Harmonisation of Biodiesel Composition via Competitive Interesterification – Transesterification

Valdis Kampars[*], Ruta Kampare, Elina Sile, Modris Roze

Institute of Applied Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena 3/7, Riga, LV-1048, Latvia
valdis.kampars@rtu.lv

A pure interesterification reaction of triglyceride with methyl acetate in the presence of potassium tert-butoxide homogeneous catalyst produces a reaction mixture containing 72.5 wt.% of fatty acid methyl esters (FAME) and 14 wt.% of triacetin. In order to harmonise the content of the reaction mixture by increasing the fatty acid alkyl esters (FAAE) and decreasing the content of triacetin, in this work a competitive interesterification – transesterification conversion of triglyceride has been made using *iso*-propanol. Due to the low reactivity of *iso*-propanol, it is possible to carry out the targeted harmonisation of biofuel composition by increasing the FAAE content up to 81.9 wt.% while retaining a relatively high triacetin content (6-9 wt.%). The lowering of the triacetin content and replacing it with the fatty acid *iso*-propyl esters provides the opportunity to obtain products that are more similar to conventional biodiesel and improve the cold flow properties of the fuel.

1. Introduction

Energy consumption in the transport sector is growing at an average annual rate of 1.4%, accounting for more than 25% of global CO_2 emissions (Transportation sector energy consumption, 2016). This sector predominantly uses conventional fuels from petroleum refining, which has a catastrophic impact on the environment and contributes to climate change. Increasing evidence of climate change and growing energy dependency has underlined the EU's commitment to becoming a low-energy economy and to consuming safe, secure, competitive, locally produced and sustainable energy (Banjaa et al., 2019). The development of renewable transportation fuels and new vehicle technologies has become incredibly urgent. Biodiesel is one of the three most important biofuels today, usually produced by transesterification with methanol in the form of a mixture of fatty acid methyl esters (FAME). However, the future of biodiesel is threatened by the use of vegetable oils (Piemonte et al., 2014) without an optimised agricultural stage (De Marco et al., 2016) as the primary feedstock, as well as the low value of the by-product glycerol (Van Damme et al., 2014) obtained in the transesterification process. Although many biodiesel technologies are known (homogeneous and heterogeneous acid or base catalysed transesterification, enzymatic catalysis, ionic liquid, non-catalytic reaction with alcohol at pressurized conditions) transesterification in presence of homogeneous basic catalysts is the main reaction used today for the biodiesel production (Fonsecaa J.M. et al., 2019). Reaction conventionally occurs as a reaction of triglycerides with methanol or other short chain alcohol in presence of basic catalysts in accordance with the reaction (1). Another reaction usable for the splitting of triglycerides is interesterification. Interesterification in almost all cases is a reaction with methyl acetate (MA) although other short chain monoesters can be used as reagents. In interesterification reaction (equation 2) with MA the same composition of FAME as in transesterification with methanol (equation 1) have to be synthesised, but another by-product triacetine appears:

$$TG + 3ROH \rightleftarrows 3FAAE + G \tag{1},$$

where TG – triglyceride, ROH – short chain alcohol (methanol for synthesis of FAME), G – glycerol.

$$TG + 3MeAc \rightleftarrows 3FAME + TA \tag{2},$$

where, MA – methyl acetate, FAME – mixture of fatty acid methyl esters, TA – triacetine.

