esters were analyzed by the UV detector (US, Waters, 486) with 205nm of wavelength in HPLC. The mobile phase was acetone and acetonitrile, and the stationary phase was octa decyl silica.

3. Results and Discussion

3.1. The Comparisons of shear stress and viscosity

The shear stress of biodisel mixture is expressed in Eq. (1) by the viscosity law of Newtonian fluid.

$$\tau = -\eta_{\text{mix}} du/dy, \quad (1)$$

where τ is the shear stress(Pa), η_{mix} (Pa s) the viscosity of biodiesel mixture, and du/dy the shear rate. The viscosity (η_{mix}) is determined by the experimental shear stress by Eq. (1).

The Irving's Eq. (2) can be applied to calculate the viscosity (η_{mix}) of biodiesel mixture on the assumption of the neglect of eventual fatty acid methyl esters associations (De Filippis, 1995).

$$\ln \eta_{mix} = \sum w_i \ln \eta_i, \quad (2)$$

where η_i is the viscosity of respective fatty acid methyl ester(Pa s) and w_i the weight fraction of fatty acid methyl ester. The viscosity(η_i) at different temperature was estimated by Orrick and Erbar's model in Eq. (3) allowing for the number of double bonds and functional groups given in the Table 1. (Prausnitz et al., 1981).

$$\ln [\eta_i / (\rho_i M_i)] = A_i + B_i / T, \quad (3)$$

$$A_i = -6.95 - 0.21 n,$$

$$B_i = 275 + 99 n \quad (4)$$

where ρ_i is the density of fatty acid methyl ester (kg/m^3), M_i the molecular weight of fatty acid methyl ester, T the Calvin's absolute temperature (K), and n the number of carbon atom.

Fig. 1 shows the comparison of shear stress and viscosity with different molar ratios during transesterification of canola oil. The shear stress and the viscosity of biodiesel mixture appeared to be constant after the reach of equilibrium. At that time, the shear stress and the viscosity for the 1:8 molar ratio were lower than the 1:4 molar ratio, and their data for the 1:8 molar ratio were 5.1Pa, 5.1×10^{-3} Pa s respectively. Therefore, the shear stress and the viscosity decreased with the increase of molar ratio of methanol to oil due to the easy breakage of triglyceride. After the completion of transesterification using 0.6wt% NaOH at 60°C, 1000s^{-1} of shear rate and the 1:6 molar ratio, the mixture of biodiesel and glycerin was separated, and the fatty acid methyl esters were cooled to 40°C. The density of biodiesel mixture was 868kg/m^3 . And its kinematic viscosity was measured as $6.2 \times 10^{-3} \text{mm}^2/\text{s}$ and estimated by Orrick and Erbar's model. The estimated kinematic viscosity ($6.1 \times 10^{-3} \text{Pa s}$) is a little higher than 1 – $6\text{mm}^2/\text{s}$ of ASTM B100 standard from D-6751 method. The kinematic viscosity for 1:8, 1:6 and 1:4 was compared on Fig.2. Orrick and Erbar's model was applied appropriately to estimate η_{mix} in my experimental ranges.

3.2. Effects of molar ratios on viscosity and overall yield

Transesterification is a reversible reaction, and the increasing molar ratio accelerates the reaction. However, higher molar ratio interferes in the separation of glycerin. Nimcevic et al. (2000) pointed the optimum molar ratio of methanol to oil is 1:6 from the transesterification of rapeseed oil using alkaline catalyst at 65°C. Nouredдини et al. (1997) showed the optimum molar ratio is 1:8 from the transesterification of soybean oil at 80 using 0.5wt% NaOH.

The effects of molar ratios on viscosity and the overall yield from the transesterification of canola oil are shown on Fig.3. The viscosity of biodiesel mixture decreased due to the presence of di- and monoglyceride, and the overall yield increased because of the irreversible transesterification with the increase of molar ratio.

