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# Optimization of rapeseed oil fatty acid esterification with methanol in the presence of sulfuric acid

**Janis Brinks*, Kristaps Malins, Valdis Kampars, Julija Prilucka, Lauma Apseniece**

*Riga Technical University, Institute of Applied Chemistry, 14/24 Azenes Str., Riga LV-1048, Latvia*
**Corresponding author: e-mail: janisbrin@gmail.com*

The interest in biodiesel production from low cost feedstocks is still increasing. Such feedstocks usually contain large amounts of free fatty acids, which make the currently employed base catalysts inefficient, thereby promoting the use of acid catalysts. Due to the high activity and low cost, sulfuric acid could become the most widely used acid catalyst for biodiesel production. Research undertaken so far using sulfuric acid for esterification of fatty acids has shown that the products obtained fail to meet the requirements of the standard EN 14214. This paper describes a systematic study of rapeseed oil fatty acids esterification in order to obtain a product complying with the standard EN 14214. The influence of sulfuric acid concentrations (0.1–3.0%), methanol molar ratios (1:1–20:1) and reaction time (0–360 min) was evaluated. Finally, a two-stage esterification process was developed, where in optimal conditions esterification yield of 97.8% and ester content of 99.6% were achieved.

**Keywords:** biodiesel, free fatty acids, sulfuric acid, methanol, esterification.

## INTRODUCTION

Biodiesel is one of the most promising alternatives to fossil fuels that is derived from renewable natural resources[1]. Currently, the largest proportion of biodiesel is produced by alkaline transesterification of edible oils that accounts for 70–95% of the total production costs[2]. Significant research direction is an attempt to obtain biodiesel using inexpensive, low quality feedstocks, such as the by-products of vegetable oil refining[3], used cooking oils[4], animal fats[5], trap grease[6] and free fatty acids (FFA) contained in crude glycerol[7]. Use of such feedstocks could be economically viable and environmentally friendly as with the decreasing price of biodiesel its competitiveness with fossil fuels would increase and reduce the amount of the produced waste[8]. Unfortunately, the high FFA content in such feedstocks prevents the effective use of alkaline catalyst[9]. In order to efficiently implement the alkaline transesterification, FFA content of the oil should not exceed 0.5 ww.% that corresponds to the acid value (AV) of ~ 1 mg KOH/g[10, 11]. It is possible to perform an alkaline transesterification of the oil that contains up to 3 ww.% of FFA (AV ~ 6 mg KOH/g) by increasing the amount of alkaline catalyst in order to compensate for FFA neutralization reaction consumption[12, 13]. In this case, additional amount of catalyst is needed, also leading to the soap formation. This results in decreasing the biodiesel separation and purification efficiency, causing an overall decrease in biodiesel yields and significantly increasing the production cost. Therefore, biodiesel production from high FFA feedstocks is better performed in the presence of acid catalysts as they can promote FFA esterification and also transesterification of triglycerides[14]. In the presence of acid catalyst biodiesel can also be obtained using FFA as the only feedstock[15, 16, 17].

FFA esterification and triglycerides transesterification are both reversible reactions[18]. The equilibrium of triglyceride transesterification reaction is shifted towards the formation of fatty acid methyl esters (FAME) because glycerin forms a separate phase and its reactivity is lower compared to methanol. However, the reversibility of FFA esterification reaction is significantly more pronounced compared to the triglycerides transesterification which is explained by a similar reactivity of methanol and water. Sulfuric acid is one of the most promising homogenous acid catalyst for industrial scale biodiesel productions, because of its high activity and low cost[19]. Therefore the possibilities for application of sulfuric acid are still being investigated, even though its usage involves several drawbacks[20, 21]. It is known that in the presence of sulfuric acid not only esterification occurs, but also such side reactions as oxidation and formation of methylsulphates and dimethyl ether[22, 23]. It is also not clear whether the use of sulfuric acid for the esterification of fatty acid mixture allows to fulfill the requirements of standard EN 14214 that requires low FFA content. For instance, Chongkhong et al.[3] conducted esterification process of palm fatty acid distillate in the presence of sulfuric acid. The lowest achieved FFA content was 2%, which does not meet the requirements of the standard.

