大豆油를 原料로 한 代替 디이젤燃料의 粘性学的 性質 +

Rheological Properities of Soybean Oil Ester of the Oil and Their Mixtures with Diesel Fuel and Additives

徐 相 龍* · 에프 디 해리스**

Suh, Sang Ryong · Harris, F. D.

摘 要

디이젤엔진의 代替燃料로서 大豆油는 大豆油의 높은 粘性에 起因하는 문제점이 지적되고 있다. 이의 해결방법으로 大豆油와 디이젤油의 混合, 大豆油의 에스테르化 그리고 디이젤油 添加剤의 添加 등이 제시되고 있다. 本研究는, 大豆油, 그의 에틸 에스테르 그리고 이러한 代替燃料의 디이젤油와 混合物 또는 그 混合物의 添加剤와의 混合物의 粘性学的 性質과 그 크기를 実験的 方法으로 구하였다. 그 결과 상기의 液体는 모두 뉴톤니안 液体이고, 添加剤는 상기 混合物의 粘性을 낮추는데 별로 효과가 없는 것으로 판단되었다.

I. INTRODUCTION

Vegetable oil and/or transesterified vegetable oil are known as promising candidates as an alternative or extender of diesel fuel since they are well suited for compression ignition engines which produce most of farm power.

The oils have been tested in the engine by many researchers (Peters et al., 1981; Harris et al., 1981; Yarbrough et al., 1982; Van de Walt and Hugo, 1982; Pienaar et al., 1982). Most of the tests show that the oils have very good potential as the engine fuel but several problems were reported. The problems are fuel filter plugging, carbon deposits on injector nozzles, carbon deposits inside cylinders and crankcase oil dilution.

Physically the oils have much higher viscosities than diesel fuel. Chemically the oils contain gum forming materials which can not be removed easily. These two differences between the oils and diesel fuel are suggested to be major sources of the engine problems.

Physical properities of the oils have been studied by many researchers. For the viscosity of soybean oil, Pryde (1980), Goering et al. (1981), Ryan et al. (1982), Vinyard et al. (1982) reported the viscosity but most of the data are only for two or three temperature conditions.

Several attempts have been made by researchers to change the physical and chemical properties of the oils but the major thrust has been to reduce the viscosity. Small amounts of diesel fuel additives in the oil and diesel fuel mixtures (Van de Walt and Hugo, 1982) and transesterification of the oil (Pienaar et al, 1982; Hawkins and Fuls, 1982) are the methods used to reduce the viscosity. The transestrification was reported as a successful method to reduce the viscosity but is known as an expensive chemical process. Some of the additives were noted effective to reduce the problems in the engine but effects of the additives on the viscosity of the oils and the mixtures were not documented.

The objective of this study is to give informations on the rheological properties of soybean oil, ester of soybean oil and blends of the above with diesel fuel and the influence of several diesel fuel additives on vicosities of the oil and blends with diesel fuel.

II. MATERIALS AND EQUIPMENT

A. Materials

The viscosities of soybean oil, ethyl ester of the oil,

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* 全南大学校 農科大学 農工学科

** University of Missouri－Columbia

diesel fuel, diesel fuel additives and mixures of the above were investigated in this study. Soybean oil was the crude soybean oil expressed by a screw press. The ethyl ester of soybean oil was produced by Emery Industries, Inc., and the diesel fuel was a general No. 2 diesel fuel. Four kinds of diesel fuel additives were studied. These additives were diesel fuel conditioners produced by Wynn's Friction Proofting Supply, Ind. and Lubrizol Corporation; one was from the Wynn's and three were from the Lubrizol, namely Lubrizol 8005, 552 and 8256A.

Selection of the additives was based on experimental results of engine tests with several kinds of diesel fuel additives perormed by Van der Walt and Hugo (1982) and on communication with the producers of the additives.

