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# Influence of refining process for the eco-friendly industrial lubricants on their rheological properties

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Today, there is an increased interest in studying the eco-friendly industrial lubricants as possible replacers of mineral oils. And this interest obliged the researchers to test the different grades of vegetable oils in order to evaluate their rheological behaviour. The paper presents the influence of shear rate and temperature on the rheological properties (viscosity, flow index and consistency index) of the rapeseed oil, in three different stage of refining process: crude, degummed and refined. Tests were done on a Brookfield cone and plate viscometer CAP 2000+, having the following test parameters: test type - shear rate imposed, shear rate (100...2000 $s^{-1}$) and temperature range of 20...75°C. The results of the tests highlight the better rheological and tribological behaviour of the rapeseed oil, thus it could be recommended in tribological applications.

**Keywords:** biodegradable lubricants, rheology, rapeseed oil

## INTRODUCTION

Because of they have relatively weaker properties, biodegradable oils have not yet an important presence in technical systems that require intensive operating regimes. To compete with petroleum based lubricants or synthetic ones, research studies should provide a viable alternative in performance and price for vegetable oils. In recent years, the regional level (such as the European Union), but also at national level they were created policies that encourage the use of lubricants based on renewable resources, but there are still problems to solve [1].

The process of replacing of "classic" lubricants can only be a gradual process, because it depends on many factors: focus research on making new performant recipes of bio lubricants, availability of farmers to produce such crops, the existence of cost-effective facilities for processing raw materials and support of big consumers in using these lubricants [2], [3].

Today, there is a growing interest in the study of rapeseed oil as potential substitute for mineral or synthetic oils. Some of the last ones are relatively expensive or more polluting to the environment. This interest compels researchers to evaluate a function of oil refining process - the rheological and tribological behaviour [4], [5], [6]. The refining process involves degumming, neutralization, drying, bleaching and deodorization. Crude oil from extraction has to be refined to obtain high quality oil. Natural impurities of crude rapeseed oil include water, dirt, phosphatide gums, free fatty acids, colour matter, odoriferous and flavorous substances, natural breakdown and oxidation products of the oil itself [7], [8].

The paper presents the influence of shear rate and temperature on the rheological properties (viscosity, flow index and consistency index) of the rapeseed oil, in three different stage of refining process: crude, degummed and refined.

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## RAPESEED OIL PROPERTIES

The biodegradable oils were supplied by the Romanian company "Prutul" from Galati. The degumming and refining processes were performed at the firm.

The degumming process extract components (phospholipids and non-triglycerides) that, if they were left in the vegetable oil, they would favor the fermentation and the generation of gum deposits [9]. The refining process includes degumming, neutralization and washing for removing some radicals of the fat acids, metallic traces and other water-soluble substances [10].

The chemical composition of the vegetable oils is given in Table 1 and was done with the aid of gas cromatography, according to the standards PN-EN ISO 5508:1996 and PN-EN ISO 12966-2:2011, at J.S. Hamilton from Poland for the company Prutul S.A from Romania.

Characteristics in Table 2 were determined in the laboratory of Prutul S.A.

**Table 1.** Composition of fat acids for the tested oils

| Fat acid, g/100 g | Crude rapeseed oil | Refined rapeseed oil |
|---|---|---|
| Myristic acid | 0.05 | < 0.1 |
| Palmitic acid | 4.84 | 5.1 |
| Palmitoleic acid | 0.06 | 0.2 |
| Margaric acid | 0.14 | < 0.1 |
| Heptadecenoic acid | - | < 0.1 |
| Stearic acid | 0.14 | 1.8 |
| Oleic acid | 62.73 | 57.1 |
| Linoleic acid | 22.4 | 27.9 |
| Linolenic acid | 7.50 | 5.9 |
| Arachidic acid | 0.50 | 0.4 |
| Eicosenoic acid | 1.25 | 1.0 |
| Behenic acid | 0.30 | 0.3 |
| Erucic acid | - | < 0.1 |
| Lignoceric acid | - | < 0.1 |

**Table 2.** Characteristics for the rapeseed oil

| Characteristic | Crude rapeseed oil | Degummed rapeseed oil | Refined rapeseed oil |
|---|---|---|---|
| Free fatty acids (% oleic acid) | 1.2 | 1.2 | 0.09 |
| Water and volatiles (%) | 0.13 | 0.13 | 0.035 |
| Impurities insoluble in ethyl ether (%) | 0.1 | 0.1 | 0.008 |
| Phosphorus (%) | 0.05 | 0.028 | - |
| Total fat (%) | | 99 | - |
| Energetic value (kcal) | - | 891 | - |
| Erucic acid (%) | - | 0 | 0 |
| Iodine value (mg.I/ 100 cm³) | - | - | 2 |
| Soap (sodium oleate) (%) | - | - | 0.004 |
| Peroxide (meq/ kg) | - | - | 0.5 |

## EXPERIMENTAL METHODOLOGY

The rheological tests were done on a cone and plate rotational viscometer “Brookfield Cap 2000+”. This is suitable for the complete characterization of Newtonian and non-Newtonian fluids including the measurement of yield points or thixotropy. The built-in display shows all relevant results and the flow-/viscosity curve could be plotted using CAPCALC32 software.