TA is compatible with FAME, can be considered as fuel additive and included into biofuel composition, ensuring higher conversion of oil to biofuel. Interesterefication of triglycerides with methyl acetate (MA) allows the simultaneous conversion of glycerol to triacetin (TA), which can be included in the biodiesel composition by up to 10 wt.% (Casas et al., 2010). Theoretically, the TA content can be as high as 19.4 wt.% (Ribeiro et al., 2017), but in experimentally obtained mixtures, it is 12-14 wt.% (Kampars et al., 2019). The production of biodiesel with the simultaneous conversion of glycerol to the fuel component caused a great deal of interest because the percentage yield of biofuel from triglyceride theoretically can exceed 120% by mass (calculated as a mass of biofuel to a mass of vegetable oil *100%) (Saka et al., 2009). Therefore the crude glycerol is included into the list of feedstock for the production of advanced biofuels by EU Directive RED II (European Commission, 2018). Although full glycerol conversion in presence of alkoxide catalysts cannot be performed in TA and the TA content does not exceed 117% (Sustere et al., 2016), the interesterification process itself remains of great interest. It is known that the content of target products (FAME and TA) and intermediates in the final reaction mixture depends on the reaction variables: the chemical composition of the catalytic system and the molar ratio of catalyst to oil (COMR), the quality of triglyceride (usually an oil) and, the molar ratio of methyl acetate to oil (MAOMR), the temperature and reaction time, the procedure of catalyst addition and removal (Casas et al., 2013). When the alkoxide catalyst is dissolved in alcohols, excluding *tert*-butanol, a competitive transesterification with the catalyst solvent proceeds (Sile et al., 2018). Reactions with *iso*-propanol proceed slowly and can be used as a competitive reaction in order to lower the TA content below 10 wt.% and increase the content of FAAE. The purpose of this study is to use different catalytic systems and the addition of *iso*-propanol to harmonise the reaction product in order to make it more similar to conventional biodiesel, ensuring partial glycerol conversion, as well as the inclusion of 5-10 wt.% triacetin and 3-5 wt.% of fatty acid *iso*-propyl ester into the fuel composition.

2. Materials and methods

2.1 Materials

Refined rapeseed oil was purchased from the local producer Iecavnieks (Iecava, Latvia). Methyl acetate (99%), phosphoric acid (85%) and potassium *tert*-butoxide 1 M solution in THF were obtained from *Sigma-Aldrich.* Materials for the GC analysis: methyl heptadecanoate (95%) was purchased 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%), dichloromethane (pure) from *ROTH.* Potassium, tetrahydrofuran and *iso*-propanol were purchased from Fisher Chemical.

2.2 Synthesis of potassium isopropoxide in the THF

2 g (51.16 mmol) potassium (in the box with argon atmosphere) was put in the three-neck flask with 50 ml of dry tetrahydrofuran (previously stored over 3Å molecular sieves). Then, in the flask equipped with a dropping funnel, an argon inlet adapter and a condenser, 8 ml (6.3 g) (104.82 mmol) of dry *iso*-propanol (previously stored over 3Å molecular sieves) were slowly added via stirring. Stirring at 45 °C was followed until all of the potassium dissolves (approximately ~ 8 hours). The resulting solution (without any further treatment) is used for the preparation of catalysts.

2.3. Experimental procedure of interesterification

Rapeseed oil and alkyl acetate were mixed and heated up to 55 ^{o}C under reflux while being stirred at 800 rpm, using a 250-mL 3-neck round bottom flask. Then a catalyst was added, and the reaction time was started. The reaction mixture was quenched after 60 min by adding the stoichiometric amount of phosphoric acid. Then the excess of reactant methyl acetate was removed by rotary evaporation, and the potassium phosphate precipitate by filtration. The obtained sample was stored in a refrigerator.

2.4. Analytical methods

The analysis of all components of each sample of interesterification products was carried out by using an *Analytical Controls* biodiesel analyser based on *Agilent Technologies* gas chromatograph 7890A. Samples were injected with Agilent Technologies 7683B Series Injector. Triglycerides (TG), diglycerides (DG), monoglycerides (MG), fatty acid methyl ester (FAME) were identified and quantified using triolein, diolein, monoolein and methyl heptadecanoate, respectively. Ester content was determined according to the modified standard method LVS EN 14103, using methyl heptadecanoate as an internal standard [9]. The capillary column employed was an HP Innowax with a length of 30 m, an internal diameter of 0.25 mm and a film thickness of 0.25 µm. The oven temperature was set at 200 °C. Glycerol, mono-(MG), di- (DG) and triglyceride (TG), diacetyl monoglyceride (DAMG), monoacetyldiglyceride (MADG), monoacetyl monoglyceride (MAMG), monoacetin (MA), diacetin (DA), triacetin (TA) and FAME were analysed using a DB5-HT column (15 m,

