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점도 모니터링에 의한 식물유의 바이오디젤화

현영진*

The Conversion of Vegetable Oils into Biodiesel by iscosity Monitoring

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ABSTRACT

The transesterification of vegetable oils such as canola oil, soybean oil and corn oil with the amount of catalyst and molar ratio of methanol to oil was performed at 60℃ and 1000s^{-1} of shear rate on the rotary viscometer. The viscosity of fatty acid methyl ester at different temperature was estimated by Orrick and Erbar's model. he 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 6.1 – 6.8mm^2/s of viscosity in 25 minutes and was predicted well by the relation of viscosity(η_{mix}) monitored.

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

Ⅰ. Introduction

Fossil fuel combustion releases a large amount of CO$_2$ blocked away from the atmosphere and contributes to a global warming. So the most significant impact of the emitting CO$_2$ level is the world climate change green house gas effect [1]. 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 bio-diesel (fatty acid methyl eaters, 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 [2,3].

During transesterification, mono and diglyceride are present and mono glyceride acts as

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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 [4]. 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 [5]. As the transesterification proceeds, the viscosity of biodiesel mixture is going down with time [6,7]. 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 [8]. Knobe [9] 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 Filipps et al. [10] 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.

II. 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 (Vermon Hill, IN).

2.2. 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℃ 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.

Ⅲ. 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.

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

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 Grunberg-Nissan 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 [8].

$$\ln\eta_{mix} = \sum_i^n w_i \ln\eta_i + \sum_i^n \sum_j^n w_i w_j A_{ij} \qquad (2)$$

where η_i is the viscosity of respective fatty acid methyl ester(Pa s) and $w_{i,j}$ the weight fraction of i,j component A_{ij} the binary interaction coefficient. 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. [11].

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

$$A_i = -6.95\ 0.21\ n,$$
$$B_i = 275 + 99n \qquad (4)$$

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.

Table 1. Orrick and Erbar group contribution for A and B

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 shows the comparison of shear stress and viscosity with different molar ratios during transesterification of canola oil. The shear stressand 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, 5.1mPa 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℃, $1000s^{-1}$ 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℃. The density of biodiesel mixture was $868kg/m^3$.

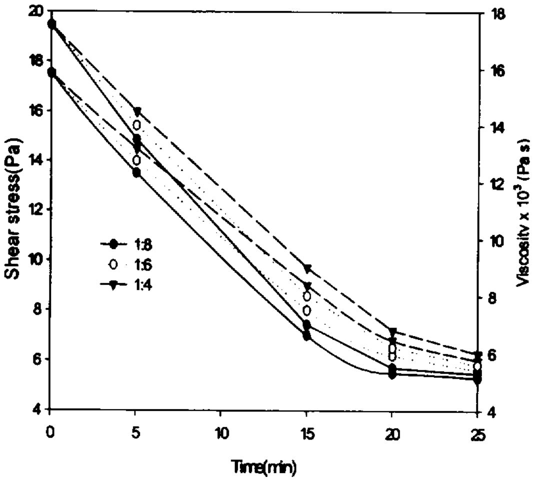

Fig. 1. Comparison of shear stress and viscosity of biodiesel mixture with molar ratio at 60℃, 0.6wt% NaOH and $1000s^{-1}$.

And its kinematic viscosity was measured as 6.2 mm^2/s and estimated by Orrick amd Erbar's model. The estimated kinematic viscosity (6.1 mm^2/s) is a little higher than 1 − 6mm^2/s of ASTM B100 standard from D-6751 method.

3.2. Effects of molar ratio on kinematic viscosity

As the transesterification goes forward with molar ratio, triglyceride converts more easily into fatty acid methyl ester than di- or mono-glyceride. The viscosity of boidesel goes down with molar ratio. The kinematic viscosity for 1:8, 1:6 and 1:4 was compared on Fig.2. The kinematic viscosities for the 1:4 molar ratio and the 1:6 and 8 molar ratio were 6.6 and about 6.1 mm^2/s.

Orrick and Erbar's model was applied appropriately to estimate ηmix in my experimental ranges.

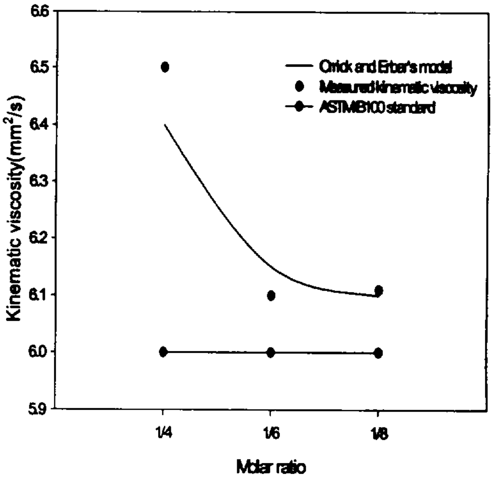

Fig. 2. Comparison of measured kinematic viscosity, Orrick and Erbar's model and ASTM B100 standard at 40℃.

3.3. Effects of unsaturation percent on viscosity

The unsaturated fatty acid methyl ester in glyceride has a lot of localized electron on the carbonyl carbon. This is why the breakage of glyceride takes place easily and trans-esterification is accelerated. The unsaturated FAME has a lower pour or cloud point than saturated FAME. The unsaturated FAME has a good fluidity while winter season.

Therefore, the unsaturation of FAME has an effect on the viscosity of it. The transesterification of canola, soybean oil and corn oil was performed using 0.6wt% NaOH at 60℃, 1000s^{-1} of shear rate and the 1:6 molar ratio. And then the mixture of biodiesel and glycerin was separated, and the fatty acid methyl esters were cooled to 30℃. Fig.3 shows the effects of unsaturation percent on viscosity at 30℃.