When the molar ratio reaches 1:8, the difficult transfer of methoxide ion to the triglyceride take place owing to the film of excess methanol formed on the surface of triglyceride. And the overall yield for the 1:8 molar ratio showed nearly constant of 95% close to the overall yield for the 1:6 molar ratio. So, the viscosity and the overall yield for the 1:6 molar ratio were 5.1×10^{-3} Pa s and 95% in 25minutes. From this result, the optimum molar ratio appeared to be 1:6.

3.3. Effects of catalysts on viscosity and overall yield

When water and free fatty acid in vegetable oil are far below its limiting level, the alkaline catalysts such as NaOCH₃, KOCH₃, NaOH, KOH and K₂CO₃ are common for transesterification (Sridharan et al., 1974). The performance of catalyst depends on the formation of strong nucleophile like alkoxide ion and water during the dissolution of catalyst into methanol.

When the alkoxide ion is formed, this nucleophilic anion attacks the carbon atom on triglyceride easily, and the tetrahedral intermediate is broken into di- and mono glyceride. So, the viscosity of biodiesel mixture decreases with the conversion of triglyceride into fatty acid methyl ester.

Fig.4 shows the effects of catalysts on viscosity and overall yield from the transesterification of canola oil. The overall yield increased with the viscosity decrease of biodiesel mixture due to the breakdown of tri – and diglyceride.

The viscosity and the overall yield for NaOCH₃ were 5.1×10^{-3} Pa s and 95% in 25 minutes. This is attributed to a little saponification, which came from less formation of water during the attack of methoxide ion to triglyceride (Freedman et al., 1984).

The order of catalyst performance in the aspect of only the overall yield is NaOCH₃>

NaOH > KOH. But the overall yield for NaOH was close to that for NaOCH₃ in 25 minutes. So, the appropriate catalyst appeared to be NaOH because of cheaper price of NaOH than NaOCH₃.

3.4. Effects of amount of NaOH on the viscosity and the overall yield

As the amount of alkaline catalyst increases, the intensity of alkoxide ion is higher, and this ion transfers easily to the surface of oil. Therefore, the overall yield increases with the decrease of viscosity due to the conversion of triglyceride into di- and mono glyceride. Further, the increase in catalytic amount does not increase the overall yield, and it might bring the saponification of biodiesel mixture. When the metal ion is not removed, the quality of biodiesel goes bad as well as the addition of extra costs to remove it

Krisnangkura et al. (1992) stated the usual range of the amount of alkaline catalyst is 0.5 – 1wt% for transesterification of vegetable oils. The effects of the amount of NaOH on viscosity and overall yield are shown on Fig.5. The overall yield and viscosity for 0.6wt% NaOH approached 95% and 5.1×10^{-3} Pa s for 0.8wt% NaOH in 25 minutes. Therefore, the optimum amount of NaOH was 0.6wt%.

3.5. Effects of vegetable oils on the viscosity and the overall yield

As the unsaturated fatty acids in triglyceride increases, the methoxide ion attacks unsaturated carbon atom on triglyceride, and the transesterification accelerates. The unsaturation of fatty acid in vegetable oil which stands for the localization of π - electrons around the double bonds is an operating factor (Ma et al., 1999).

Vegetable oils such as canola oil, soybean oil and corn oil, which contain different number of double bonds to symbolize the unsaturated fatty acid were chosen as triglyceride in my research. The effects of vegetable oils on the viscosity and the overall yield are shown on Fig.6. Canola oil (65% oleic acid, 23% linoleic acid, 6% linolenic acid) showed 5.1×10^{-3} Pa s and 95% due to the more unsaturation of fatty acid than soybean oil (23% oleic acid, 55% linoleic acid, 6% linolenic acid) and corn oil (25% oleic acid, 6% linoleic acid). From this result, canola oil is an appropriate vegetable oil for transesterification.

