



RAPE SEED OIL TETRAHYDROFURFURYLESTERS RAPŠU EĻĻAS TETRAHIDROFURFURILESTERA IEGŪŠANAS METODES

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Abstract: *The transesterification of vegetable oil using various kinds of alcohols is a simple and efficient renewable fuel synthesis technique. Products obtained by modifying natural triglycerides in transesterification reaction substitute fossil fuels and mineral oils. Currently the most significant is the biodiesel, a mixture of fatty acid methyl esters, which is obtained in a reaction with methanol, which in turn is obtained from fossil raw materials. In biodiesel production it would be more appropriate to use alcohols which can be obtained from renewable local raw materials. Ethanol rouses interest as a possible reagent, however, its production locally is based on the use of grain and therefore competes with food production so it would implicitly cause increase in food prices. Another raw material option is alcohols that can be obtained from furfurole. Furfurole is obtained in dehydration process from pentose sugars which can be extracted from crop straw, husk and other residues of agricultural production. From furfurole the tetrahydrofurfuryl alcohol (THFA), a raw material for biodiesel, can be produced. By transesterifying rapeseed oil with THFA it would be possible to obtain completely renewable biodiesel with properties very close to diesel [2-4]. With the purpose of developing the synthesis of such fuel, in this work a three-stage synthesis of rapeseed oil tetrahydrofurfurylestes (ROTHFE) in sulphuric acid presence has been performed, achieving product with purity over 98%. The most important qualitative factors of ROTHFE have been determined - cold filter plugging point, cetane number, water content, Iodine value, phosphorus content, density, viscosity and oxidative stability.*

Keywords: *biodiesel, rape seed oil, tetrahydrofurfuryl alcohol.*

Introduction

Biodiesel is currently one of the most popular renewable fuels and it has the following advantages in comparison with diesel [1]:

1. Biodiesel is environmentally friendlier than fossil fuel since the CO₂ produced during the operation of an internal combustion engine creates very little greenhouse effect, because significant part of it has been consumed during the vegetation period of the plants;
2. Running diesel engines on biodiesel reduces most of the harmful emissions;
3. If the production and use of biodiesel is increased, the energy independency of the countries lacking or having limited fossil energy sources increases as well;
4. The production of biodiesel provides for more balanced development of national economy.

The transesterification of vegetable oil using various kinds of alcohols is a simple and efficient renewable fuel synthesis technique. Products obtained by modifying natural triglycerides in transesterification reaction substitute fossil fuels and mineral oils. Currently the most significant is the biodiesel, a mixture of fatty acid methyl esters, which is obtained in a reaction with methanol, which in turn is obtained from fossil raw materials. In biodiesel production it would be more appropriate to use alcohols which can be obtained from renewable local raw materials. Ethanol rouses interest as a possible reagent, however, its production locally is based on the use of grain and therefore competes with food production so it would implicitly cause increase in food prices. Another raw material option is alcohols

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Materials and methods

To obtain the biodiesel, a refined rapeseed oil produced by SIA "Iecavnieks" was used. THFA was purchased from *Alfa Aesar GmbH & CO KG*. Paramagnetic resonance (PMR) spectrums were recorded with *Varian 600MHz* spectrometer, using CDCl_3 as a solvent.

The three-stage technique for obtaining ROTHFE in sulphuric acid medium with content over 98% was developed on the basis of publication [3] and incorporates the following:

In Stage 1, 58g of THFA is gradually mixed with 4g of concentrated H_2SO_4 . 100g of oil is heated in a round flask to 100°C , and then the THFA and sulphuric acid are added. Reaction pulp is intensively mixed using a magnetic stirrer at 100°C for 3 hours, then it is poured into a detachable funnel and after 24 hours, the remains of glycerin and sulphuric acid are separated. After this stage, the product concentration reaches 85%, according to PMR analysis.

Stage 2 is carried out by the same technique as Stage 1. The biodiesel and oil solution layer obtained in Stage 1 is transesterified with 15g of THFA, in which 1g of concentrated sulphuric acid has been dissolved. After separation of glycerin, biodiesel layer is washed using 1l 15% sodium carbonate until pH is neutral, then it is washed with 300 ml of distilled water. To accelerate separation, 200g of sodium chloride is added to the emulsion, and then it is heated to 100°C . After separation of layers, the water is evaporated using rotation evaporator. Biodiesel layer according to PMR contains approx. 95% ROTHFE.

