STUDY ON THE RHEOLOGY OF CORN OIL SUBJECTED TO FORCED OXIDATION

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ABSTRACT

This paper reflects a study on the rheology of corn oil in unoxidized state, subjected to forced oxidation treatment. Using the Rheotest2 system, the variation of dynamic viscosity with temperature and shear rate, using oxidized and non-oxidized corn oil, was determined. The oils were heated to 110 °C and 120 °C and the temperature was maintained for 5 to 10 hours. The experiments showed the decrease of dynamic viscosity with temperature and shear rate. The oxidation process causes a sharp increase in the dynamic viscosity of the oxidized corn oil for 10 hours at 120 °C. The measurement of the dynamic viscosity of the oils subjected to the oxidation process is an indicator of the degree of oxidative degradation of vegetable oils.

KEYWORDS: corn oil, lubrication, biodegradable, shear rate, viscosity, oxidation

1. Introduction

Currently, 50% of all lubricants used in the world end up in the environment, by total loss, volatility or major accidents. Before the year 2000, 95% of these materials were based on mineral oils. Due to their ecotoxicity and low biodegradability, they constitute a considerable threat to the environment, although they are efficient lubricants, with good tribological properties [1]. Biodegradable oils are, at the moment, a high achievement in the field of lubrication in equipment and machinery mainly working under conditions that may result in environmental pollution. Lately, the emphasis is on the use of vegetable oils as the basis of biodegradable lubricants. The rheological properties of vegetable oils depend on many factors, including temperature, shear rate, concentration, density, pressure, time of application, chemical properties, additives and catalysts, molecular weight, degree of unsaturation of fatty acids, melting point [2-6]. Most research has been directed to study the effects of temperature, shear rate, concentration and pressure. The most important factor affecting viscosity is temperature. The viscosity of oils and fats decreases with the increase of temperature [7-10]. Wan Nik, Ani, Masjuki and Eng Giap [11] evaluated the effects of shear rate and temperature on the rheological properties of vegetable oils from sun flower, corn, canola, coconut and superolein.

2. Experimental results

Viscosity was determined with the help of a Rheotest 2 system, shear rates ranging between 3.3 s^{-1} and 80 s^{-1}, the test temperatures being between 40 °C and 80 °C (determinations were done for each step of 10 °C, in this range).

To perform forced oxidation, a system was built, as presented in Figure 1. It consists of: 1 - air pump, 2 - air flow meter, 3 - air filter, 4 - tube with oil sample, 5 - thermostatic bath. For each oxidation test, 25 ml of oil were used. The flow rate of air introduced into the oil sample was 20 l/h.

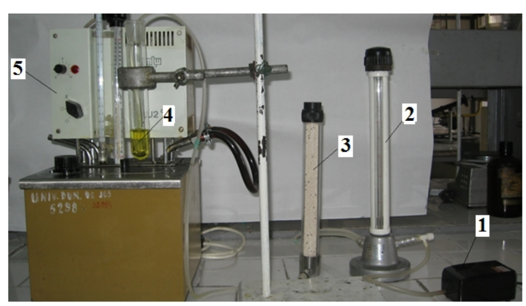

Fig. 1. *Oxidation equipment*

The corn oil was oxidized at temperatures of 110 ºC and 120 ºC for 5 hours and 10 hours. The results obtained are presented in Figures 2-5. They show variations in dynamic viscosity depending on the shear rate corresponding to the test temperatures of 40 ºC and 80 ºC.

2.1. Dynamic viscosity changes depending on shear rate

At both temperatures and periods of oxidation, as well as test temperatures, dynamic viscosity decreases when the shear rate increases. The decrease in dynamic viscosity is much more accentuated at low shear rates.

Corn oil oxidation at 110 ºC and 120 ºC for 5 hours and 10 hours causes increases in the dynamic viscosity of the oils in comparison with unoxidized oil, a phenomenon observed at both temperatures.