B. Equipment

The viscometer used in this study was a model "Haake Rotovisco RV2" manufactured by Haak Instruments, Inc. It is a coaxial cylinder rotational viscometer with a speed range of 0.1 to 724 rpm. The viscometer consists of 4 parts; the driving unit, the measuring head, the viscosity sensor system with a tempering vessel, and tne control console.

Two measuring heads are available. Model "MK 50" which has a maximum torque of 49,000 dyne-cm was used in this research.

Several types of sensor systems can be used with this viscometer to extend its measuring capability. Model "MVI" sufficed for this study. The MVI system consists of a regular cup and rotor with recessed top and bottom surfaces which minimize influences on torque; in particular, the influence of air bubbles retained in the bottom recess and excess sample in the upper recess. It is equipped with a jacket type tempering vessel for maintaining a constant temperature.

The control console controls the speed of the rotor either by setting constant rpm or increasing or decreasing rpm at a selected rate with respect to time.

A model "7040A" Hewlett Packard x-y recorder was used in connection with the above viscometer to record either time versus shear stress or shear rate versus shear stress.

A constant temperature bath was used to control the temperatur of the substance in the sensor system. The bath was a model "NB" of Colora Ultra Thermostats supplied by Brookfield Engineering Laboratories, Inc. Cooling is provided with either a built in cooling coil or an external coil that can be immersed in the water.

A bath cooler, model "PBC-4" manufactured by Neslab Instruments Co. was used in combination with the constant temperature bath to obtain a temperature below ambient.

III. PROCEDURE

The experimental plan for viscosity determinations was divided into three parts. The first part was for rheological classification of soybean oil, the ethyl ester, diesel fuel and blends of the above. The second part compared viscosities of soybean oil, ethyl ester of soybean oil, diesel fuel and blends of the three fluids mixed with the additives in order to observe effects of the additives on viscosity of the blends. The third part was to determine the viscosities of blends of soybean oil-diesel fuel and the ester-diesel fuel at various temperatures.

The first part of the experiment was for soybean oil (SB), ethyl ester of soybean oil (ES), diesel fuel (DS), 50/50 soybean oil-diesel fuel (SD1:1), and 50/50 soybean oil-the ethyl ester (SE1:1).

The second part of the experiment was carried out with the fluids shown in Table 1. As shown, mixing ratio of all the additives was 5 percent by volume. Producers of the additives recommended much lower mixing ratios – 0.04 percent for Wynn's diesel fuel conditioner, 0.25 percent for Lubrizol 8005, 0.03 percent for Lubrizol 552, and 0.01 percent for Lubrizol 8256A. The reason of using the higher mixing ratio in the experiment was to mangnify the effect of the additives to make comparisons easier.

In the first and second parts of the experiment, the viscosity was determined by reading the speed of the rotor and a scale which can be converted directly into shear rate and shear stress, respectively. A curve for the

Table 1. A list of soybean oil, soybean oil ester and diesel fuel blends mixed with diesel fuel additives tested for viscosity comparison.

Oil Code No.	Composition, percent by Volume						
	Soy Oil	Diesel	Ester	Ad. 1 [a]	Ad. 2 [b]	Ad. 3 [c]	Ad. 4 [d]
100	100						
10		100					
20			100				
1				100			
2					100		
3						100	
4							100
110	50	50					
120	50		50				
210		50	50				
101	100			5			
102	100				5		
103	100					5	
104	100						5
111	50	50		5			
112	50	50			5		
113	50	50				5	
114	50	50					5
121	50		50	5			
122	50		50		5		
123	50		50			5	
124	50		50				5

a Ad. 1=Wynn's diesel fuel conditioner
b Ad. 2=Lubrizol 8005
c Ad. 3=Lubrizol 552
d Ad. 4=Lubrizol 8256 A

relation between the speed (shear rate) and the scale (shear stress) was obtained for each fluid. Shear rate was changed in the range of 0 – 936 1/sec by changing speed of the rotor from 0 to 400 rpm. The test temperature was 37.8°C.