0.32 mm, 0.10 μm) under conditions prescribed in standard LVS EN 14105. The oven temperature was set to 50 °C for 5 min, and then it was increased up to 180 °C at the rate of 15 °C/min, then up to 230 °C at the rate of 7 °C/min and finally up to 370 °C at the rate of 10 °C/min. Helium was used as a carrier gas with a flow rate of 20 mL/min, and the detector temperature was set to 390 °C in both methods. Chromatographic analysis of each sample was performed two times, and the arithmetical average was used as a characteristic. The mass fraction of products into the reaction mixture is provided in wt.%. The per cent error for chromatographic analysis was 4%. The density of fuel (15 °C) was determined with the use of Anton Paar DMA 4500 density meter according to the standard method LVS EN ISO 12185. The kinematic viscosity (40 °C) was determined with the use of Anton Paar SVM 3000 viscosity meter according to the standard method LVS EN ISO 3104. The measurements of cold filter plugging point (CFPP) were performed on the basis of LVS DIN EN 116 standard method with the use of ISL FPP 5Gs equipment. The carbon residue was determined with the use of Alcor MCRT-160 tester according to the standard method LVS ASTM D 4530 without any previous treatment of reaction mixture. Each measurement was made in twice, and the average value was calculated.

2. Results and discussion

The homogeneous base-catalysed transesterification reactions take place in short (60 min) reaction times and proceeds at low temperature. The reactions are usually carried out at atmospheric pressure and, in the case of FAME synthesis, the reaction temperature is determined by the boiling point of methanol (64.7 °C). Sodium hydroxide, potassium hydroxide and sodium methoxide are used as active homogeneous catalysts, the efficiency of which is determined by the presence of impurities, especially free fatty acids, which cause the formation of soap (Avhad et all., 2015). Interesterification reactions also proceeds during a short time (usually 60 min) and the reaction temperature in the case of FAME synthesis, is determined by the boiling point of methyl acetate (56.9 °C). Of the above catalysts, only sodium methoxide is active in interesterification and it efficiency also is determined by the presence of impurities. Since sodium methoxide is used in the form of a methanolic solution, the presence of methanol in the reaction medium and a parallel transesterification reaction with methanol cannot be avoided. The best homogeneous basic catalyst for carrying out a pure interesterification reaction is potassium *tert*-butoxide in *tert*-butanol or THF (Sustere et al., 2016).

Based on our previous studies (Sile et al., 2018) all reactions were performed at a temperature of 55 °C for 1h, using the reactant to oil molar ratio (MAOMR) of 18 or 30, the catalyst to oil molar ratio (COMR) of 0.1 or 0.12 and an invariable procedure for obtaining the samples for further investigation (Table 1).

Table 1: Mass fraction of the final composition in wt.% of the reaction mixtures obtained by variation of catalysts and amount of iso-propanol.

Catalyst	MAOMR/ COMR[1]	FAME/ FAAE[2]	TA	Target Products[3]
t-BuOK/ THF, 1M	18/0.1	69.8/69.8	12	80.8
t-BuOK/ THF, 1M	30/0.12	72.5/72.5	14	86.5
iPrOK/THF, 1M, S[3]	30/0.1	73.8/75.9	12.5	88.4
iPrOK/THF, 1M, S	30/0.12	74.2/76.3	12	88.3
MeOK/iPrOH, 1M	18/0.1	69.9/74.2	3.3	77.5
MeOK/iPrOH, 1M	18/0.12	70.5/75.7	2.5	78.2
MeOK/iPrOH, 0.5 M	18/0.1	70.2/76.9	1.3	78.2
MeOK/iPrOH, 0.5 M	18/0.12	75.5/83.5	0.8	84.3
iPrOK/iPrOH/THF[4]	30/0.1	77.8/81.6	6.4	88
iPrOK/iPrOH/THF	30/0.12	77.9/81.9	5.5	87.4
tBuOK/THF 1M[4] + O.5 iPrOH/oil	30/0.12	73.3/76.1	8.9	85
tBuOK/THF 1M + 1 iPrOH/oil	30/0.12	75.0/78.6	6.3	84.9
tBuOK/THF 1M + 1.5 iPrOH/oil	30/0.12	77.8/82.4	3.9	86.3