In this work systematic studies of FAME synthesis from rapeseed oil fatty acids (RFA) in the presence of concentrated sulfuric acid were accomplished. Finally, a two stage process was developed that allows to obtain a product that complies with the standard EN 14214.

## EXPERIMENTAL

### Materials

A refined rapeseed oil (RO), whose properties are given in Table 1, was used in experiments. Fatty acid profile was determined by the composition of the FAME yielded by esterification, according to ISO 5509 methyl ester synthesis and chromatographic EN 14103 standard methods. RFA was derived from RO by acid hydrolysis reaction with water (AV 199.91 mg KOH/g determined in accordance with EN 14104 standard). Sulfuric acid and methanol (water content 0.16%, established by the EN ISO 12937 standard method) was purchased from *Sigma – Aldrich Chemie GmbH* and their purity > 98%.

**Table 1.** Properties of RO

| Property | Value | Method |
|---|---|---|
| Monoglyceride ww.% | 0.3 | Modified EN 14105 |
| Diglyceride ww.% | 0.8 | |
| Triglyceride ww.% | 97.7 | |
| Saponification value, mg KOH/g | 191.62 | EN ISO 3657 |
| Acid value, mg KOH/g | 0.01 | EN 14104 |
| Water content, ww.% | 0.06 | EN ISO 12937 |
| Unsaponifiable matter, ww.% | 1.2 | EN ISO 3596 |
| Iodine value, $gI_2$/100g | 117 | EN 14111 |
| Refractive index | 1.4663 | EN ISO 6320 |
| Density at 15°C, g/cm$^3$ | 0.917 | EN ISO 3675 |
| Fatty acid composition in RO (ww.%) | | |
| Palmitic acid (C16:0) | 3.9 | ISO 5509 and EN 14103 |
| Stearic acid (C18:0) | 1.3 | |
| Oleic acid (C18:1) | 62.1 | |
| Linoleic acid (C18:2) | 21.3 | |
| α-Linolenic acid (C18:3) | 8.4 | |
| Arachidic acid (C20:0) | 0.3 | |
| Eicosenoic acid (C20:1) | 0.6 | |
| Other fatty acids | 0.7 | |

### Experimental methods

A series of experiments were conducted at 70.0±1.0°C temperature in order to investigate and optimize the process of obtaining rapeseed oil fatty acid methyl ester (RME) from RFA. Esterification reaction produces a significant amount of water thereby creating water--methanol-sulfuric acid system whose boiling temperature increases over 70°C. After 10 min of reaction no boiling or volumetric decrease of esterification mixture were visually observed. The effects of sulfuric acid concentrations (0.1–3.0% by weight of RFA), molar ratio of methanol:FFA (20:1) and reaction time (0–360 min) were investigated. 50 g of RFA were used in each experiment. Experimental reactions were conducted using a three-neck round-bottom flask equipped with reflux condenser. RFA was heated to 70.0±1.0°C temperature then sulfuric acid in methanol was added, which was considered as the starting point of reaction. The reaction progress was controlled by taking a 2 ml sample of the reaction mixture at regular time intervals (10, 20, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330, 360±0.1 min). Test samples were washed with 30 ml of distilled water, thus stopping RFA esterification reaction and ensuring the removal of unwanted impurities such as methanol, sulfuric acid, methyl sulfate and crude glycerol. Afterwards the samples were placed in the thermostat for 10 min (60°C). The upper biodiesel phase was separated once the emulsion settled. The last remains of water and methanol were distilled using a rotary evaporator at a pressure 900 Pa, 90°C for 10 min. Finally, AV was determined for the samples obtained. A similar research methodology for FFA esterification process was described by Nakpong et al.[24] and Parkara et al.[25].

### Testing methods

AV was determined for all the samples. Additionally, RME content was determined for part of the samples. The esterification process was analyzed on the basis of FFA content that was calculated using formula (1). The same formula was used in Marchetti et al. publication[20].

$$FFA(\%) = \frac{AV_{100\%} - AV(t)}{AV_{100\%}} \times 100 \quad (1)$$

Furthermore, Dias et al.[5] and Veljković et al.[26] also in their works used a similar esterification reaction control by monitoring AV in samples.