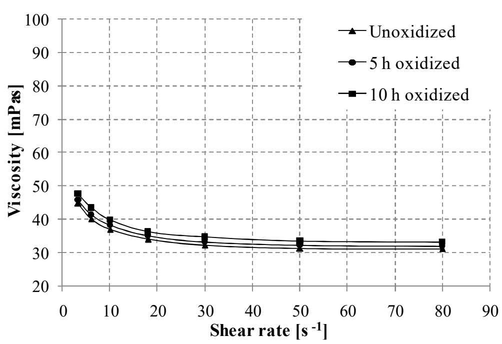

Fig. 2. *Variation of viscosity with shear rate, at 40 ºC, for corn oil oxidized at 110 ºC*

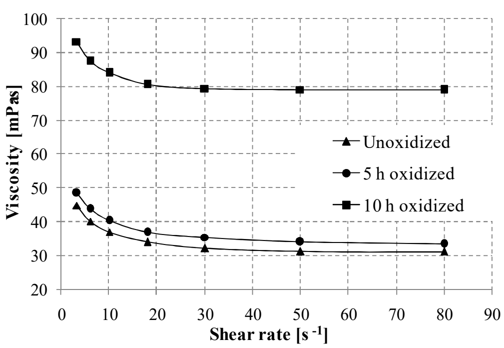

Fig. 3. *Variation of viscosity with shear rate, at 40 ºC, for corn oil oxidized at 120 ºC*

A large increase in dynamic viscosity can be observed with an increase in the oxidation period, from 5 hours to 10 hours. The largest increase in dynamic viscosity is recorded at a temperature of oxidation of 120 ºC, for oil oxidized for 10 hours, the temperature of the test being of 40 ºC.

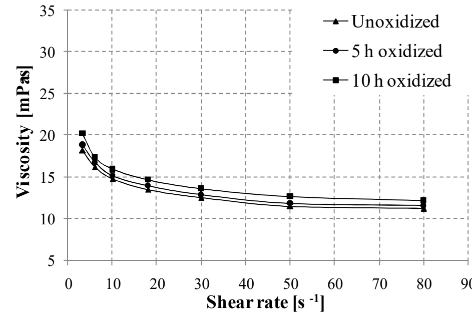

Fig. 4. *Variation of viscosity with shear rate, at 80 ºC, for corn oil oxidized at 110 ºC*

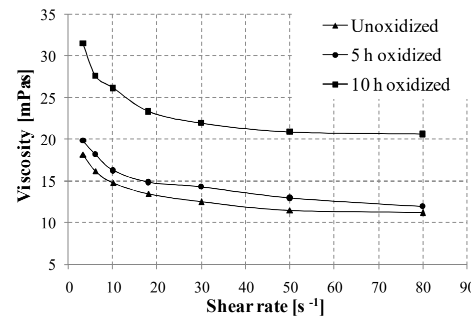

Fig. 5. *Variation of viscosity with shear rate, at 80 ºC, for corn oil oxidized at 120 ºC*

By increasing the test temperature from 40 ºC to 80 ºC, a less significant increase of the dynamic viscosity could be noticed.

2.2. Dynamic viscosity changes depending on temperature

In Figures 6-9 the dynamic viscosity changes depending on temperature were represented, for corn oils oxidized at temperatures of 110 ºC and 120 ºC for 5 hours and 10 hours, corresponding to shear rates of 6 s^{-1} and 50 s^{-1}.

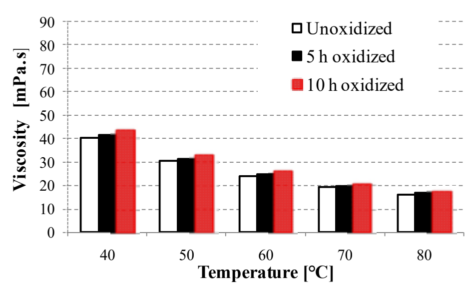

Fig. 6. *Variation of viscosity with temperature, at 6^{-1} shear rate, for corn oil oxidized at 110 ºC*

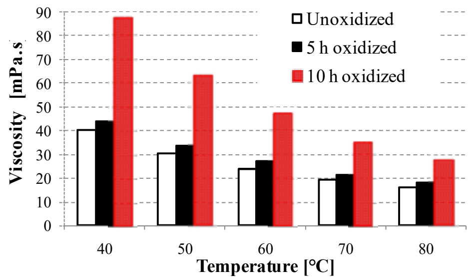

Fig. 7. *Variation of viscosity with temperature, at 6^{-1} shear rate, for corn oil oxidized at 120 ºC*

For both temperatures and periods of oxidation, as well as shear rates, the dynamic viscosity decreases with the increase in the temperature at which the oils have been tested.