MAOMR/COMR[1] – reaction conditions, FAME/FAAE[2] - mass fraction of FAME and FAAE in the final reaction mixture, target productsl[3] - content of FAAE + TA; S[4] – synthesised as part of this work; iPrOK/iPrOH/THF[3] stock solution of catalyst was obtained by dilution of 20% solution of iPrOK/iPrOH with THF up to 1mol/L, 1M tBuOK/THF[4] stock solution of catalyst is 1M solution of tBuOK in THF. Before the catalyst, iPrOH was added to iPrOH/oil molar ratio of 0.5.

A change in the composition of the final mixture, while maintaining a high target product (FAAE and TA) content, was achieved by changing the catalyst and its amount, as well as the amount of *iso*-propanol present in the initial composition of the reaction. As illustrated in Table 1, pure interesterification in the presence of t-BuOK/ THF provides the opportunity to obtain biofuel with the FAME content of 72.5 and the TA content of 14 wt.% (FAAE + TA 86.6 wt.%).

The FAME content is far from the necessary 96.5 wt.% required by biodiesel standard LVS EN 14214. The increase of MAOMR to 30 resulted in a sharp increase of the target product content of transesterification, but the increase of added *iso*-propanol volume increased the competitive interesterification and the FAAE content to 77 wt%.

The highest content of target products (88.4%) has been obtained by performing the interesterification reaction in the presence of a synthesised catalyst iPrOK/THF by the synthesis of fatty acid isopropylesters in the presence of high content of TA (12.5 wt.%).

Reactions in the presence of iPrOK/iPrOH/THF catalyst and tBuOK/THF catalyst with the addition of the selected amount of iso-propanol show that the TA content can be easily destroyed to the level of 5-9% together with the increase of FAAE content up to 81.9 wt.%. In general, the obtained results show that the lowering of triacetin content and replacement of it with FAiPrE provides the opportunity to obtain products more similar to conventional biodiesel, because the content of FAAE in the reaction mixture can be increased approximately by 10% (from 72.5 to 82.4 wt %).

All reactions take place within 60 minutes at low temperature and do not require special equipment. They allow the realization of a partial glycerol conversion to fuel additive and reduce the low-value by-product. The conversion of glycerol into fuel additives or fuels has been widely studied as a process separated from biodiesel production, and the conditions for the implementation of these processes are not so simple and the efficiency is in many cases not high. The main obtained fuel additives (glycerol esters, glycerol ethers, glycerol formal, solketal, acetal) maintain either high oxygen content, high viscosity, or low heat value and cannot be used directly as a fuel because poor combustion performance (Nda-Umar et al., 2019). Direct conversion of glycerol to hydrocarbons (GTH – process) is technically complex and far from real use (Xiao Y. at al., 2016).

Data illustrated in Table 1 shows that there are 4 reaction mixtures with a relatively low intermediate content (15 wt.% and lower), relatively high FAAE content (up to 81.9 wt.%) and a TA content between 5 and 6 %. These reactions are more appropriate for obtaining high-quality fuels with a TA content below 10%; therefore, the obtained reaction mixtures were characterised as fuels (Table 2).

3.1 Fuel properties

It is clear that neither full nor partial conversion of glycerol to fuel component cannot allow obtaining biofuel with properties meeting the requirements of standard LVS EN 14214. This standard requests a very high FAAE content (96.5%) and does not permit to use additives in remarkable volume. The same, but to a lesser extent applies to the other characteristics, defined in the standard in very short range. For example, TA has a density (1150 kg/m^3) that is remarkably higher than that of biodiesel, and the stoichiometric mixture (FAME 80.6 and TA 19.4 mass %) will have a density of about 920 kg/m^3 which is not allowed (see Table 2).