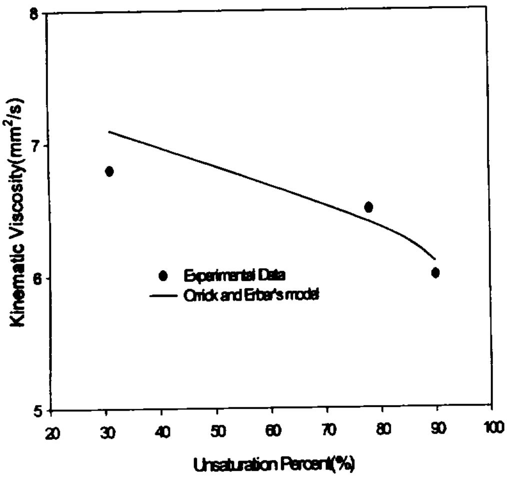

Fig. 3. Effects of unsaturation percent on viscosity at 30℃.

As the unsaturation goes up to 90%, the kinematic viscosity goes down to 6.1mm^2/s due to low pour point. Experimental data were fitted well by Orick and Erbar's model.

3.4. 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. [12] pointed the optimum molar ratio of methanol to oil is 1:6 from the transesterification of rapeseed oil using alkaline catalyst at 65℃. Noureddini et al. [13] 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.4.

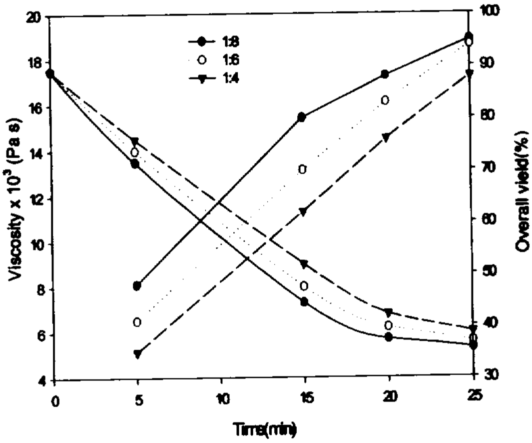

Fig. 4. Effects of molar ratios of methanol to oil on viscosity and overall yield at 60℃, 0.6wt% NaOH and 1000s^{-1}.

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 mPa s and 95% in 25minutes. From this result, the optimum molar ratio appeared to be 1:6.

3.5. 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 triglycride 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. [14] 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.

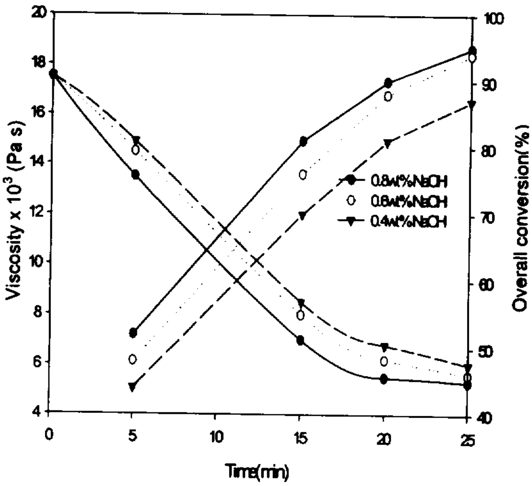

Fig. 5. Effects of amount of NaOH on viscosity and overall yield at 60℃, the 1:6 molar ratio and 1000s^{-1}.

The overall yield and viscosity for 0.6wt% NaOH approached 95% and 5.1 mPa s for 0.8wt% NaOH in 25 minutes. Therefore, the optimum amount of NaOH was 0.6wt%.

3.6. Effects of viscosity which is dependent on unsaturation percent on overall yield

The overall yield is defined as Eq.(5).

$$Y_{overall} = M_f / M_o \tag{5}$$

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).

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

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 mi and ln η_{mix} .

Fig.6 shows the effects of viscosity dependent on unsaturation percenton overall yield.

As we can see Eq. (6), the overall yield increases with the decrease of viscosity (ηmix). The overall yield was 85-95% and the unsaturation percent was 40-91% for the ranges (6.1-6.8mm^2/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.

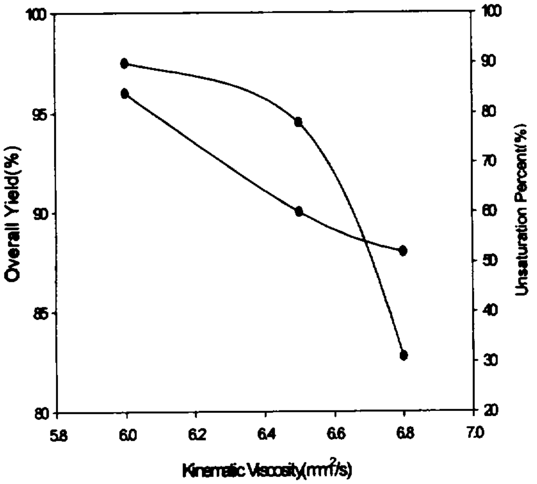

Fig. 6. Effects of viscosity dependent Overall yield at 60℃, the 1:6 molar ratio, 0.6wt% NaOH on unsaturation percent on and $1000s^{-1}$.

Ⅳ. Conclusions

The transesterification of vegetable oils using alkaline catalysts was done at 60℃ 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 mm^2/s)) at 40℃was a little higher than the upper limit(1 – 6 mm^2/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 (6.1–6.8mm^2/s) of viscosity in 25 minutes. The overall yield was predicted by the relation depended on the terms of mi and η_{mix}, in Eq.(6).

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