3.6. Effects of viscosity on overall yield

The overall yield (Y_{overall}) is defined as Eq. (5).

$$Y_{\text{overall}} = M_f / M_o \quad (5)$$

where M_f is total amounts (kg) of final fatty acids calculated from experimental fatty acid methyl esters, M_o total amounts (kg) of initial fatty acids in vegetable oils. The stoichiometric molar ratio contributes to the conversion of the triglyceride into fatty acid methyl esters. The relation which correlates overall yield with viscosity is derived as Eq. (6) from the substitution of Eq. (3) and Eq. (4) into Eq. (5).

$$Y_{\text{overall}} = \sum m_i [\ln_i (\rho_i M_i) + A_i + B_i / T] / (M_o \ln \eta_{\text{mix}}), \quad (6)$$

where m_i is the amount(kg) of fatty acid calculated from experimental fatty acid methyl ester. So, the overall yield of fatty acid methyl esters is dependent on the terms of m_i and $\ln \eta_{\text{mix}}$.

Fig.7 shows the effects of vegetable oils and viscosity on overall yield.

As we can see Eq. (6), the overall yield increases with the decrease of viscosity (η_{mix}) regardless of vegetable oils. The overall yield was 85% - 95% for the ranges ($5.1 - 7.1 \times 10^{-3}$ Pa s) of viscosity after the steady state to reach in 25minutes. And the overall yield increased with the amount of unsaturated fatty acid.

We can infer the viscosity (η_{mix}) have an effect on the overall yield from the discussion and the operating range to meet minimum viscosity should be chosen.

4. Conclusions

The transesterification of vegetable oils using alkaline catalysts was done at 60°C and 1000s^{-1} of shear rate in rotary viscometer. The viscosity changes of biodiesel mixture were monitored, and the effects of its viscosity on the overall yield were examined. The viscosity of biodiesel mixture was calculated by the experimental shear stress and was well estimated by Orrick and Erbar's model allowing for the number of double bonds and functional groups in biodiesel mixture. And its kinematic viscosity ($6.1 \text{ mm}^2/\text{s}$) at 40°C was a little higher than the upper limit ($1 - 6 \text{ mm}^2/\text{s}$) of ASTM B100 standard. The optimum variables ranges were determined on a minimum point of the viscosity (η_{mix}) only monitored. For the optimum conditions of the 1:6 molar ratio and 0.6wt% NaOH, the overall yield for vegetable oils was 85% - 95% for the ranges ($5.1 - 7.1 \text{ Pa s}$) of viscosity in 25 minutes. The overall yield was predicted by the relation depended on the terms of m_i and η_{mix} , in Eq.(6).

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Table 1.

Orrick and Erbar group contribution for A and B

Fig.1. Comparison of shear stress and viscosity of biodiesel mixture with molar ratio at 60°C, 0.6wt% NaOH and 1000s⁻¹.

Fig.2.Comparison of measured kinematic viscosity, Orrick and Erbar's model and ASTM B100 standard at 40°C.

Fig.3. Effects of molar ratios of methanol to oil on viscosity and overall yield at 60°C, 0.6wt% NaOH and 1000s⁻¹.

Fig.4. Effects of catalysts on viscosity and overall yield at 60°C, the 1:6 molar ratio, 0.6wt% catalysts and 1000s⁻¹.

Fig.5. Effects of amount of NaOH on viscosity and overall yield at 60°C, the 1:6 molar ratio and 1000s⁻¹.

Fig.6. Effects of vegetable oils on viscosity and overall yield at 60°C, the 1:6 molar ratio, 0.6wt% NaOH and 1000s⁻¹.

Fig.7. Effects of viscosity on overall yield at 60°C, the 1:6 molar ratio, 0.6wt% NaOH and 1000s⁻¹.

