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Properties of rapeseed oil fatty acid alkyl esters derived from different alcohols

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HIGHLIGHTS

- Sulphuric acid is suitable catalyst for fatty acid alkyl esters preparation from different alcohols.
- Ester content of distilled fatty acid alkyl esters was increased over ⩾96.5%.
- Fatty acid alkyl esters obtained from branched higher alcohols have great cold flow properties.

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ABSTRACT

One of the ways to improve the cold flow properties of biodiesel is to derive it from other alcohols instead of methanol. In this research a three step synthesis of fatty acid alkyl esters (FAAE) in the presence of sulfuric acid was performed via transesterification of rapeseed oil using 11 different linear or branched alcohols (C_1—C_6) – methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylbutan-1-ol, pentan-1-ol, 2,2-dimethylpropan-1-ol, 4-methylpentan-2-ol. Furthermore, a vacuum distillation was carried out to increase ester content over ⩾96.5 wt.%. It was concluded that an increase of the length of FAAE hydrocarbon chain in alcohol moiety significantly helps to improve the cold flow properties of FAAE distillates. From linear alcohols the minimal values of (cold filter plugging point (CFPP) −17 °C, cloud point (CP) −16 °C and pour point (PP) −18 °C were reached using FAAE derived from butan-1-ol. From branched alcohols the lowest CFPP −24 °C, CP −28 °C and PP −37 °C were achieved by obtaining FAAE from 4-methylpentan-2-ol.

1. Introduction

With the increase of worldwide petroleum consumption and its price there is also an increase in demand and need for biofuels in order to reduce environmental and economic instability problems [1,2]. Biodiesel is one of the most promising renewable liquid fuels. It can be obtained from any raw material containing vegetable oil and fatty acids [3]. As such feedstock can be used edible [4,5] as well as non-edible vegetable oils [6–8]. Thus, a significant number of scientific studies have been done to demonstrate that a variety of feedstock, considered as a waste of the food industries, classify to be suitable for biodiesel production [3]. As such food industry wastes are considered to be animal fats, tallow, waste greases, used cooking oils and vegetable oil refining wastes. Hence, the world's largest part of biodiesel is produced using edible vegetable oils. For instance, in Asia the main biodiesel feedstock is palm oil, whereas in USA it is soybean oil [4]. In European Union biodiesel production is mainly done using rapeseed oil (RO) [9]. This is due to the suitable climate for the seed growth and the quality of the obtained biodiesel is similar to diesel fuel [10].

Methanol is the most common alcohol used for biodiesel production process due to its relatively low cost and availability [1,11]. Biodiesel production processes utilize a wide variety of homogeneous and heterogeneous catalysts (basic or acidic) [12]. The most widely used are homogeneous alkaline catalysts (NaOH, KOH, $NaOCH_3$), those catalysts have higher catalytic activity than acidic [13,14]. However, homogeneous acid catalysts (sulfuric acid, hydrochloric acid, phosphoric acid, sulfonated organic acids, etc.) are less sensitive to impurities in raw material [15,16]. Therefore, they are more effective for the biodiesel production process when the raw materials have elevated free fatty acid and water content [17]. Despite the fact that a transesterification reaction rate using homogeneous acid catalyst is significantly slower than with

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alkaline catalysts, the obtained yield of the biodiesel for both processes can be similar [18]. This can be achieved with an increase of the reaction time, temperature, catalyst concentration and the molar ratio of alcohol to triglyceride [19–21]. The increase of reaction temperature is especially important when the alcohols with the higher boiling points are used [22]. In reference [23] the authors have extensively studied the influence of H_2SO_4 on vegetable oil transesterification reaction. When 1 wt.% of H_2SO_4 is used with molar ratio of methanol to oil (30:1) it was possible to obtain fatty acids methyl esters (FAME) in 99% yield over 69 h. However, when 4 wt.% of H_2SO_4 catalyst was utilized to the reaction of one mole of used cooking oil with 20 mol of methanol over 10 h $\geqslant$ 90% yield of FAME was obtained [21]. In our previous work we investigated the influence of esterification reaction conditions on the yield of alkyl esters of rapeseed oil fatty acids in the presence of sulfuric acid [24]. The use of vacuum distillation was required in order to increase fatty acid alkyl esters (FAAE) content in final product [25,26].