Using the cone-plate viscometer, highly viscous liquids and pastes from many differing fields of industry can be characterized according to ISO 3219. Flow curves deliver a rheological determination of Newtonian and non-Newtonian behaviour. The features of the viscometer are:

- Automatic recording of flow curves;
- Time measurements;
- Temperature programs;
- Viscosity measurements according to ISO 3219.

To determine the lubricant rheological model for rapeseed oil, in all three states, it was used an “imposed velocity gradient” test, with the variation limits 100 ... 2000 $s^{-1}$ and temperature range of 20...75°C. The tests were carried out by loading to 2000 $s^{-1}$ and downloading to 100 $s^{-1}$, in order to highlight the effects of lubricant thixotropy.

There were tested the three samples of fluid and were calculated the lubricant rheological parameters, using the rheometer software, beyond the non-Newtonian fluids model, for the power law:

$$\tau = m\left(\frac{du}{dy}\right)^n, \tag{1}$$

where:

$\tau$ - shear stress, Pa;

$\frac{du}{dy}$ - shear rate, 1/s;

$m$ - consistency index (which is equivalent to the Newtonian fluid viscosity), Pa.$s^n$;

$n$ - flow index (equal to 1 if the fluid is Newtonian).

To determine the apparent viscosity variation of law versus temperature for analyzed lubricants, there were made tests for four imposed velocity gradients: 500 $s^{-1}$, 1000 $s^{-1}$, 1500 $s^{-1}$ and 2000 $s^{-1}$ and for a temperature range of 20 ... 75$^0$C. The law of variation which has been assumed was Reynolds law:

$$\eta = \eta_{50} e^{m(t-50)}, \tag{2}$$

where:

$\eta$ – viscosity, Pa.s;

$\eta_{50}$ – viscosity at 50 $^0$C, Pa.s;

$m$ – temperature parameter, 1/$^0$C;

$t$ – temperature, $^0$C.

The parameters values of the variation laws were determined using the regression analysis method, using MathCAD software.

## RESULTS AND DISCUSSION

Lubricant rheograms for rapeseed oil, in crude, degummed and refined state, are presented in Fig.1, Fig.2 and Fig.3. The results for lubricant rheological parameters for all three states are directly obtained by using the rheometer software (Capcalc V3.0), being centralized in Table 3.

**Table 3.** The lubricant rheological parameters for rapeseed oil, in different states

| States of rapeseed oil | Consistency index ($m$), Pa·s$^n$ | Flow index ($n$) | Correlation coefficient - |
|---|---|---|---|
| Crude | 0.257 | 0.794 | 59.8% |
| Degummed | 0.291 | 0.767 | 52.7% |
| Refined | 0.521 | 0.672 | 49.6% |