In the third part of the experiment, the SB, ES, DS, and 25/75, 50/50 and 75/26 blends of SB-DS and ES-DS were tested in the same manner of the first and second part of this experiment except with variable temperature. The observed temperatures were 10°, 38°, 68° and 93°C.

The viscosity of the selected fluids was determined from the shear rate and shear stress values using equation (1).

$$\mu = \frac{\tau}{\gamma} \tag{1}$$

where, μ = absolute viscosity,

τ = shear stress, and

γ = shear rate.

To obtain the kinematic viscosity from the absolute viscosity, the density of soybean oil and soybean oil and soybean ester blends were measured at temperatures ranging from 12.2°C to 104°C. The tested blends were the SB, ES, DS, SD1:1, and SE1:1. The densities were measured using a balance for mass and a volumetric flask for volume.

The kinematic viscosity was determined using the definition:

$$\nu = \frac{\mu}{\rho} \tag{2}$$

where, ν = the kinematic viscosity, and

ρ = density.

IV. RESULTS AND DISCUSSION

A. Rheological Classification

The shear rate and shear stress were plotted with the x-y recorder for the fluids tested. The experiment resulted in a linear relationship between shear rate and shear stress passing through the origin for all the fluids tested. The curves were reproduced by reading the shear rate and shear stress at 8 points with shear rates of 117, 234, 351, 468, 585, 702, 819 and 936 1/sec for each fluid and are shown in Figs. 1 and 2. The curve for diesel fuel shows some deviations from the observation plots, however, the result was considered due to low values of the shear stress which were difficult to measure precisely with the viscometer. Therefore, because of the linearity, it was concluded that all the fluids tested can be classified as Newtonian fluids.

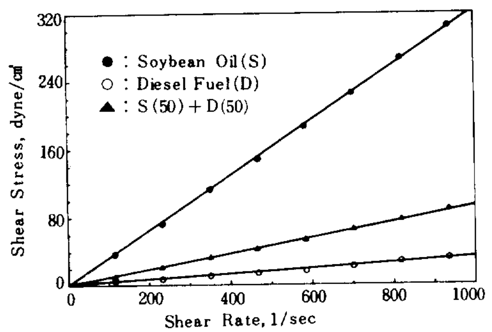

Fig. 1. Relations between shear rate and shear stress of soybean oil, diesel fuel and 50/50 blend.

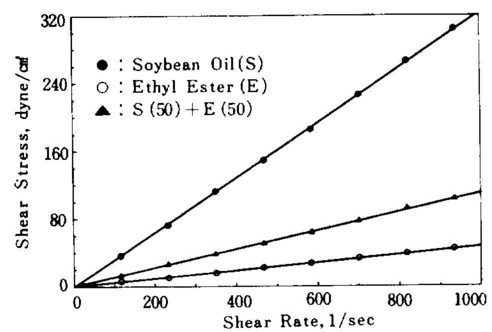

Fig. 2. Relations between shear rate and shear stress of soybean oil, ethyl ester of soybean oil and 50/50 blend.

B. Comparison of Viscosities of the Selected Fluids

The viscosities of the fluids listed in Table 1 were determined with the viscometer, and curves for shear rate versus shear stress were obtained. Shear stresses were read from the viscometer at 8 point of shear rate as the same manner as before and the viscosities were determined using euqation (1). The 8 values were averaged.

Mean values of viscosity are listed in Table 2 with the standard deviations of the observed values and corresponding coefficients of variation. The coefficients of variaton for most of the fluids are less than 5 percent except diesel fuel, Wynn's diesel conditioner and blends of the ethyl ester-diesel fuel which have very low viscosity.

Most of the mixtures resulted in lower values of viscosity than those estimated form the viscosities of the fluids used to make the mixtures. To show this, a viscosity, named expected viscosity (μ_e), was calculated for each mixture using viscosities and portions of the fluids which were used to make the mixtures by an euqation of interpolation.

$$\mu_e = \frac{\mu_1 P_1 + \mu_2 P_2}{P_1 + P_2} \qquad (3)$$

where, μ = viscosity of fluids used to make the mixture, and

P = portion of the fluid in the mixture by decimal.