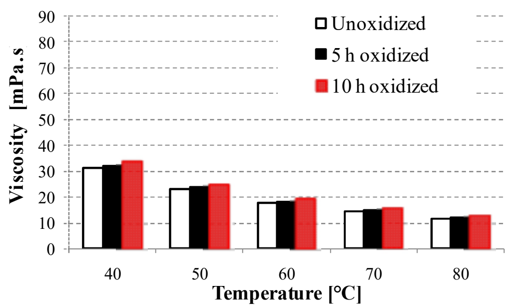

Fig. 8. *Variation of viscosity with temperature, at 50^{-1} shear rate, for corn oil oxidized at 110 ºC*

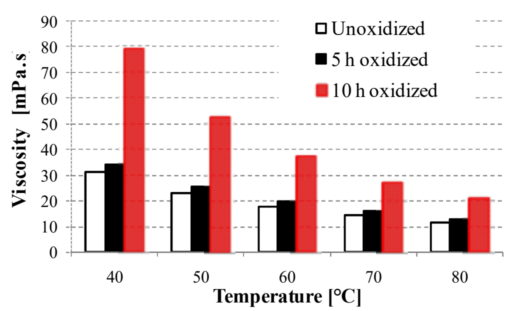

Fig. 9. *Variation of viscosity with temperature, at 50^{-1} shear rate, for corn oil oxidized at 120 ºC*

Corn oil oxidation at a temperature of 110 ºC for 5 and 10 hours, tried to shear rates of 6 s^{-1} and 50 s^{-1}, does not cause significant increase in dynamic viscosity in comparison to unoxidized oil.

The increase in the temperature of the oxidation from 110 ºC to 120 ºC leads to a strong rise in the dynamic viscosity of the oil oxidized for 10 hours. Tested at a temperature of 40 ºC, the viscosity of the oil oxidized for 10 hours at a temperature of 110 ºC and a shear rate of 6 s^{-1} is 8.1% higher than that of unoxidized oil, while after 5 hours of oxidation, the viscosity increased by only 3.1%. At the same test temperature, the viscosity of the oil oxidized for 10 hours at a temperature of 120 ºC and a shear rate of 6 s^{-1} is 117.7% higher than that of unoxidized oil, while after 5 hours of oxidation, the viscosity increased by only 8.8 %. In the case of the test temperature of 80 ºC, the viscosity of the oil oxidized for 10 hours at a temperature of 110 ºC and a shear rate of 6 s^{-1} is 7.3% higher than that of unoxidized oil, while after 5 hours of oxidation, the viscosity increased by only 3.5%.

At the same temperature of the test, the viscosity of the oil oxidized for 10 hours at a temperature of 120 ºC and a shear rate of 6 s^{-1} is 70.7% higher than that of unoxidized oil, while after 5 hours of oxidation, the viscosity increased by only 12.5%.

In the case of corn oil oxidized for 10 hours at a temperature of 110 ºC and a shear rate of 6 s^{-1}, the increase in the temperature of the test from 40 ºC to 80 ºC causes a decrease in the dynamic viscosity by 60.1%, while for the shear rate of 50 $s^{-1,}$ the decrease is 62.2% (comparable with that recorded at a shear rate of 6 s^{-1}).

Increasing the oxidation temperature to 120 ºC for the corn oil oxidized for 10 hours, the percentage variation in dynamic viscosity, between the temperatures of 40 ºC and 80 ºC, is 68.46% for the shear rate of 6 s^{-1} and 73.6% for the shear rate of 50 s^{-1}.

To support our results regarding the variation in viscosity depending on temperature, the Andrade equation (1) and the Azian equation (2) [12-16] were used:

$$\ln \eta = \ln A + \frac{B}{T} \quad (1)$$

$$\ln \eta = A + \frac{B}{T} + \frac{C}{T^2} \quad (2)$$

where T is the absolute temperature and A, B and C are material constants.