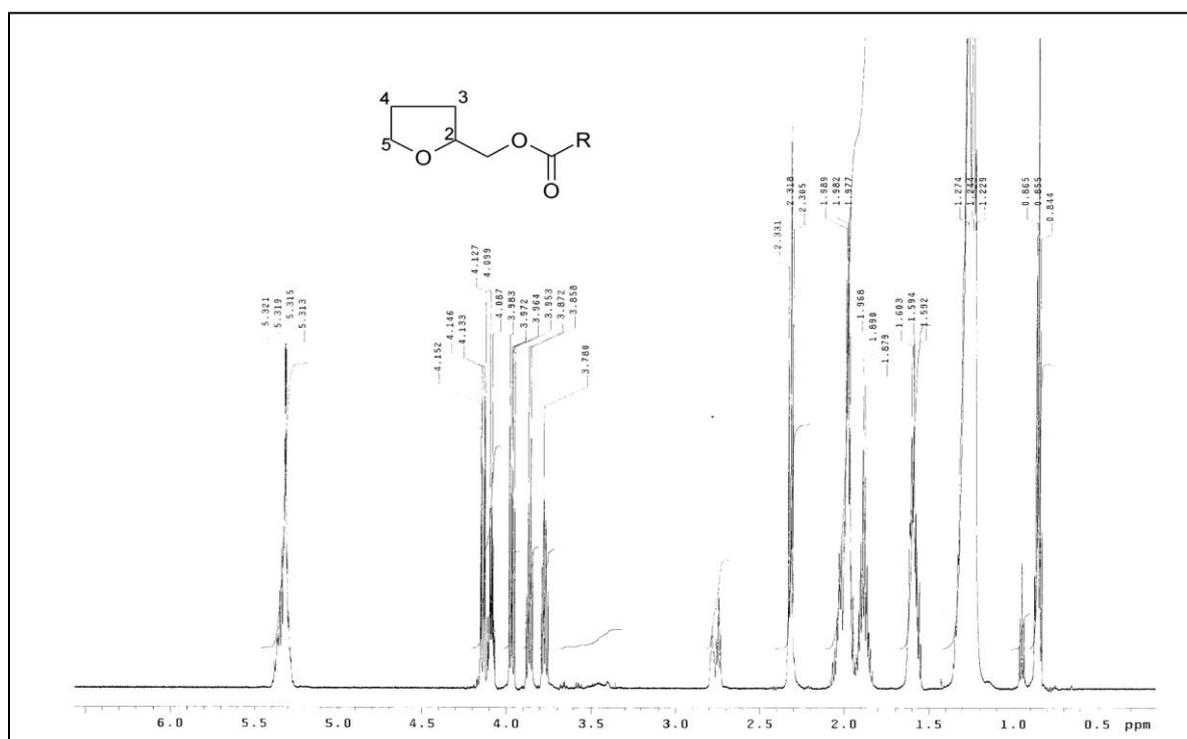


Fig. 1. ROTHFE PMR spectrum

In Stage 3, reagent concentrations, conditions and product separation are the same as in Stage 2, but ROTHFE washing is carried out 3 more times with 500ml of water to maximally separate the remains of acid and salts. After water is evaporated in vacuum, ROTHFE is dissolved in ¼ portion of petroleum ether and filtered through 0.8µm filter, then petroleum ether is evaporated and the outcome is 74g of product with ROTHFE concentration over 98%. PMR spectrum of the product is provided in Figure 1 and qualitative factors in Table 1. PMR ROTHFE signal attribution was performed as follows: THFA part: 1,9 and 1,6 (m and m, 3-CH₂); 1,9 and 1,8 (m and m, 4-CH₂); 3,86 and 3,77 (m, 5-CH₂); 4,09 (m, 2CH); 4,14 and 3,97 (dd and dd, -CH₂-O-C(O)-); fatty acid part: 1,0 – 0,8 (t, CH₃ group); 5,4 – 5,2 (m, -CH=CH-); 2,8 – 2,7 (m, =C-CH₂-C=); 2,32 (t, ³J=7Hz, -C(O)-CH₂-); 1,98 (m, -CH₂-C=C-CH₂-); 1,6 (m, -C(O)-C-CH₂-); 1,4 – 1,2 (m, the other CH₂ groups).

Results and discussion

The most important qualitative factors of ROTHFE determined in accordance with requirements of European biodiesel standard EN 14124 are shown in Table 1. According to the data in table, a conclusion can be drawn that ROTHFE cold filter plugging point, cetane number, water content, Iodine value and phosphorus content comply with the standard. Surprising is the fact that the sulphur content in ROTHFE has increased remarkably. It can be attributed to the sulphuric acid (transesterification catalyst) remains in the biodiesel which are very hard to separate efficiently. The process of washing with water or Na₂CO₃ solution is labor-consuming and causes considerable product losses. ROTHFE also has increased density and viscosity, which can be attributed to its molecular weight, since it is higher than that of the corresponding rapeseed oil methyl and ethyl esters.