The expected viscosities for the mixtures are listed in Table 2 for comparison.

The effect of the additives on the viscosities of soybean oil and its blends with diesel fuel and the ethyl ester is observable. As shown, viscosities of the mixtures with the additives reflect the viscosities of the additives – if an additive of low viscosity is mixed, the viscosity of the mixture is lowered and vice versa. However, because of the small amount of the additives in the mixtures, the effect is not much. Moreover, if the producers' recommended mixing ratios are used, it is expected that the effect is almost insignificant.

Among the additives, only Wynn's diesel conditioner lowered the viscosities of soybean oil and the blends. The result is clearly due to the low viscosity of the conditioner compared with the viscosities of soybean oil and the blends. With the other additives, even though the viscosities of the mixtures show lower values than the expected values, the viscosities of the mixtures are higher than the viscosities of soybean oil and the blends used to make the mixtures.

Table 2. Mean values, standard deviations, coefficients of variation and the expected values of viscosity of the selected fluids at a temperature of 37.8℃.

Unit : centipoise

Oil Code No.	Mean	Std. Dev.	C. V. (%)	Expected Viscosity
100	31.4	0.83	2.6	
10	2.9	0.56	19.3	
20	4.6	0.12	2.6	
1	1.6	0.75	46.3	
2	93.5	1.14	1.2	
3	343.9	12.69	3.7	
4	79.4	0.31	0.4	
110	9.3	0.40	4.3	17.2
120	11.1	0.46	4.2	18.0
210	3.5	0.35	9.9	3.8
101	27.3	0.79	2.9	30.0
102	34.2	0.90	2.6	34.4
103	37.1	0.38	1.0	46.3
104	34.0	0.79	2.3	33.7
111	7.9	0.32	4.0	8.9
112	10.3	0.39	3.8	13.3
113	12.5	0.76	6.1	25.2
114	8.9	0.25	2.8	12.6
121	9.6	0.46	4.8	10.6
122	13.5	0.29	2.2	15.0
123	13.3	0.38	2.9	26.9
124	12.1	0.37	3.1	14.4

It was concluded that some of the diesel fuel additives which have low viscosity, like Wynn's diesel conditioner, can be used to lower the viscosities of soybean oil and the blends but the effect of the additives is insignificant practically because of the small portions of the additives in the mixtures.

C. Viscosity at Various Temperatures

Viscosities of various blends of the SB-DS and ES-DS were determined at various temperatures. The experiment was intended to provide information which might be useful in further research on modified fuels and/or modified engins using soybean oil. The results are shown in Table 3.

Densities of soybean oil, the ethyl ester, diesel fuel and blends of the above were observed at various temperatures in order to obtain the kinematic viscosities of the fiuids from the absolute viscosities.

The results are shown in Fig. 3. As shown, the

Table 3. Viscosity of the selected fluids

Fluid	Viscosity (centipoise)			
	10.0℃	37.8℃	68.3℃	93.3℃
Soybean Oil (SB)	93.6	31.4	13.8	7.8
Diesel Fuel (DS)	4.7	2.9	2.4	2.1
SB (25) + DS (75)	9.9	5.1	3.5	2.3
SB (50) + DS (50)	20.6	9.3	5.0	3.4
SB (75) + DS (25)	43.6	17.2	8.9	5.4
Ethyl Ester (ES)	9.0	4.6	3.1	2.6
ES (25) + DS (75)	5.7	3.4	2.5	2.2
ES (50) + DS (50)	6.5	3.5	2.7	2.4
ES (75) + DS (25)	7.1	4.1	2.8	2.4

selected fluids show linear relations with temperature. The relations were obtained by regression analyses, and are listed in the figure with the coefficients of correlation.