The rheological parameters of the Andrade and Azian equations as well as the correlation coefficients are presented in Tables 1 and 2.

It should be noted that the resulting correlation coefficients are higher for the Azian equation (values between 0.99954 and 0.99996). This equation approximates very well the experimental results, and can be used to determine the variation of the dynamic viscosity of the vegetable oils depending on their temperature.

3. Conclusions

This study focuses on the variation of dynamic viscosity with temperature and shear rate for corn oil in unoxidized state, as well as oxidized for 5 and 10 hours at 110 °C and 120 °C.

It was noted that the viscosity decreases with increasing shear rate and temperature. A significant decrease in viscosity is recorded at low shear rates. During the process of forced oxidation, there occurs a formation of hidroperoxides which causes the appearance of non-volatile compounds (dimers, trimers and compounds of high molecular weight), the result being the increase of the oil’s viscosity. The largest increases in dynamic viscosity were observed at a temperature of oxidation of 120 ºC maintained for 10 hours.

The measurement of the dynamic viscosity of the oils subjected to the oxidation process could be an indicator of the degree of oxidative degradation of vegetable oils. To study the change of dynamic viscosity depending on temperature, the Andrade and Azian equations were used to determine the rheological parameters and the correlation coefficients. From the analysis of the latter, there were noted values of the correlation coefficients closer to 1 when using the Azian equation. This equation gives the best approximation on the experimental data and can be used to assess the change in the dynamic viscosity of oils depending on temperature variation.

Table 1. *Parameters of the Andrade equation*

Shear rate [s^{-1}]	*Parameters*		*lnA*	*B*	*Correlation coefficients*
6	*Unoxidized*		-4.39013	$2.5252\cdot10^3$	0.9986
	Oxidized at 110 ºC	*5 h*	-4.35212	$2.5228\cdot10^3$	0.9982
		10 h	-4.42020	$2.5602\cdot10^3$	0.9987
	Oxidized at 120 ºC	*5 h*	-4.08455	$2.4592\cdot10^3$	0.9989
		10 h	-5.7845	$3.2101\cdot10^3$	0.9997
50	*Unoxidized*		-5.3312	$2.7406\cdot10^3$	0.9991
	Oxidized at 110 ºC	*5 h*	-5.2907	$2.7373\cdot10^3$	0.9991
		10 h	-5.0489	$2.6734\cdot10^3$	0.9987
	Oxidized at 120 ºC	*5 h*	-5.0166	$2.6698\cdot10^3$	0.9988
		10 h	-7.4141	$3.6826\cdot10^3$	0.9991

Table 2. *Parameters of the Azian equation*

Shear rate [s^{-1}]	*Parameters*		*A*	*B*	*C*	*Correlation coefficients*
6	*Unoxidized*		6.4875	$-4.7087\cdot10^3$	$1.2\cdot10^6$	0.99992
	Oxidized at 110 ºC	*5 h*	7.8593	$-5.5983\cdot10^3$	$1.347\cdot10^6$	0.99987
		10 h	5.6859	$-4.1607\cdot10^3$	$1.115\cdot10^6$	0.99985
	Oxidized at 120 ºC	*5 h*	3.2163	$-2.3961\cdot10^3$	$0.805\cdot10^6$	0.99954
		10 h	3.7262	$-2.7621\cdot10^2$	$1.039\cdot10^6$	0.99985
50	*Unoxidized*		3.9037	$-3.41\cdot10^3$	$1.019\cdot10^6$	0.99981
	Oxidized at 110 ºC	*5 h*	3.9961	$-3.4387\cdot10^3$	$1.025\cdot10^6$	0.99984
		10 h	6.0421	$-4.7026\cdot10^3$	$1.224\cdot10^6$	0.99992
	Oxidized at 120 ºC	*5 h*	5.4683	$-4.3031\cdot10^3$	$1.156\cdot10^6$	0.99994
		10 h	5.8371	$-5.129\cdot10^3$	$1.462\cdot10^6$	0.99996

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