Samples were analyzed according to the procedures enclosed in EN 14214 standard. AV and iodine value were determined by volumetric titration with KOH solution and Wijs solution. Density and viscosity were determined using Anton Paar DMA 4500 density meter (accuracy 0.0005 g/cm$^3$) and Anton Paar SVM 3000 SVM 3000 Stabinger viscometer (relative uncertainty 0.35%). Carbon residue was determined using PAC ISL MCRT – 160 micro carbon residue tester. The flash point was evaluated using Stanope-Seta 30000-0 (accuracy ±1°C). Water content was determined using Karl Fisher coulometer Mettler Toledo DL39 (accuracy 0.05%). Total contamination was calculated by remaining mass on filter after sample filtration. Ester content was determined using Agilent Technologies 7890A gas chromatograph, equipped with a flame ionization detector and a HP Innowax capillary column (30 m x 0.25 mm x 0.25 $\mu$m). The content of free and total glycerine and mono-, di- and triglycerides were determined using Agilent Technologies 7890A gas chromatograph, equipped with a flame ionization detector and a HT DB-5 (15 m x 0.32 mm x 0.1 $\mu$m).

## RESULTS AND DISCUSSION

There are several key parameters that influence the results of the esterification process as temperature, reaction time, catalyst concentration, methanol:FFA molar ratio, stirring speed and raw material composition. To minimize the count of experiments, all kinetic curves were obtained using the constant stirring rate and temperature. On the basis of the previous research it was assumed that at a given stirring speed the reaction mixture is completely homogenized and selected reaction temperature is close to optimal[27].

### Effect of sulfuric acid concentration

Figure 1 shows the kinetic curves from RFA esterification process using different concentrations of sulfuric acid while maintaining the triple methanol excess in relation to the stoichiometric methanol:FFA molar ratio.

Using sulfuric acid concentrations between 1.0–3.0%, FFA content in biodiesel phase dropped below 20% in 60 min. A similar observation was described by Che et

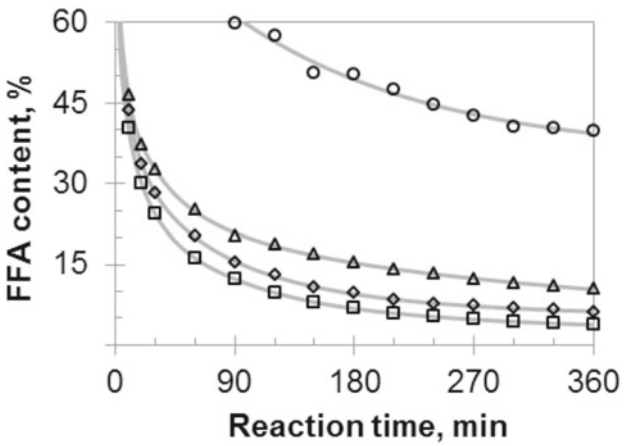



**Figure 1.** Effect of sulfuric acid concentration on RFA esterification process ((○) 0.1%, (△) 1.0%, (◇) 2.0%, (□) 3.0%; methanol:FFA 3:1; 70°C)

al.[28] where in the first 30 min the FFA content decreased by 50–80%. The lowest FFA content of 3.8% that corresponds to AV of 7.58 mg KOH/g was obtained by performing an esterification for 360 min with sulfuric acid concentration of 3.0%. While the use of sulfuric acid concentrations of 1.0 and 2.0% allowed to reach FFA content of 10.4 and 6.2% in 360 min, respectively. The worst results were obtained in the presence of 0.1% sulfuric acid where the FFA content decreased to 39.9% in 360 min. Consequently, higher sulfuric acid concentration leads to the increase of reaction rate and the equilibrium shift towards the formation of esters that could be explained by sulfuric acid ability to bind water. The overall process in the presence of sulfuric acid could be displayed by the following equilibrium reactions:

$$FFA + CH_3OH \overset{H_2SO_4}{\rightleftharpoons} RME + H_2O \quad (2)$$

$$H_2SO_4 + xH_2O \rightleftharpoons H_2SO_4 \cdot xH_2O \quad (3)$$

Interaction between sulfuric acid and water (3) decreases freely available water in the system, therefore shifting the reaction (2) equilibrium towards the products. At the same time, reaction (3) decreases sulfuric acid amount available for catalysis, thus decreasing esterification reaction rate.

The obtained products were dark brown colour when high sulfuric acid concentration was used, thus indicating an existence of oxidation process. However, the results of experiments show that oxidation processes are negligible when sulfuric acid concentration does not exceed 1.0%.

