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Chemical interesterification of rapeseed oil with methyl, ethyl, propyl and isopropyl acetates and fuel properties of obtained mixtures

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ABSTRACT

An alternative method for the synthesis of biodiesel fuel from rapeseed oil that prevents formation of glycerol and produces the fuel in mass exceeding the mass of oil has been proposed. Upon the interesterification reaction with different alkyl acetates triacetin is formed (instead of glycerol) which can be considered as a valuable additive and do not have to be removed from the reaction mixture. In this study the influence of the alcohol moiety of alkyl acetate on the interesterification process was studied using sodium methoxide solution in methanol as catalyst. The reactivity of the acetates in the interesterification reactions decrease in the following order: methyl- ; ethyl- ; propyl- ≫ isopropyl acetate. However, performing reactions with these alkyl acetates at its boiling points for 1 h using optimal amount of catalyst with alkyl acetate to oil molar ratio of 36:1, reaction mixtures with high content of fatty acid alkyl esters can be obtained. Fuel properties of the obtained mixtures were investigated. Obtained renewable fuels do not meet the requirements of standard EN 14214 for biodiesel, although the main characteristics of the biodiesel obtained in the reaction with methyl acetate are marginally close to the standard requirements.

1. Introduction

Due to the excess of glycerol and its processing problems, a new method of biodiesel production that prevents glycerol synthesis should be developed [1,2]. The interesterification of triglycerides with methyl acetate provides a promising alternative of transesterification, because triacetylglycerol (triacetin) is formed instead of glycerol [3,4]. When the triacetin is included in the formulation of biodiesel, the amount of biofuel obtained from triglyceride (TG) increases [5]. Recent studies have shown that addition of triacetin to the biodiesel for up to 10 wt.% do not affect the quality of biofuel and it still meets the requirements of quality standard EN14214. Casas et al. studied the influence of wide-ranging triacetin content on the fuel properties of reaction product obtained after the reaction of different vegetable oil with methyl acetate [5]. Goembira et al. also studied the properties of fatty acid ethyl ester (FAEE) blended with triacetin [6]. There are many reports on the influence of different alcohol moieties on the fuel properties of fatty acid esters [7,8] obtained by transesterification. It is clear that fatty acid alkyl esters (FAAE) with longer and branched alcohol moiety improve low temperature properties. Nevertheless the properties of biofuels obtained through interesterification with ethyl acetate (FAEE), propyl acetate (FAPE) and isopropylacetate (FAiPE) have not been studied.

Interesterification of oils and fats for biodiesel and triacetin production are extensively studied in recent years. In order to improve process effectiveness, a lot of research capabilities are devoted to the interesterification studies, which utilizes waste cooking oils [9,10], supercritical methyl acetate [11,12] and heterogeneous biocatalysts [13]. The obtained yields of FAAE do not excess 96.6% [12], 95% [14] or 90% [4], and the content of triacetin also differ. Usually the authors study kinetics of the interesterification process on the basis of the change of FAAE content without quantification of intermediates and determination the fuel properties of the end product.

The catalysts studied for interesterification reactions are potassium hydroxide, potassium methoxide and polyethylene glycolate [14]. Casas et al. studied catalyst dependency on interesterification reaction conditions. The authors discovered that the presence of methanol in the case of use of potassium methoxide solution in methanol increased the reaction rate of interesterification [3].

Due to its low cost and physical and chemical advantages methanol and ethanol are the most used popular reactants in the transesterification process. [15]. Sanchez et al. studied the influence of different short chain alcohols – methanol, ethanol, butanol and isopropanol on the yield and composition of fatty acid alkyl esters using *Jatropha* oil and potassium methoxide as catalyst. The authors reported that the transesterification with methanol provides the highest yield, while the lowest yield is obtained when isopropanol is used. This matter was explained with higher reactivity of linear alcohols over branched ones [16]. Enzymatic

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Abbreviations: FAAE, fatty acid alkyl ester; FAME, fatty acid methyl ester; FAEE, fatty acid ethyl ester; FAPE, fatty acid propyl ester; FAiPE, fatty acid isopropyl ester; MADG, monoacetyldiglyceride; DAMG, diacetylmonoglyceride; TG, triglyceride.

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synthesis of rapeseed biodiesel with methyl, ethyl, butyl and vinyl acetates was investigated by Jeong et al. [17]. Methyl and ethyl acetates gave the highest ester content – 58.0 wt.% and 62.6 wt.% at 40 °C after 19 h, respectively [17], therefore ethyl acetate is oftenly used as a reactant in enzymatic interesterification [18,19]. Furthermore in the supercritical interesterification of rapeseed oil with methyl, ethyl, propyl and butyl acetates, propionates and butyrates, high yield of esters was reached only with methyl acetate. Longer alkyl chains in both alcohol and acyl moieties of alkyl esters gave lower product yields [6]. The interesterification of rapeseed oil with methyl acetate over tin octanoate gave higher FAAE yield than with ethyl acetate (at 210 °C) [20].The main task of this study is to ascertain the influence of chemical structure of alcohol moieties of alkyl acetates (methyl, ethyl, propyl and isopropyl) on the proceeding the interesterification reaction (see Fig. 1) and composition of products. It would be interesting to compare the results with data from supercritical interesterification with different alkyl acetates. The properties such as density, viscosity, carbon residue, cold filter plugging point (CFPP), cloud point (CP) and pour point (PP) of the obtained products were investigated.