Table1

Group	A	B
Carbon atoms	$-(6.95 + 0.21 n)$	$275 + 99 n$
Double bond	0.24	-90
-OH	-3.00	1600
-COOH	-0.90	770
C=O	-0.5	350
-COOH	-1.00	420

Fig.1

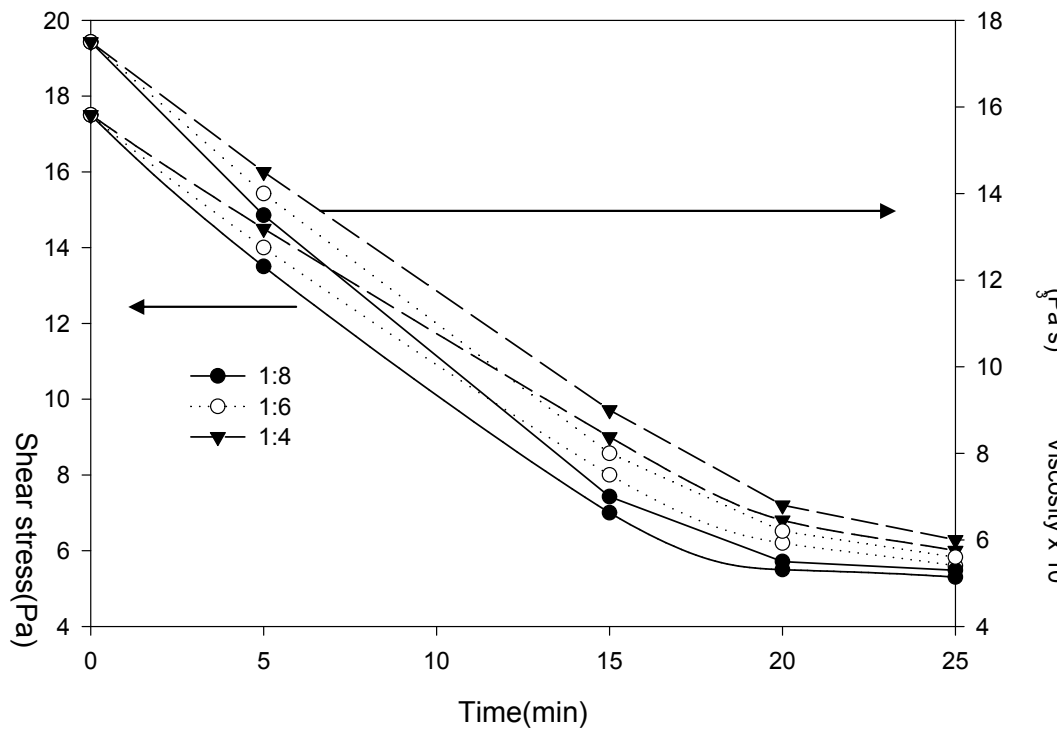


Fig.2

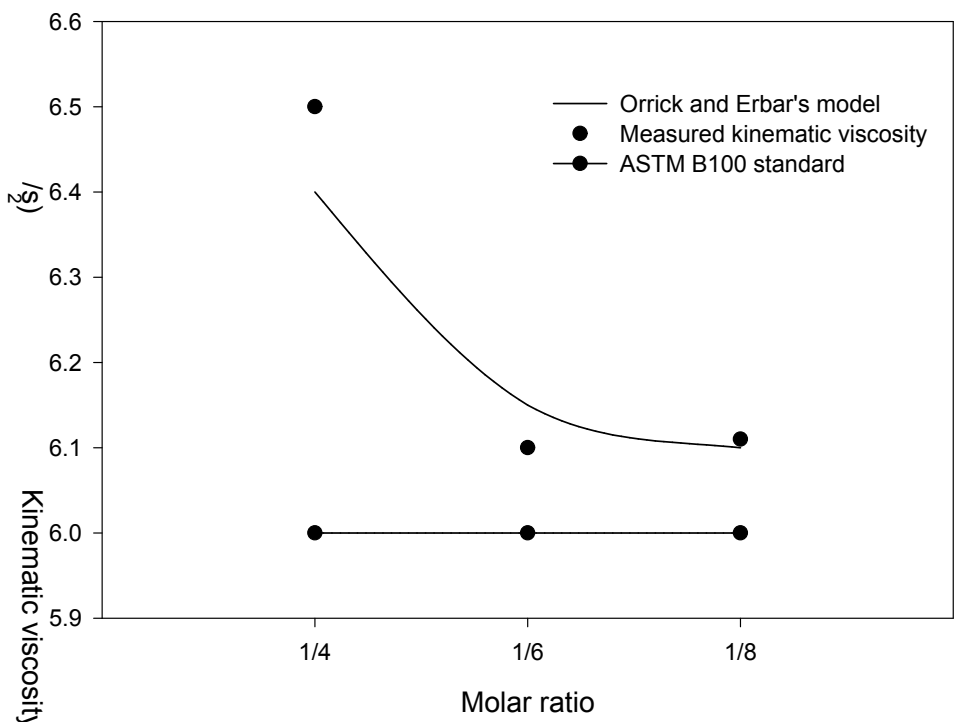