**Effect of methanol molar ratio**

Figure 2 shows kinetic curves of RFA esterification using different methanol:FFA molar ratios but constant sulfuric acid concentration. The increase of methanol:FFA molar ratio from 1:1 to 20:1 resulted in a decrease of unreacted FFA content from 32.1 to 1.1% in 360 min, respectively. In the first 30 min the FFA content in the biodiesel phase decreases rapidly regardless of the methanol molar ratio used. However, using methanol:FFA molar ratio of 20:1 the equilibrium of esterification can be achieved after 90 min, reaching at the same time 1.1% FFA content. While the use of a lower methanol:FFA molar ratio allows to achieve an equilibrium of esterification only after 300 min. 3.5 and 2.8% high FFA content was achieved using, respectively, 5:1 and 6:1 methanol:FFA molar ratio in 300 min. The use of even lower molar ratio than mentioned above causes a rapid decrease in the yield of esterification reaction. Unfortunately, the use of increased methanol:FFA molar ratio of 20:1 does not ensure a compliance with the standard EN 14214. Besides, even a greater increase in excess of methanol would only make the process economically disadvantaged, as it will be necessary to recover large quantities of methanol. Therefore, the second esterification stage would be needed to ensure a compliance with the standard EN 14214. Assuming that sulfuric acid concentration of 1.0% is sufficient to bind water according to reaction (3) and this reaction's influence on all kinetic curves is similar, impact of methanol excess on overall process can formally be explained by the equilibrium reaction (2).

**Optimization of a two-stage esterification process**

In all the cases, the obtained AV of the final product (biodiesel) exceeds the requirements of EN 14214 standard that defines the maximum allowable limit of 0.5 mg KOH/g[29]. In order to obtain AV that corresponds to the standard it is necessary to perform a second esterification stage. Furthermore, a two stage esterification of RFA would be more efficient than producing biodiesel in a single stage using high concentrations of reagents. A similar conclusion was also made by Ghadge et al.[30]. A large molar excess of methanol would raise the cost of its recovery, but high concentration of sulfuric acid contributes to the oxidation of the reaction mixture components. By analyzing the results obtained it was concluded that for the first RFA esterification stage it is advantageous to use methanol:FFA molar ratio of 5:1 and the sulfuric acid concentration of 1.0% at 70°C. Under these reaction conditions RFA conversion reached ~ 96.5% and the content of FFA decreased to 3.5% (6.9 mg KOH/g) during 300 min. In order to optimize the second stage of RME obtaining process, a series of experiments were performed using 5% RFA/RO mixture.

Figure 3–5 shows the 5% RFA/RO mixture's esterification kinetic curves. The use of increased methanol:FFA molar ratio of 20:1 and sulfuric acid concentration of 0.1% allowed to achieve equilibrium of esterification after approximately 240 min, thereby reducing FFA content to 0.2% (Fig. 3). Using a methanol:FFA molar

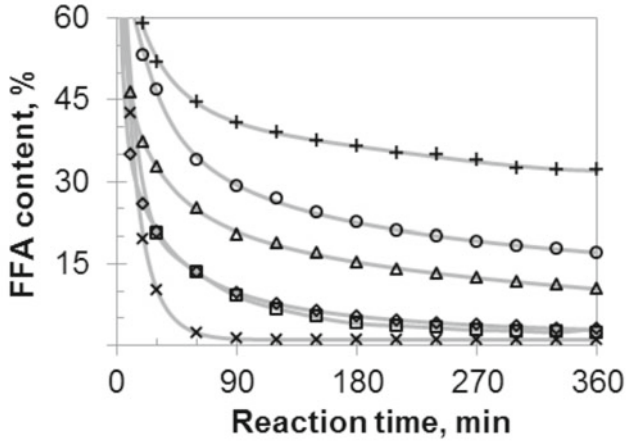



**Figure 2.** Effect of methanol:FFA molar ratio on RFA esterification process ((+) 1:1, (○) 2:1, (△) 3:1, (◇) 5:1, (□) 6:1, (×) 20:1; 1.0% $H_2SO_4$; 70°C)