The density of the fuel is used to calculate the precise volume of the fuel necessary to supply an adequate combustion (Silitonga et al., 2013), but it is not clear whether the density, for example, at the higher level causes any issues. As seen in Table 2, the density of the obtained fuels is higher than allowed by the standard, and it rises with the increase of the TA content. Kinematic viscosity is the main reason why vegetable oils or fats are converted to biodiesel and is a key factor in ensuring optimal diesel fuel atomisation (Knothe et al., 2005). Both low and high viscosities can have negative effects on an engine's performance. If fuel viscosity is low, the outflow will correspond to a power loss for the engine and if fuel viscosity is high, the injection pump will be unable to supply enough fuel to fill the pumping chamber. If the viscosity is too high, it causes poor atomisation of fuel, worse combustion, loss of power and an increase of the HC and CO emission. High viscosity causes the formation of engine deposits as it affects the atomization and leads to the formation of large droplets on injection. The high viscosity of biodiesel and its blends alter the pattern of injector spray in the engine, also leading to the formation of carbon deposits in the engine (Isioma et all., 2013). If fuel viscosity is extremely excessive the production of black smoke proceeds. Low viscosities do not provide sufficient lubrication for the precision fit of fuel injection pumps. Kinematic viscosity characteristic of all obtained biofuels meets the requirements of the standard and that is very important. Carbon residue characterises the carbon depositing tendencies of the fuel, and for the obtained fuels it is higher than for pure biodiesel. This increase could be caused by the presence of glycerol derivatives with free hydroxyl groups. The cold flow properties of the obtained fuels meet the requirements of the standard for C class diesel fuel, although they are as good as those of pure biodiesel obtained from the same feedstock. It is interesting that for the last sample, the main cold flow properties CFPP and PP are a little better than for others. It could be caused by the higher content of fatty acid *iso*-propyl esters. Obtained results show that competitive

interesterification–transesterification reactions can be successful used to find a compromise between the inclusion of glycerol in biofuels in the form of TA and the compliance of biofuel properties with the requirements of standard EN 14214.

Table 2: Fuel properties

Sample or standard	Density, kg/m^3	Viscosity, mm^2/s	Carbon residue, %	CFPP; CP, ^{o}C
Standard LVS EN 14214	860-900	3.5-5.0	-	-5
Distilled biodiesel from the same feedstock	882	4.09	< 0.01	-10;-13
iPrOK/THF, 1M, S^3 COMR 0.1	923.3	4.99	0.1	-7:-12
iPrOK/iPrOH/THF COMR 0.12	913.3	4.98	0.1	-7:-12
tBuOK/THF 1M +1 iPrOH/oil COMR 0.12	910.5	4.99	0.06	-8;-13

4. Conclusions

Interesterification reactions with methyl acetate in the presence of a homogeneous alkoxide catalyst and a selected amount of *iso*-propanol proceed as competitive interesterification–transesterification reaction. A competitive conversion of rapeseed oil allows obtaining biofuel with a high fatty acid ester content (up to 81.9 wt.%) including fatty acid *iso*-propyl ester content (3-5 wt.%) and triacetin (5 - 8 wt. %). Due to the low reactivity of *iso*-propanol, it possible to make a targeted harmonisation of the fuel composition by replacing triacetin with fatty acid *iso*-propyl esters. Lowering of triacetin content and replacing it by fatty acid *iso*-propyl esters provides the opportunity to obtain products with a higher fatty acid ester content which makes it more similar to conventional biodiesel. Despite the complicated composition of the mixtures, its fuel characteristics completely or nearly comply with the requirements of LVS EN 14214, excluding the requirements for FAME, as well as intermediate content and density. Including of the fatty acid *iso*-propyl esters at approximately 5 wt. % begins to improve the cold flow properties of the fuel.

Acknowledgements

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