The interesterification reaction is shown in Fig. 1. The intermediates in TG interesterification reaction with alkyl acetates are monoacetyldiglyceride (MADG) and diacetylmonoglyceride (DAMG).

2. Materials and methods

2.1. Materials

The refined rapeseed oil was purchased from a local producer *Iecavnieks*. The methyl acetate (99%) and ethyl acetate (99%) were obtained from *ROTH*, propyl and isopropyl acetates (99%) were obtained from *Alfa Aesar*. Phosphoric acid (85%) was obtained from *Sigma-Aldrich.* Catalyst 28.6 wt.% sodium methoxide solution in methanol was supplied from *Sigma-Aldrich*. Materials for GC analysis - methyl heptadecanoate (95%) were supplied from *Sigma-Aldrich*, 1,2,4-butanetriol (96%) and MSTFA (*N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide, 97%) – from *Alfa Aesar*, tricaprin (98%) – from *TCI Europe*, heptane (95%), and dichloromethane (99%) – were supplied by *ROTH.*

The characterisations of rapeseed oil used in experiments were determined and published earlier [7] and are given in Table 1.

2.2. Experimental procedure

The rapeseed oil and alkyl acetate were mixed and heated up to 55 °C or close to boiling point temperature of alkyl acetate (methyl 55 °C, ethyl 75 °C, propyl 98 °C, isopropyl 87 °C) in the 250 mL or 500 mL 3-necked flask, equipped with a reflux condenser, thermometer and magnetic stirrer-heater. The rotational speed was set at 800 rpm. Then catalyst was added and the reaction time was started. Reaction mixture was quenched after 60 min by adding the stoichiometric amount of phosphoric acid and emerged salts were filtered. In the kinetics experiments 5 mL sample from reaction mixture was removed and also stoichiometric amount of phosphoric acid was added. Then excess of reagent was removed by rotary evaporation and stored in refrigerator. Each experiment was carried out two times and the average value was calculated. The concentration (amount) of catalyst is measured as molar ratio to oil and amount of reactant as molar ratio of reactant to oil.

2.3. Analytical methods

The analysis of all components of each sample was carried out by using *Analytical Controls* biodiesel analyzer based on *Agilent Technologies* gas chromatograph 7890A, equipped with 2 columns. The capillary column employed was a HP Innowax with a length of 30 m, an internal diameter of 0.25 mm and a film thickness of 0.25 μm. Oven temperature was set at 200 °C. The content of esters was determined according to procedure of standard EN 14103. The calibration was done by methyl heptadecanoate as internal standard, as retention time of its peak does not overlap to peaks of all type of esters.

Glycerol, monoglycerides, diglycerides (from TG transesterification), TG, MADG, DAMG, monoacetylglycerol (monoacetin), diacetylglycerol (diacetin) and triacetin were analysed using DB5-HT column (15 m, 0.32 mm, 0.10 μm) under conditions prescribed in standard EN 14105 and quantified as in our previous report [21]. The oven temperature was set to 50 °C for 5 min and then temperature was first increased to

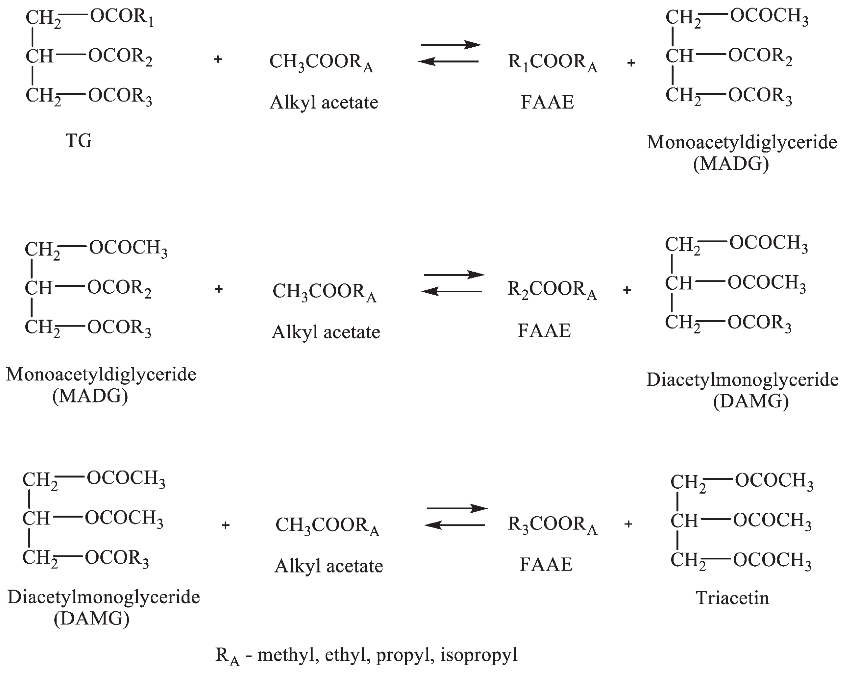

Fig. 1. The interesterification of TG with alkyl acetates.