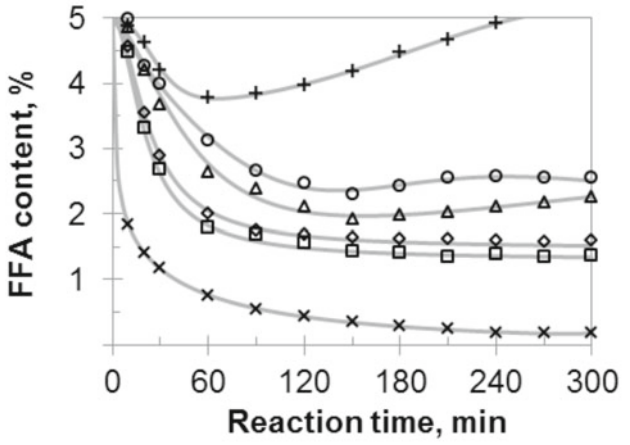



**Figure 3.** Effect of methanol:FFA molar ratio on 5% RFA/RO mixture's esterification process ((+) 1:1, (○) 3:1, (△) 4:1, (◇) 5:1, (□) 6:1, (×) 20:1; 0.1% $H_2SO_4$; 70°C)

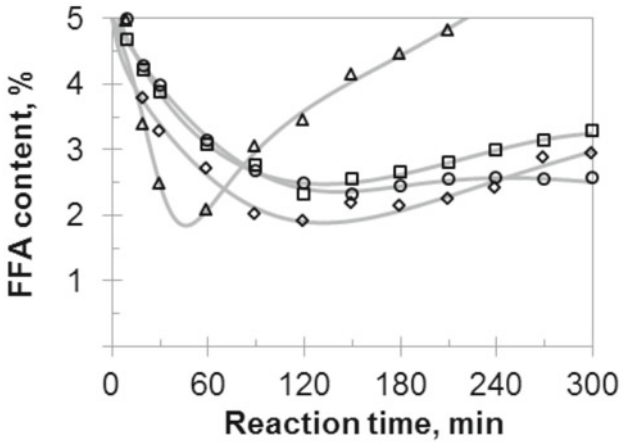



**Figure 4.** Effect of sulfuric acid concentration on 5% RFA/RO mixture's esterification process ((○) 0.1%, (□) 0.2%, (◇) 0.5%, (△) 1.0%; methanol:FFA 3:1; 70°C)

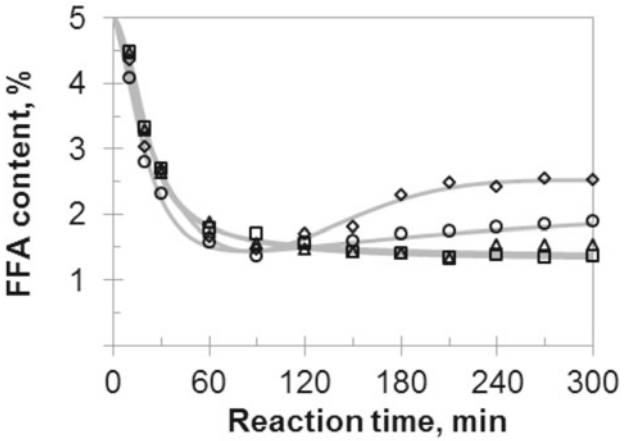



**Figure 5.** Effect of sulfuric acid concentration on 5% RFA/RO mixture's esterification process ((□) 0.1%, (△) 0.2%, (○) 0.5%, (◇) 1.0%; methanol:FFA 6:1; 70°C)

ratio of 3:1–6:1, the reaction equilibrium was reached at reaction times 150 min, reducing the FFA content to 1.4–2.3%. Similar results were obtained by Marchetti et al.[20]. The esterification reaction that was performed using stoichiometric methanol:FFA molar ratio of 1:1 showed that the minimum FFA content of 3.8% can be achieved in 60 min but afterwards the FFA content of the reaction mixture rises above the initial 5%.

It was observed that FFA content after reaching its minimum point increases when the methanol:FFA molar ratio of 3:1 is used, irrespective of sulfuric acid concentration applied during reaction (Fig. 4). This effect is reduced by increasing the methanol excess (Fig. 3, 5). A relatively rapid RFA esterification occurs in the first 45 min when using a 1.0% concentration of sulfuric acid. It results in reaching the minimum FFA content of 1.8% that is followed by the increase of FFA content even exceeding its initial level in the raw material.

