

## COMPARATIVE STUDY OF SELECTED LUBRICATING PROPERTIES OF BIOFUELS

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### ABSTRACT

The paper presents the research results of lubricity of selected vegetable oils, rapeseed oil methyl esters, and esters with addition of oleic acid. Higher wear of samples during lubrication by rapeseed oil methyl esters in comparison to the tested vegetable oils was obtained. The addition of oleic acid to esters resulted in the improvement of their lubricating properties.

**Keywords:** vegetable oils, rapeseed oil methyl esters, lubricating properties.

### INTRODUCTION

Ability to limit access to the ON (shortage or depletion of oil in the world), as well as political issues and environmental hazards associated with the extraction and processing of oil, inspired the search for alternative fuels of vegetable origin to power diesel engines. To supply diesel engines (CI) most commonly used are biofuels the following: vegetable oils, fatty acid alkyl esters and bioethanol [1].

The world produces mostly soybean and palm oil, and rapeseed oil, along with sunflower oil, is only on the third-fourth place. [2]

The work carried out on the use of vegetable oils as fuels depends on the geographic region. In temperate climates soybean and sunflower oil are tested, in the northern temperate zone other oils are tested: rapeseed, linseed and corn oil, and in warm climates: palm, peanut, cotton, sesame and coconut oil [1].

Vegetable oils are the glycerol esters and fatty acids of chemical nature containing from 14 to 22 carbon atoms in the molecule. Fatty acids are composed of carbon chains of different lengths and different number of double bonds between the carbon atoms [3].

In the studies described in [4], it was observed that the lubricity of pure fatty acid compounds increases to some extent with the length of the carbon chain. However, greater improvement in lubricity was achieved with the increased number of double bonds than in the case of increasing the chain length. Triglycerides of oleic acid also showed a better lubricity than the corresponding methyl ester, in contrast to literature reports [5]. The carboxyl group is likely to be most effective in improving the lubricity [4]. Electrons of double bonds at the end of the carbon chain are also very effective in improving lubricity [6]. The sequence of oxygenated groups to improve lubricity according to [4] is as follows: COOH > CHO > OH > COOCH<sub>3</sub> > C=O > C-O-C. Improved lubricity caused by COOH and OH groups correlates with the known observation of ionic interaction of the metal substrate with the lubricant molecules caused by hydrogen bonds and the Debye orientation forces, which are much stronger than the interaction based on the van der Waals forces [7].

The lubricating properties of alkyl esters are lower, because it does not give the ionic interaction with the metal, because of the absence of free OH groups. In the tests described in [4] is pointed

out, that the lubricity decreases with decreasing number of OH groups, and that the addition of free fatty acids for fuels with low lubricity improves lubricity, which is consistent with literature reports [8, 9, 10]. Geller and Goodrum [11] in 2004 formed the initial correlation between the degree of unsaturation and lubricity. In a number of investigated fatty acid methyl ester: stearic acid ester (C18: 0), oleic acid ester (C18: 1), linoleic acid ester (C18: 2) and linolenic acid ester (C18: 3), with the increase of the degree of unsaturation, the increase of lubricity was observed. However, the research [12] shows that with the increase of the degree of unsaturation of fatty acids in sunflower oil, the lubricating properties of the oil decreased.

This paper presents the results of lubricity of selected vegetable oils, rapeseed oil fatty acid methyl esters and esters with oleic acid added for potential use as a fuel or fuel additives for petroleum products.

## MATERIALS AND METHODS

The study was conducted on a test stand presented in detail in [13]. The method of testing was to simultaneously wear three samples ( $\Phi$  diameter about 5 mm) by means of a rotating counter-sample in a form of a flat ring, in the lubrication conditions with the test agent at the temperature of 333K, by friction of about  $2 \cdot 10^4$  m, at a pressure of 29.43 kN. Samples and counter-samples were made of steel 100Cr6 (H15SG), which is a very common material used for the production of injection equipment. The test agent during the test circulated in a closed loop, in the amount of 30 dm<sup>3</sup>, which was thermally filtered and stabilized. The measure of lubricating properties is the mass and surface loss of samples. The study determined the coefficient of friction.

Refined vegetable oils: sunflower, soybean, rice, peanut, corn and rapeseed (characteristics in Table 1), as well as fatty acid methyl esters of rapeseed oil Trzebinia and esters produced at Lublin University of Technology were used in the research. The rapeseed oil methyl esters Trzebinia with the addition of free fatty acid in the form of oleic acid were also tested.

## RESULTS

First of all, the vegetable oils were subjected to the tests. The result charts concerning the lubricating properties of these oils are presented below.

The graphs in Figure 1 indicates that the soybean has got the best lubrication properties, measured by the degree of wear of the steel among the tested vegetable oils. The biggest loss of mass and the largest surface of trace of cooperation was observed for the sunflower oil, which means the worst lubricating properties of the oil.

Then rapeseed oil methyl esters Trzebinia were tested to define their characteristics, which are shown in Table 2. The study was conducted in the laboratory of the University of Life Sciences in Lublin. Results of the lubricating properties of pure rapeseed oil methyl esters are summarized in Table 3.