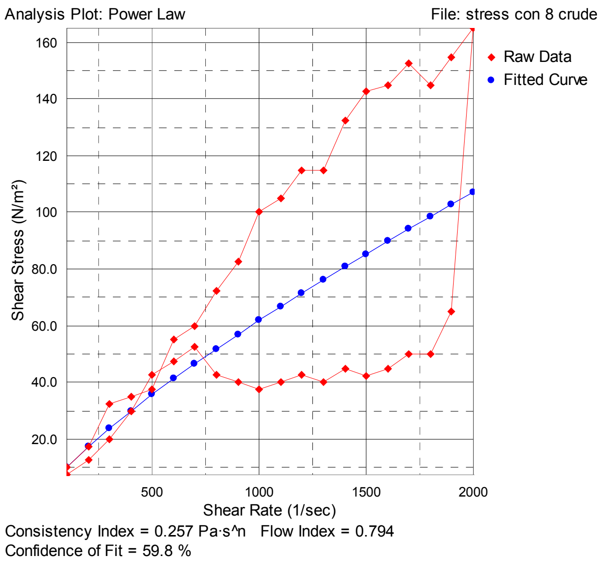


**Fig.1.** Lubricant rheogram for crude rapeseed oil

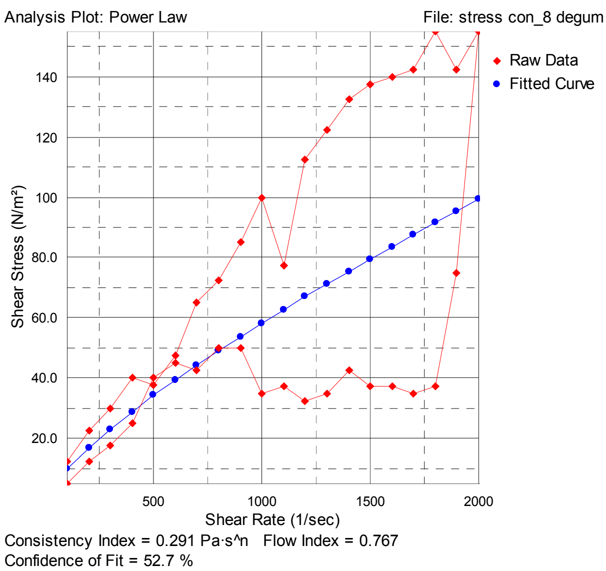


**Fig.2.** Lubricant rheogram for degummed rapeseed oil

Analysing the values of the the rheological parameters, it can observe that the characteristic rheological model for all three states of rapeseed oil (crude, degummed and refined) is the power law model, but with a low correlation coefficient. This is due to the pronounced thixotropy phenomenon, which occurs regardless the refining degree of the lubricant.

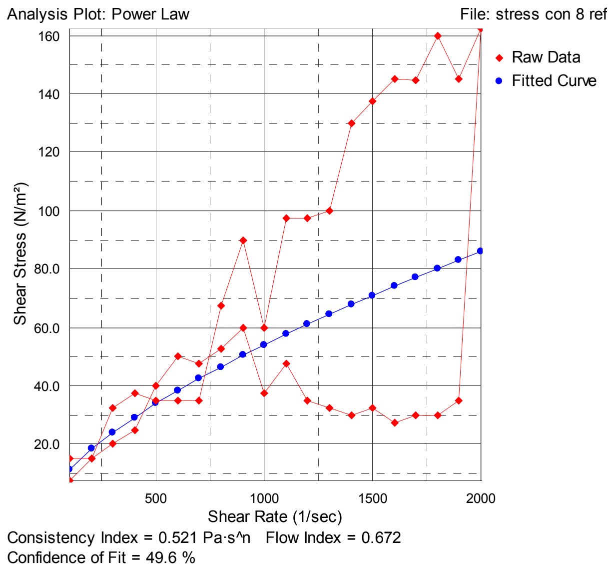


**Fig.3.** Lubricant rheogram for refined rapeseed oil

In the case of crude, degummed and refined rapeseed oils, pronounced oscillations of tangential stresses were observed, which means that their structure is relatively unstable and heterogeneous.

The results concerning the variation of apparent viscosity versus temperature, for all three states of rapeseed oil, are presented in Fig.4, Fig.5 and Fig.6.

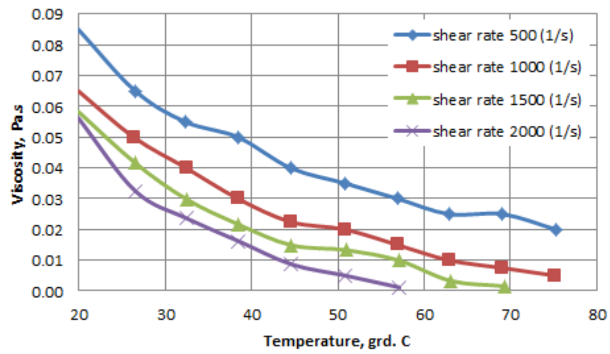


**Fig.4.** Variation of apparent viscosity versus temperature for crude rapeseed oil

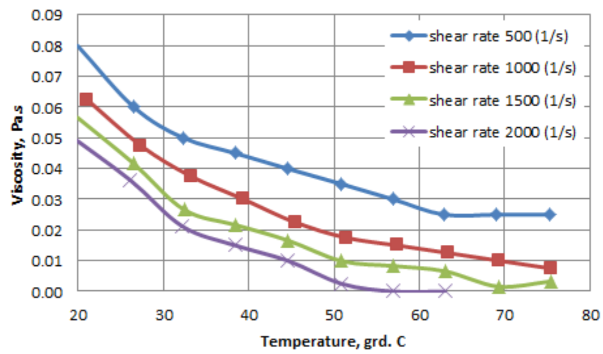


**Fig.5.** Variation of apparent viscosity versus temperature for degummed rapeseed oil

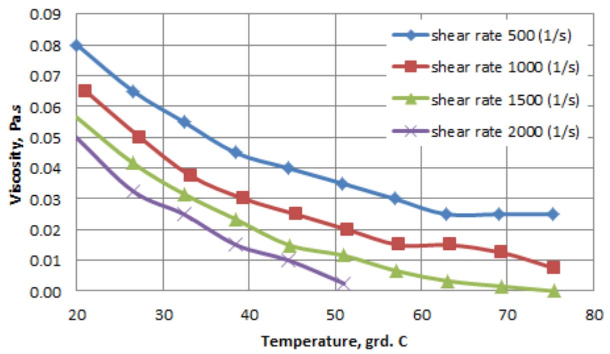


**Fig.6.** Variation of apparent viscosity versus temperature for refined rapeseed oil

The characteristic parameters for the Reynolds model corresponding to all three states of rapeseed oils (eq. 2) are presented in Table 4.