Fig. 3

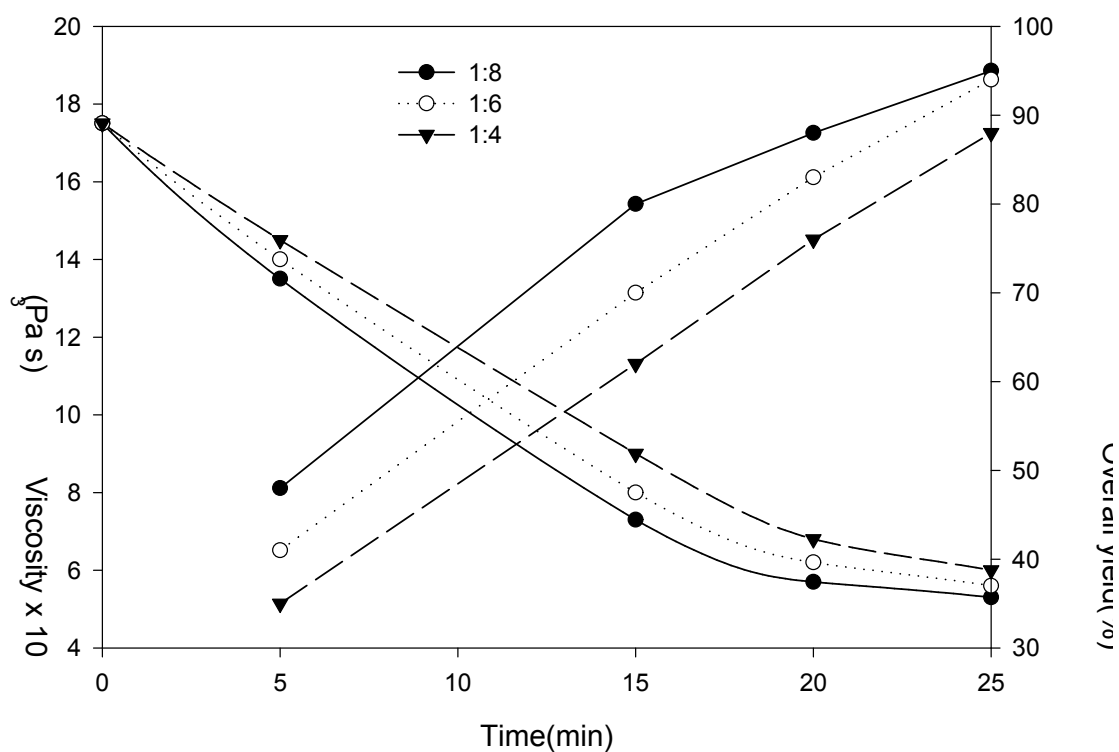


Fig.4

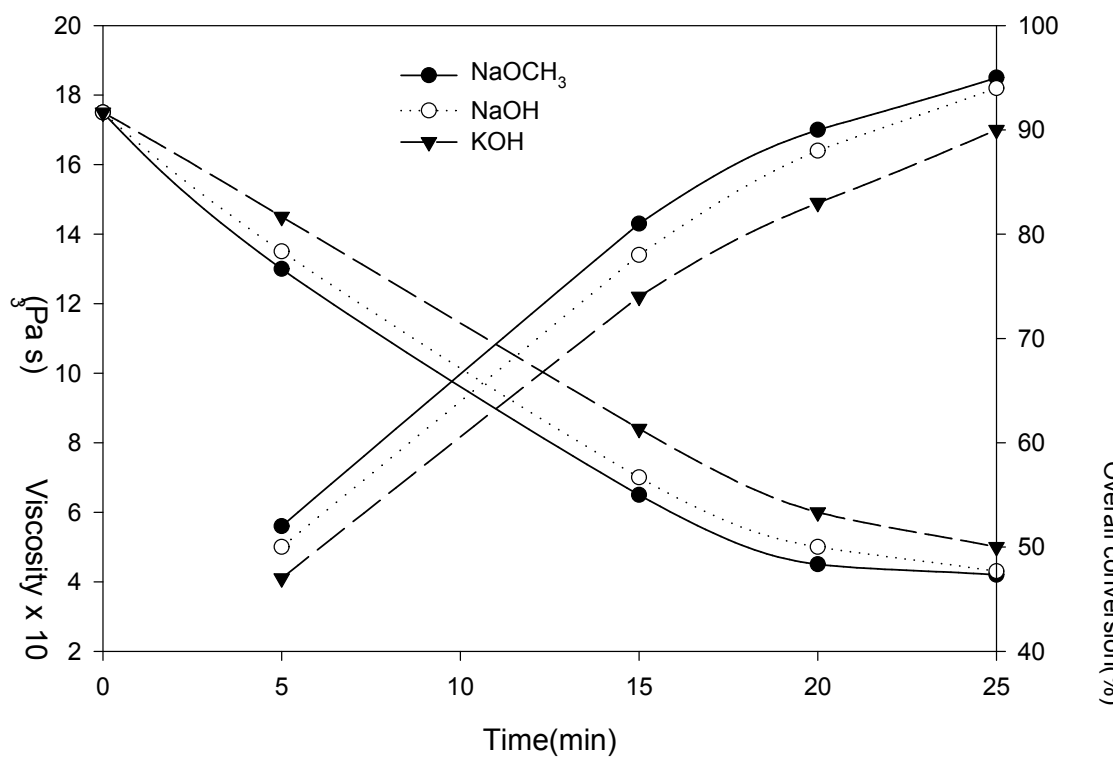