The research shows that rapeseed oil methyl esters are characterized by poorer lubrication properties than the tested vegetable oils. A similar degree of wear of test samples in conditions of ester lubrication, regardless of manufacturer, was obtained.

The third group subjected to the tests consisted of rapeseed oil methyl esters Trzebinia with addition of oleic acid, for which the results are shown in Figure 2.

Rapeseed methyl esters with the addition of oleic acid have got better lubricating properties than pure esters. The addition of oleic acid in the

**Table 1.** The fatty acid content in vegetable oils tested, % of mass [1]

| Oil types     | C18: 0 stearic acid | C18: 1 oleic acid | C18: 2 linoleic acid | C18: 3 linolenic acid |
|---------------|---------------------|-------------------|----------------------|-----------------------|
| Rapeseed oil  | 1.2–2.0             | 60–73             | 19–22                | 9–10                  |
| Soybean oil   | 2.1–6               | 22–34             | 53–60                | 2–10<br>8 [2]         |
| Sunflower oil | 2.9–4               | 17–18<br>22 [2]   | 71–74<br>66 [2]      | 0.5                   |
| Corn oil      | 1.5–4               | 30–50<br>28 [2]   | 34–56<br>58 [2]      | 1.0                   |
| Peanut oil    | 2.0–2.4             | 48–48.5           | 32–34                | 0.9–1.0               |
| Rice oil [14] | 1.9                 | 42.5              | 39.1                 | 1.1                   |

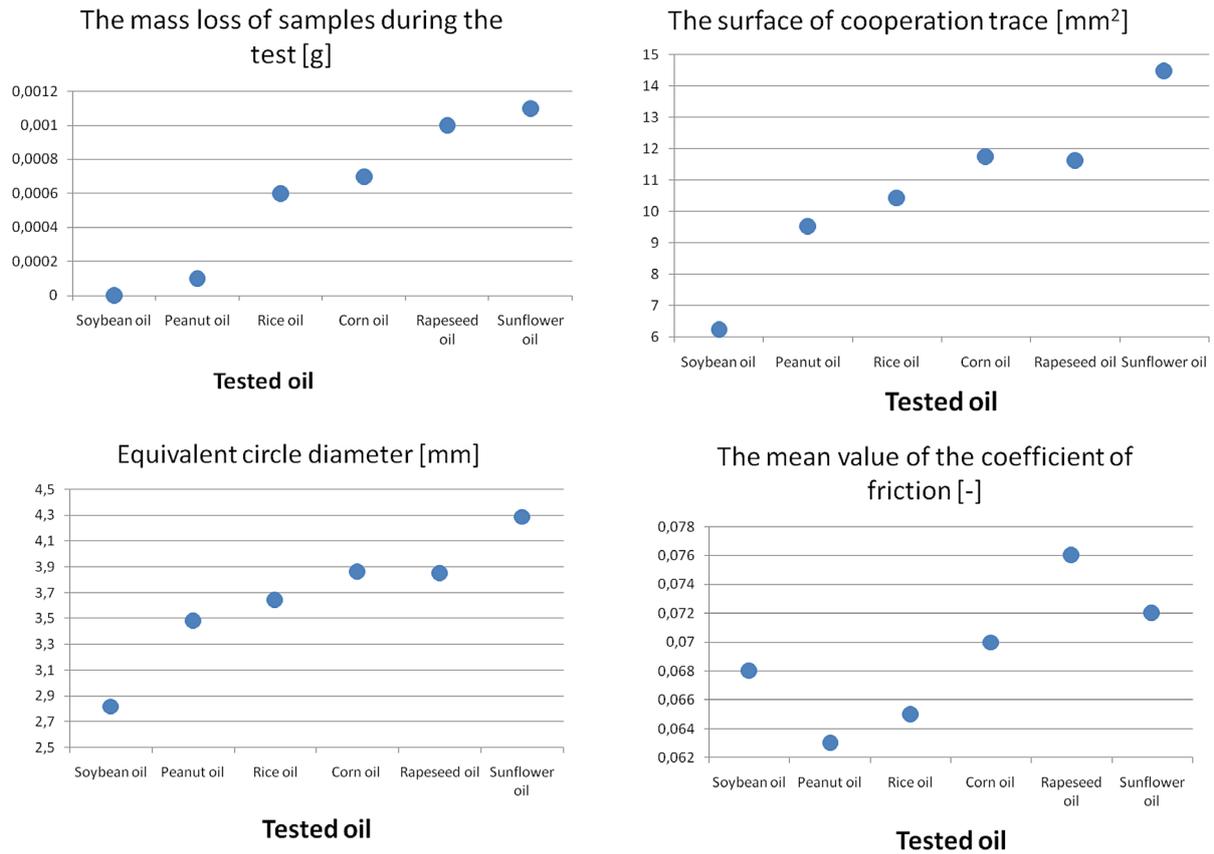


Fig. 1. Summary of the results of the lubricating properties of vegetable oils tested