**Table 4.** Characteristic parameters for the variation of the apparent viscosity versus temperature, according to Reynolds model, for rapeseed oil in different states

| Parameter / Shear rate, 1/s | Crude rapeseed oil | | |
|---|---|---|---|
| | $\eta_{50}$, Pa·s | m, $1/^0$C | Correlation coefficient |
| 500 | 0.0367 | -0.025 | 98.62% |
| 1000 | 0.0179 | -0.045 | 98.99% |
| 1500 | 0.0095 | -0.067 | 93.07% |
| 2000 | 0.0040 | -0.095 | 93.88% |
| **Parameter / Shear rate, 1/s** | **Degummed rapeseed oil** | | |
| | $\eta_{50}$, Pa·s | m, $1/^0$C | Correlation coefficient |
| 500 | 0.0366 | -0.021 | 95.41% |
| 1000 | 0.0194 | -0.037 | 99.65% |
| 1500 | 0.0105 | -0.058 | 92.58% |
| 2000 | 0.0042 | -0.090 | 92.43% |
| **Parameter / Shear rate, 1/s** | **Refined rapeseed oil** | | |
| | $\eta_{50}$, Pa·s | m, $1/^0$C | Correlation coefficient |
| 500 | 0.0372 | -0.022 | 96.01% |
| 1000 | 0.0210 | -0.036 | 98.08% |
| 1500 | 0.0089 | -0.070 | 96.44% |
| 2000 | 0.0043 | -0.089 | 91.45% |

Analysing Table 4, it can be observed that the Reynolds model for the variation of apparent viscosity with temperature is valid for all states of the oil, with values of correlation coefficients higher than 90%.

## CONCLUSIONS

At present, the eco-friendly industrial lubricants could be serious possible replacers of mineral and synthetic oils. In this category, an important place is taken by the vegetable oils, because of the fact that they are biodegradable, generally less toxic and renewable. Rapeseed oil production occupies third place in the world production of vegetable and marine oils. This oil is characterized by excellent lubricity, a very high viscosity index (VI) and high flash point.

On the negative side, rapeseed oil in crude state has a lack of sufficient oxidative stability for lubricant use. Low oxidative stability means the oil oxidizes rather quickly during use, if it is untreated, becoming thick and polymerizing to a plastic-like consistency.

The solution for this problem is chemical modification by refining and adding antioxidant additives. The presence of additives could reduce the phenomenon of thixotropy and increase the structural stability of the lubricant. Anyway, the thixotropy of rapeseed oil disappears at low shear rates (less than 500 $s^{-1}$), regardless the refining degree of the lubricant.

Regarding the thermal behaviour of the rapeseed oils, it can be observed a strong decrease of apparent viscosity with increasing of shear rate, for all three states of lubricant. This shows an important pseudo plastic behaviour of the rapeseed oil.

## REFERENCES

1 S. C. Cermak, G. Biresaw, T. A. Isbell, R. L. Evangelista, S. F. Vaughn, R. Murray, *Ind. Crops Prod.,* 44, 232, (2013).
2 N. J. Fox, G. W. Stachowiak, *Tribol. Int.*, 40, 1035, (2007).
3 B. Krzan, J. Vizintin, *Tribol. Int.*, 36, No. 11, 827, (2003).
4 F. M. T. Luna, B. S. Rocha, Jr. E. M. Rola, M. C. G. Albuquerque, D. C. S. Azevedo, Jr. C. L. Cavalcante, *Ind. Crops Prod.,* 33, 579, (2011).
5 B. Lyu, X. B. Duan, D. G. Gao, J. Z. Ma, X. Y. Hou, J. Zhang, *Ind. Crops Prod.,* 70, 292, (2015).
6 H. M. Mobarak, M. Chowdhury, *Tribology in Industry*, 36, No. 2, 163 (2014).
7 E. M. J. Deffense, *Ol., Corps Gras, Lipides*, 16, 14, (2009).
8 I. Pirna, C. Lica, M. Nicolescu, E. Voicu, M. Radu, G. Gageanu, Ch. Fürll, *INMATEH - Agricultural Engineering*, 32, No. 3, 84, (2010).
9 X. Ji, Y. Chen, X. Wang, W. Liu, *Ind. Lubr. Tribol.,* 64, No. 6, 315, (2012).
10 R. M. Mortier, M. F. Fox, S. T. Orszulik, Chemistry and Technology of Lubricants, Springer, Third Edition, 209, (2010).