Table 1.

ROTHFE characteristics

<i>Parameter</i>	<i>Value</i>	<i>Method</i>	<i>Standard</i>	<i>Unit of measurement</i>
Cold filter plugging point	-7°	EN 116	Depending on climatic zone	°C
Cetane number	53,2	EN ISO 5165	min 51	-
Sulphur content	80,5	EN ISO 20846	max. 10	mg/kg
Water content	100	EN ISO 12937	max 500	mg/kg
Density at 15°C	0,937	EN ISO 3675	min 860, max 900	kg/m ³
Viscosity at 40°C	12,19	EN ISO 3104	min 3,5, max 50	mm ² /s
Iodine value	91,1	EN 14111	max 130	g iodine/100g
Phosphorus content	3	EN 14107	max 10	mg/kg
Oxidative stability at 110°C	<0,2	EN 14112	min 6,0	h

Oxidative stability of ROTHFE proved to be very low (see Table 1). Figure 2 shows that the curve representing ROTHFE oxidation process according to standard EN 14112 is very close to that of tetrahydrofurfuryl acetate. Tetrahydrofurfuryl acetate and ROTHFE oxidize without interruption, starting from the point of reference, and do not form the convexity typical to rapeseed methyl esters (RME) at the end of induction. This implies that the low oxidation stability of ROTHFE is due to the remains of tetrahydrofurfuryl alcohol and use of such esters will require the use of efficient antioxidants.

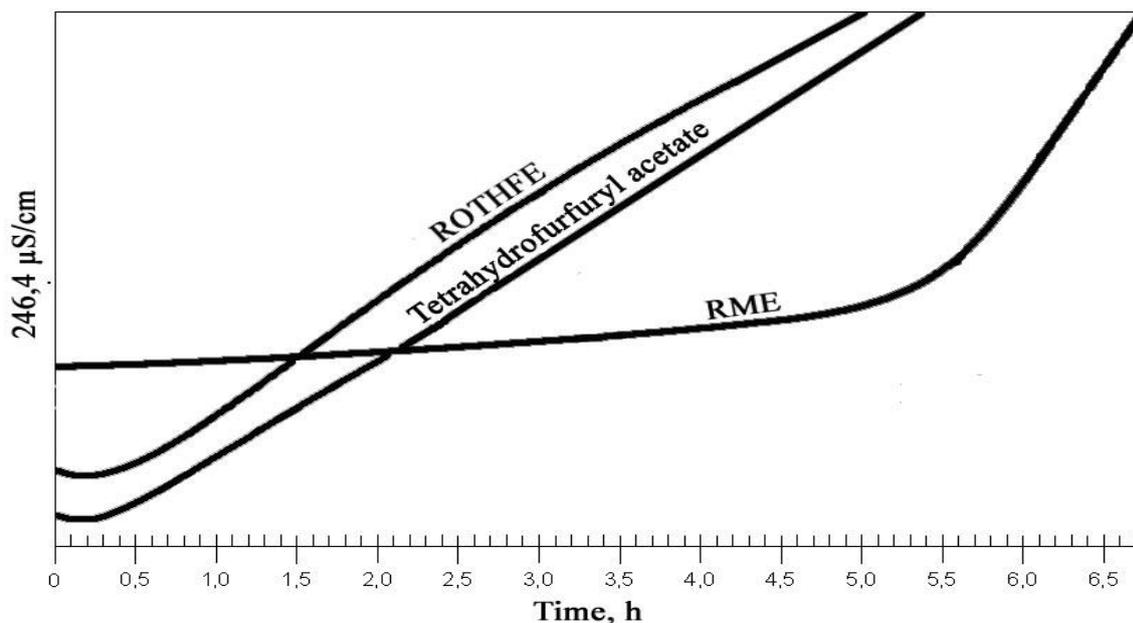


Fig. 2. ROTHFE, Oxidative stability curve of Tetrahydrofurfuryl acetate and RME

Conclusions

1. A three-stage process for ROTHFE synthesis in sulphuric acid presence including multistage separation and purification of the reaction product with the following PMR control has been developed, permitting to obtain product with purity over >98%.
2. ROTHFE cold filter plugging point, cetane number, water content, Iodine value and phosphorus content comply with biodiesel standard EN 14124.
3. In comparison with RME, ROTHFE has increased viscosity and density.
4. Oxidative stability of ROTHFE is low mostly due to tetrahydrofurfuryl fragment.
5. Using sulphuric acid as a transesterification catalyst, the product has increased sulphur content which can be reduced by washing with water or Na_2CO_3 solvent, but achieving very low sulphur content is a labor-consuming process which also reduces the final amount of product.

References

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