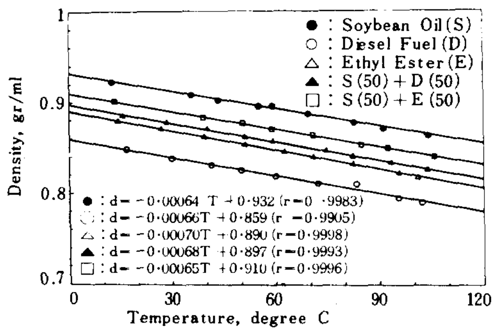

Fig. 3. Relations between temperature and density of soybean oil, ethyl esterof soybean oil, diesel fuel and the blends (T: temperature in ℃; d: density in gr/ml; r: coefficient of correlation).

Densities of blends (ρ_b) of soybean oil-diesel fuel and soybean oil-ethyl ester of soybean oil were calculated using densities of soybean oil, the ester and diesel fuel by an equation below.

$$\rho_b = \frac{\rho_1 P_1 + \rho_2 P_2}{P_1 + P_2} \quad (4)$$

where, ρ = density of fluid used to make the blend, and

P = portion of the fluid in the blend by decimal.

The calculated values were compared with the observed values of the blends. The result showed less than 0.3 percent maximum difference between the calculated and observed. The experimental data were compared with the reported data and resulted in good agreement.

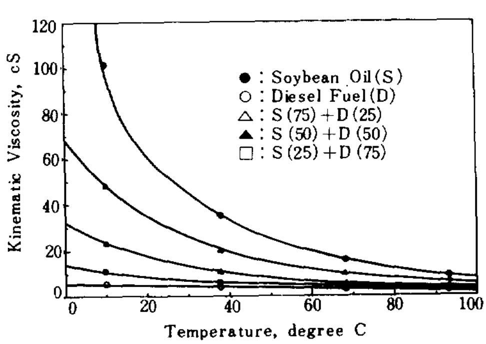

Fig. 4. Relations between temperature and the kinematic viscsoity of soybean oil, diesel fuel and the blends.

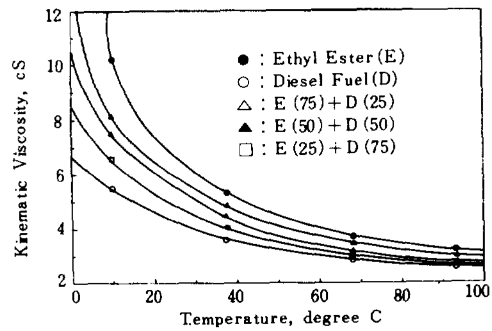

Fig. 5. Relations between temperature and the kinematic viscosity of ethyl ester of soybean oil, diesel fuel and the blends.

The kinematic viscosities of soybean oil, the ethyl ester, diesel fuel and the blends were obtained using equation (2) with the data for viscosity and density. Densities of the blends were obtained using the regression equation for each fluid and equation (4). The results are shown in Fig. 4. and 5.

The data were compared with the data reported, For soybean oil at 37.8°C, the viscosity by this study is 34.6 centistokes while the reported data are in the range of 32.6 – 36.8 centistokes. At low and high temperatures, the viscosities of the two sources are fairly consistent. For ethyl ester of soybean oil at 40°C, the viscosity by this study is 5.2 centistokes while the reported data range from 4.2 to 4.7 centistokes. Data could not be found for low or high temperatures. The viscosity of diesel fuel at 40°C is 3.5 centistokes while the reported data are in a range of 2.43 – 4.1 centistokes. At low and high temperatures, the viscosities of this study result in a little higher values than the reported values. Hence, it was concluded that the experimental data are acceptable to determine the viscosities of the fluids.

V. CONCLUSIONS

1. Soybean oil, ethyl ester of soybean oil, diesel fuel and blends of the above are Newtonian fluids

rheologically.

2. Diesel fuel additives having low viscosities can be used to lower the viscosities of soybean oil and blends with diesel fuel but the effect on the viscosity is insignificant practically.

3. The presented data for densities and viscosities of the tested fluids at various temperature conditions are acceptable to be used.

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