Fig.5

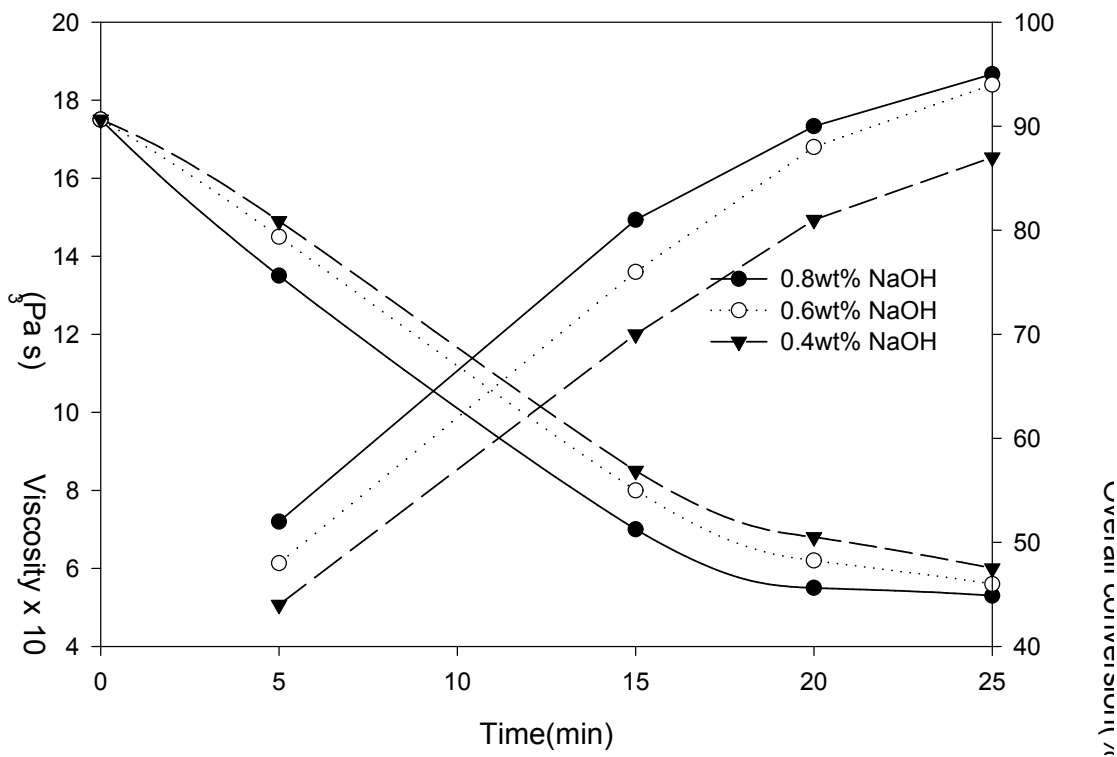


Fig.6

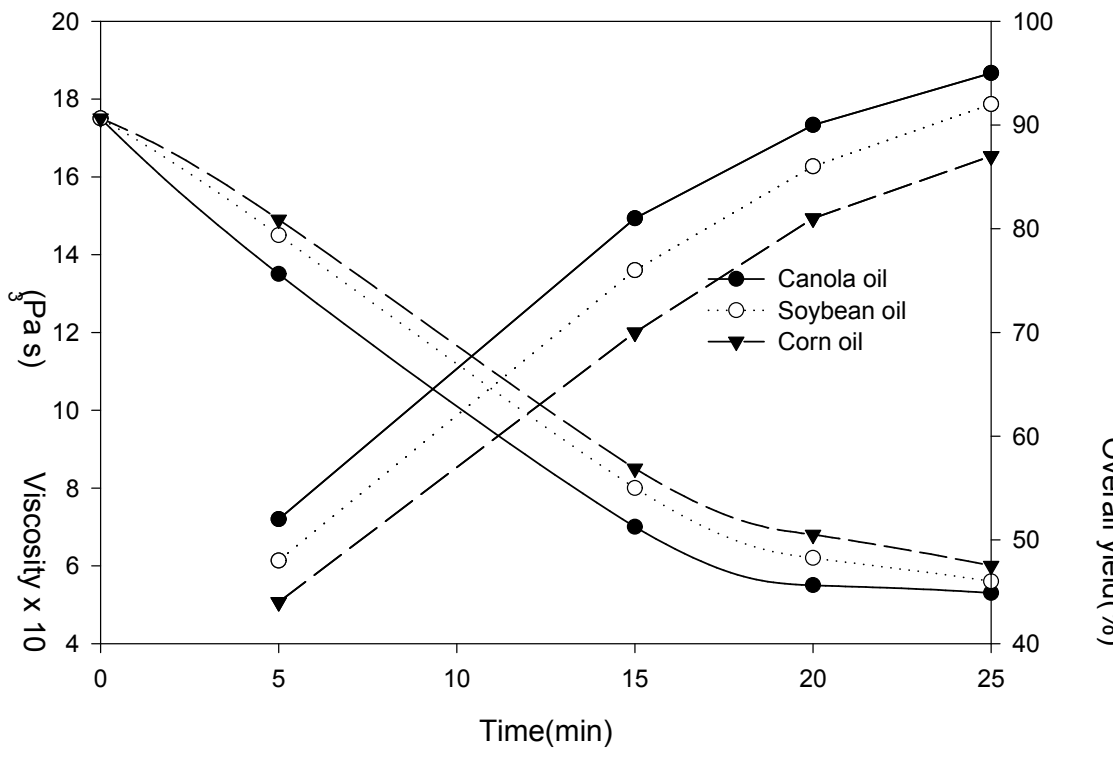


Fig.7