From the results obtained it can be concluded that methanol:FFA molar ratio of 3:1 is not suitable for 5% RFA/RO mixture's esterification in order to obtain high quality end product. Situation is improved by using the excess of methanol 6:1 (Fig. 5). However, even then the content of FFA is too high. Thereby, the excess of methanol should be further increased.

Eventually, it was concluded that the second stage of RFA esterification should be accomplished using a methanol:FFA molar ratio of 20:1 and sulfuric acid concentration of 0.1% at 70°C for 240 min. This two stage esterification method could provide the reduction of an initial AV from 199.91 to ~ 0.37 mg KOH/g, resulting in a biodiesel with RME content of 99.8%. In order to verify the scalability of the process, a two stage process was realized using 1000 g of RFA mixture. Esterification reaction's yield reached 97.8% by acquiring a biodiesel with RME content of 99.6%. Finally, the most important quality parameters of the standard EN 14214 were established for obtained RME (Table 2), all of which met the requirements of the standard. Therefore, the resulting process is scalable and allows to realize a high quality biodiesel synthesis from RFA.

## CONCLUSIONS

It is impossible to obtain a product whose FFA content is less than 1.1% (AV 2.1 mg KOH/g) in a single esterification stage where RFA esterification reaction is performed using sulfuric acid in concentration range of 0.1–3.0% and methanol:FFA molar ratio of ≤ 20:1. The equilibrium of the reaction at 70°C is achieved during 300 to 360 min. The reaction yield increases by increasing the concentration of sulfuric acid and methanol excess. Sulfuric acid concentration > 1.0% is not suitable for the synthesis of RME as the sulfuric acid used at such high concentrations leads to the undesirable oxidation processes. In order to obtain a product from RFA that complies with the standard EN 14214, a two stage esterification process should be applied. At the first stage an RFA esterification should be performed by using methanol:FFA molar ratio of 5:1, sulfuric acid concentration of 1.0% at 70°C for 300 min. In the second stage an esterification of obtained RME/RFA mixture

**Table 2.** Quality parameters in accordance with EN 14214 obtained for RME under optimal synthesis conditions

| Property | Unit | Result | Specification EN 14214 | Method |
|---|---|---|---|---|
| Ester content | % (m/m) | 99.6 | 96.5 (min) | EN 14103 |
| Density 15°C | kg/m³ | 872 | 860–900 | EN ISO 12185 |
| Viscosity 40°C | $mm^2/s$ | 3.8 | 3.5–5.0 | EN ISO 3105 |
| Carbon residue (on 10% distillation residue) | % (m/m) | 0.09 | 0.30 (max) | EN ISO 10370 |
| Flash point | °C | 173 | 120 (min) | EN ISO 3679 |
| Water content | mg/kg | 54 | 500 (max) | EN ISO 12937 |
| Acid value | mgKOH/g | 0.37 | 0.50 (max) | EN 14104 |
| Total contamination | mg/kg | 8 | 24 (max) | EN 12662 |
| Iodine value | $gI_2/100g$ | 117 | 120 (max) | EN 14111 |
| Monoglyceride content | % (m/m) | 0.16 | 0.80 (max) | EN 14105 |
| Diglyceride content | % (m/m) | 0.04 | 0.20 (max) | EN 14105 |
| Triglyceride content | % (m/m) | 0.00 | 0.20 (max) | EN 14105 |
| Free glycerol | % (m/m) | 0.00 | 0.02 (max) | EN 14105 |
| Total glycerol | % (m/m) | 0.05 | 0.25 (max) | EN 14105 |

should be realized with methanol:FFA molar ratio of 20:1, sulfuric acid concentration of 0.1% at 70°C for 240 min. Under these conditions the optimal two stage esterification process was achieved, resulting in 97.8% of biodiesel yield which characteristics corresponded to EN 14214 standard.

**Abbreviation**

AV – acid value,
$AV_{100\%}$ – acid value of the raw material, mgKOH/g,
AV(t) – acid value of reaction mixture after a time period t, mgKOH/g,
FAME – fatty acid methyl ester,
FFA – free fatty acids,
RFA – rapeseed oil fatty acids,
RME – rapeseed oil fatty acid methyl ester,
RO – rapeseed oil.

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