THE SPECIFIC PECULIARITIES OF RAPESEED FUEL USAGE DEPENDING ON OIL CHEMICAL STRUCTURE

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Abstract. Vegetable oils by 95 to 97 % consist of fatty acid triglycerides. The residues of fatty acids are responsible for the chemical and physical properties of oils. If the length of the fatty acid chains is the same, increasing of double bound quantity lowers the melting and solidification temperature that allows the use of vegetable oil containing unsaturated fatty acids as a fuel without warming up at lower ambient temperatures. The Sixth Community Environment Action Programme (2007/2204(INI)) gives the EU environmental policy direction from 01.07.2002 till 01.07.2012. Alternative fuel sphere researches in the whole world are directed on decreasing the dependence on oil extraction industry, updating world economics and defending environment from pollution. Environmental pressures demand cleaner processes, and there is a market for new 'green' chemistry products. The usage of pure plant oils (PPO) is a way to live in close connection with nature. Generally, renewable fuels are produced to reduce greenhouse gas emissions, improve combustion of fuels, and extend supplies of fossil fuels, although their production may also be used to subsidize the production of agricultural commodities and improve the balance of trade for countries that produce little fossil fuel. The subject of research is changing of pure rapeseed oil physical properties depending on the fatty acid triglyceride structure. So, the main goal is to find more effective modification of pure rapeseed oil.

Keywords: rapeseed oil, triacilglycerols, fractionation.

Introduction

Triacilglycerols (TAGs) may be incorporated in diesel fuels without chemical modification, but they have higher fuel viscosity then traditional fossil fuel. So, the problem of producing a fuel with lower viscosity, which may be used as a direct replacement for diesel fuel, is very topical.

Fatty acids, esterified to glycerol, are the main constituents of pure plant oils and such kind of fats as fish oil. The chemical modification for industrial exploitation of PPO is based on the most reactive sites in fatty acids as the carboxyl group and double bonds. Saturated chains mainly show inreactivity [1, 2].

Fatty acids vary in chain length and unsaturation level. The most common natural fatty acid chain lengths are between C16 and C22, with C18 fatty acids dominating in most plant oils. Below this range, they are characterized as a short or medium chain type, above – as long-chain acids. Naturally occurring fatty acids have *cis*-double bonds, because the chain is built during the process of biosynthesis from two carbon units, and it is inserted by enzymes of desaturase group at specific positions relative to the carboxyl group. Animal fats have a wider range of chain length, and high erucic varieties of rape are rich in this C22 monoene acid.

Saturated fatty acids have a straight hydrocarbon chain. A *trans*-double bond is accommodated with little change in shape, but natural fatty acid residues of PPO are usually located in *cis*-configuration of the molecular form. *Cis*–configuration is the dimensional position, when the radicals are located on one side of the double bond. This situation causes 'the windings' in the molecular geometry – therefore the chains cannot go closer and establish hydrophobic intermolecular contacts. Rapeseed oil contains a large amount of *cis*–configured unsaturated fatty acids as linolenic acid; therefore it has higher fluidity [3-5].

Trans-acids have melting points much closer to those of the corresponding saturates. Polymorphism results in two or more solid phases with different melting points. Methyl esters are lower melting than fatty acids but follow similar trends.

The melting point increases with the chain length, but increasing of double bound quantity (if the length of the fatty acid chains is the same) lowers the melting and solidification temperature, what allows the use of vegetable oil containing unsaturated fatty acids as fuel (without warming up) at lower ambient temperatures. However, when vegetable oils are highly unsaturated (have a high iodine value, such as linseed and cannabis oil) – they solidify at lower temperatures, but have high oxidative instability – they quickly break down.

If the compounds have quite a large quantity of double bounds (they have a low iodine value, such as palm oil, which usually is already hard at room temperature), such kind of biofuel will have higher stability – it will be decaying more slowly [2, 4, 5].

Ackman and *Eaton* indicated that a different proportion between eicosenoic (C20:1) and octadecanoic, polyunsaturated fatty acids could be a major factor in changing the relative density of canola oil [5].

The high tolerance of erucic acid to temperature makes it suitable for transmission oil. Its ability to polymerize and dry means: it can be and is used as a binder for oil paints. Being a hydrocarbon of a high calorific value, with a very low flash point, high cetane number, and good lubrication qualities, erucic acid can be a valuable component of bio-diesel. But as high erucic varieties of rape are rich in this C22 monoene acid, the viscosity of *HEAR* (high erucic acid rapeseed) oil is significantly higher than that of canola oil – from this point of view *LEAR* (low erucic acid rapeseed) can be more perspective for usage as a biofuel [1, 4].

It is possible to divide rapeseed oil into fractions after solidification. Fractionation (winterizing as it is sometimes called) helps to remove the highmelting-point TAGs. The process involves chilling the fat and then separating the two phases by filtration. One of the key factors determining the success of the fractionation process is the efficiency of separation. During this cycle, agitation is introduced by either very slow rotation of mechanical agitators or by bubbling cold air through the cell. After a certain period, the temperature difference is changed for the crystal maturing phase, and the agitation may be reduced or stopped.

Although the TAGs form the main crystalline phase, the minor components, or impurities, can often play a large role in how crystallization occurs and crystallization may be substantially different in refined oil than in the unrefined starting material.

Lutton stated that if the fatty acids of a TAG differ in length by more than four carbons, it forms a triple chain-length structure. Triple chain-length packing is also observed in TAG containing a *cis*-unsaturated fatty acid because this causes a kink in the structure. *Cis*-unsaturated fatty acids do not mix in one layer with saturated fatty acids, and triple chain-length crystals are formed. It should be noted that *trans*-unsaturated fatty acids incorporate into a crystal structure in the same way as the saturated fatty acids [5].