Table 2. Characteristics of rapeseed oil methyl esters Trzebinia (Biodiesel B-FAME). Research date 23.03.2012

| 1. | Research parameter                         | Research method   | Requirements according to standards | Result % (m/m) | Expanded uncertainty |
|----|--|---|-------------------------------------|----------------|----------------------|
| 2. | The content of fatty acid methyl esters    | Procedure CLA-GC-17-2011 based on the PN-EN 14103:2004 standard | min. 96.5                           | 91.95          | 15.34                |
| 3. | The content of linolenic acid methyl ester | Procedure CLA-GC-17-2011 based on the PN-EN 14103:2004 standard | max. 12                             | 9.7            | 1.56                 |
| 4. | Methyl alcohol content                     | Procedure CLA-GC-15-2011 based on the PN-EN 14110:2004 standard | max. 0.2                            | 0.004          | 0.0005               |
| 5. | Total glycerol content                     | Procedure CLA-GC-13-2011 based on the PN-EN 14105:2004          | max. 0.25                           | 0              | 0                    |

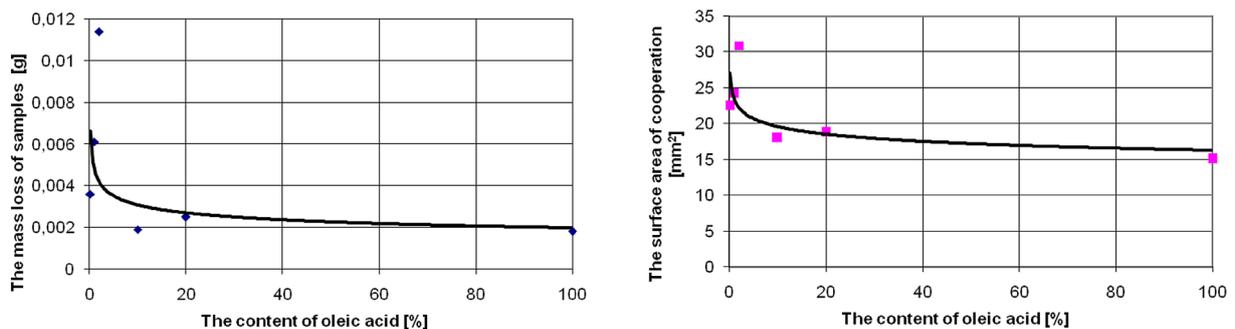


Fig. 2. Summary of the results of the lubricating properties of rapeseed oil methyl esters with addition of oleic acid according to [15]

**Table 3.** The results of lubricating properties of rapeseed oil methyl esters

| The test agent                                | Loss [g] | The surface of trace of cooperation [mm <sup>2</sup> ] | Equivalent circle diameter [mm] | Final pressure [MPa] | The coefficient of friction [-] |
|---|----------|--|---------------------------------|----------------------|---------------------------------|
| ESTER I (Trzebinia)                           | 0.0049   | 23.02  | 5.41                            | 129                  | 0.082                           |
| ESTER II (Lublin University of Technology 1)  | 0.0049   | 25.78  | 5.73                            | 114                  | 0.089                           |
| ESTER III (Lublin University of Technology 2) | 0.0036   | 22.47  | 5.35                            | 131                  | 0.101                           |

amount of several percent provides improved lubricating properties of rapeseed oil fatty acid methyl esters.

### ANALYSIS OF RESULTS

Best lubricating properties among the tested vegetable oils were observed in the case of soybean oil, for which there has been almost no mass loss of the samples. The explanation of the observed effect of the best lubricating properties can be based on the correlation between the degree of unsaturation and lubricity, because soybean oil contains the highest number of unsaturated fatty acid esters among all of the tested oils.

It was found out that regardless of the manufacturer, the increased wear of samples during lubrication by pure fatty acid methyl esters of rapeseed oil was reported.

Free fatty acids [2] are present in the vegetable oils in small amounts (0.1–2%) that are acids containing COOH group, which according to the group sequences improving the lubricity [4] is the strongest one. The presence of the group COOCH<sub>3</sub> determines the lubrication properties of esters, and so the group of further positions in the sequence. The obtained results of vegetable oils and pure rapeseed oil methyl esters are compatible with the above-mentioned sequence of oxygenated groups, which indicates that a small amount of free fatty acids provides lubricity of vegetable oils. An addition of free fatty acid (oleic acid) to methyl esters of rapeseed oil also had a positive effect on the lubricating properties and confirmed the accuracy of the sequence. Wherein, it is reasonable to add it in the amount of several percent (similar to the content in vegetable oils). Over 10% increase in the content of this addition will virtually have no effect on the result. Free fatty acids are, therefore, the materials to improve lubricity, but they are believed to be contamination and are limited by the standard.

### CONCLUSIONS

On the basis of the conducted research, we can draw the following conclusions:

- Among the tested vegetable oils, the soybean oil is characterized by the best lubrication properties, which contains the highest number of unsaturated fatty acid esters.
- Increased wear of the samples in the lubrication conditions of rapeseed oil methyl esters in comparison to vegetable oils was obtained, which is consistent with the sequence of oxygenated groups improving lubricity.
- The addition of oleic acid to methyl esters of rapeseed oil ester increased lubricating properties of esters, confirming the validity of the said sequence.

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