With the rapid expansion of the biodiesel as a commercial product in many countries, there has also been a development in standards in order to ensure its quality [1]. The most widely used standard for the biodiesel quality is EN 14214 (EU) [27] and ASTM D6751 (USA) [28], but for diesel fuel EN 590 (EU) [29] standard and ASTM D975 (USA). Cold filter plugging point (CFPP) is also one of the key parameters for biodiesel that determines in which climatic zones it is suitable for use. The properties of biodiesel are affected by the content of the esters and their chemical structure. The authors from a study [30] provided CFPP values for various FAME derived from different vegetable oils. The lowest CFPP values were for corn (−12 °C) and RO (−10 °C) derived FAME. Alternative way to improve the biodiesel cold flow properties such as CFPP, cloud point (CP) or pour point (PP) is to add various additives. For example, 1.0 wt.% Viscoplex 10-305 additive decreases rapeseed methyl esters CFPP to −26 °C [31]. In the report [32] properties of branched oleic acid 2-propyl, 2-butyl and 2-ethylhexyl esters were postulated. It was revealed that CFPP of oleic acid 2-ethylhexyl esters reaches −23 °C. Report [33] provides information about physical properties of fatty acid methyl, ethyl, 1-propyl, 2-propyl, 1-butyl and 2-butyl esters. The cold flow properties of FAAE derived from branched chain alcohols are significantly better than those of linear chain alcohols [34]. Also, cetane number increases with the length of the hydrocarbon chain in the alcohol moiety.

In the current scientific literature there are studies that investigate the use of branched and linear alcohols for the synthesis of biodiesel in order to improve its properties. However, these investigations are difficult to compare due to the difference of FAAE preparation conditions and used feedstock.

The aim of our research is to investigate the main properties (density (15 °C), viscosity (40 °C), carbon residue, flash point, heat of combustion, CFPP, CP and PP) of 11 different FAAE obtained in similar conditions from RO and various alcohols (methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylbutan-1-ol, pentan-1-ol, 2,2-dimethylpropan-1-ol, 4-methylpentan-2-ol) in three step synthesis in the presence of sulfuric acid.

2. Materials and methods

2.1. Materials

In FAAE syntheses a high quality refined RO was used. The main properties of RO are given in Table 1. All alcohols (methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylbutan-1-ol, pentan-1-ol, 2,2-dimethylpropan-1-ol, 4-methylpentan-2-ol), sulfuric acid as well as internal standards for GC were purchased from Sigma–Aldrich Chemie GmbH and their purity $\geqslant$98 wt.%.

Table 1
The main properties of rapeseed oil.

Property	Value
Monoglycerides, wt.%	0.3
Diglycerides, wt.%	0.7
Triglycerides, wt.%	97.9
Saponification value, mg KOH/g	191.71
Acid value, mg KOH/g	0.01
Heat of combustion, MJ/kg	39.67
Fatty acid composition, wt.%	
Palmitic acid (C16:0)	4.1
Stearic acid (C18:0)	1.4
Oleic acid (C18:1)	62.5
Linoleic acid (C18:2)	21.7
α-Linolenic acid (C18:3)	8.7
Arachidic acid (C20:0)	0.4
Other fatty acids	1.2

2.2. Preparation method of FAAE

FAAE were obtained from RO (700 g) by performing three step synthesis in the presence of sulfuric acid. Syntheses of FAAE were carried out in the round – bottomed flask equipped with a reflux condenser. Furthermore, each step of the synthesis was carried out at boiling (reflux) temperature of alcohols for 3 h (Table 2) with the constant mechanical stirring at 600 rpm.

In the first, second and third step of FAAE synthesis were used 5, 1.3 and 1.3 mol of alcohol to 1 mol of RO (700 g) and 4.0, 2.0 and 1.0 (wt.% of oil) H_2SO_4, respectively. The necessary amount of alcohol was estimated on the basis of RO saponification value (Table 1). After each step the resulting mixture was poured into separating funnel where crude glycerol and H_2SO_4 remains (lower layer) were separated after 24 h. After third step upper layer (mixture of FAAE, RO and alcohol) was washed three times with 700 ml of distilled water. Subsequently, remaining water and alcohol were removed from FAAE by distillation process using rotary evaporator at 6.75 mm Hg pressure, 50–130 °C temperature for 30 min. In order to acquire all FAAE samples in similar conditions and achieve the final ester content of $\geqslant$96.5 wt.%, FAAE content was increased using B/R Instrument Corporation Spinning Band Fractional Vacuum Distillation System. The pressure of 0.001 mm Hg was obtained using Edwards RV8 vacuum pump. Conditions used for FAAE vacuum distillation are given in Table 3.

In this research all analysis results were defined as an average value from two independently repeated experiments. A third independent experiment was performed in cases when previous two experimental values differed more than 3%, then the average result of experiment was determined using two closest experimental values.

2.3. Analytical methods

2.3.1. Content of monoglycerides (MG), diglycerides (DG) and triglycerides (TG)

MG, DG and TG content in FAAE and RO was confirmed by means of gas chromatography according to a standard method EN14105. A gas chromatograph (Agilent Technologies 7890A) with a capillary column HT DB-5 (15 m × 0.32 mm × 0.1 μm) and a flame ionization detector (FID) were used. The column temperature program was: 50 °C hold for 1 min; 15 °C/min up to 180 °C; 7 °C/min up to 230 °C; 10 °C/min up to 370 °C; final temperature hold for 5 min. Helium was used as a carrier gas at a flow rate of 2 ml/min. Injection volume was 1.0 μl.