Transformation of unstable to stable polymorphs can be achieved by a slight increase in temperature above the melting point of the less stable forms. This increase in temperature first causes the melting of the unstable forms and then solidification in a more stable form [3, 5].

Materials and methods

During the experiment the *LEAR* type rapeseed oil from rape grown in Latvia was used. It can be used for both purposes: as a food product and biofuel.

Initially nonrefined rapeseed oil was divided into 3 portions about 500 ml each and poured into dark glass jars. Dark glass pots were selected to lower possible polymerisation and oxidation in the way that could be used in our conditions. One jar was kept at room temperature; other two were placed into refrigerator freezer with temperature –12 ˚C. These two pots (one – for fractionation purpose, the second – for control analysis) were in the refrigerator for 5 hours.

Low agitation took place every hour (totally – 4 times per cooling time). Agitation was used as very slow rotation of metal hand agitator. After a period of 5 hours, when the forms observed were stable and after separation of unsaturated phase the process of agitation was stopped.

After that the part, which was not frozen, was separated by the gauze folded up for firming 4 layers of the filtering material. The residue of solid phase of rapeseed oil at gauze was not pressed up to avoid the contamination with saturate fraction of rapeseed oil (and the possible *trans*-unsaturated fraction) and was dumped. The gauze was chosen as an inert material with enough large ability either to funnel high viscosity fluid or to retain and cope with pressure of semisolid phase of frozen rapeseed oil.

Figure 1 shows the jar of rapeseed oil with higher solidification point and the pot with residue of hard, frozen oil.

Fig. 1. **Fractionation product volume:**
1 – 310 ml of separated fraction; 2 – 500 ml of oil

The jar with the newly separated sample and the control testing pot were kept in refrigerator 5 hours more without agitation. After that the testing of viscosity with the capillary glass viscometer *ВПЖ-4* was applied for sample staying at room temperature (calibrated thermometer showed 24 °C), frozen control and separated layer's samples. Formula 1 was used for calculation of the viscosity value for all cases.

$$V = \frac{g}{9.807} \cdot T \cdot K, \quad (1)$$

where K – viscometer constant, 0.8837 $mm^2 \cdot s^{-2}$;
V – kinematical viscosity of fluid, $mm^2 \cdot s^{-1}$;
T – expiration time of the liquid, s;
g – acceleration of gravity, $m \cdot s^{-2}$.

Results and discussion

After 5 hours of deep freezing at –12 ˚C from the first 500 ml rapeseed oil sample 310 ml fraction with higher solidification point and higher unsaturation level was obtained. This part was stable for 2 hours before the decision to separate it (because of freezing camera specification the temperature could not be changed step by step, so the one was being constant during the experiment). After 5 hours from fractionation separated fraction and control sample were deeply frozen (at –20 ˚C): the fraction with higher unsaturation level in 3 hours was as very viscous homogenous fluid, at the same time in the control pot the freezing centre was seen, which formed because of the agitation process (centripetal acceleration made unstable polymorphs to stable). Figure 2 shows the rapeseed oil solidification process. After 5 hours of deep freezing (without agitation) both samples (selected fraction and control) were deeply frozen.

Fig. 2. **The freezing centre in the right jar**

After 15 minutes at temperature 24 ˚C (time for preparing for the measurement – as is prescribed in the capillary glass viscometer *ВПЖ-4* instruction) the separated fraction was without any visible signs of being frozen, but the control sample was still non-uniform. Only after 30 minutes in the control sample pot rapeseed oil was seen as fully homogeneous substance.

During the process of viscosity measuring results were obtained for all 3 samples (Table 1). For every sample 4 measurements were done, and the average was calculated. The first sample in the table is oil, which stayed on the table at room temperature during 10 hours, the second – divided fraction, the third – control sample without division, but after deep freezing.

Table 1

Results of measurements and calculated viscosity

No.	Expiration time of the liquid T, s	Kinematical viscosity of the fluid V, $mm^2 \cdot s^{-1}$
1	67.4	59.56
2	66.5	58.78
3	68.1	60.20

Entertaining result was the control sample's longest expiration time of the liquid. Kinematical viscosity can be increased with elongation of chains, hydrogenation, polymerisation or oxidation. First two reactions need specific conditions, but heating stimulates the polymerisation or oxidation process. So, it can be suggested that it was observed that deep freezing stimulated conversion of *cis*-unsaturated forms into *trans*-unsaturated TAGs' forms as these structures have viscosity comparable with fully saturated. The expiration time of the divided fraction of the liquid shows significant separation of unsaturated TAGs.

Conclusions

1. After 5 hours of deep freezing at –12 ˚C from the first 500 ml rapeseed oil sample 310 ml fraction with higher solidification point and higher unsaturation level was obtained. The separated fraction stayed without of any visible signs of being fully frozen (fully homogeneous oily substance) in 15 minutes at temperature 24 ˚C, but the control sample – only in 30 minutes.
2. The expiration time of the liquid, which was divided, shows that fractionation in such conditions can be significantly used for separation of rapeseed oil unsaturated TAGs with higher solidification point (on purpose to improve the rapeseed oil quality for using as biofuel).
3. The results of the experiment allow suggesting that deep freezing and subsequent defrosting stimulate conversion of *cis*-unsaturated forms into *trans*-unsaturated TAGs' forms, so rapeseed oil physical peculiarities are deteriorating after deep freezing and subsequent defrosting.

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