

THE INFLUENCE OF ACYL AND ALCOHOL MOIETIES OF CARBOXYLATE ESTERS ON RAPESEED OIL CHEMICAL INTERESTERIFICATION

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Abstract

*An alternative method for the synthesis of biodiesel fuel (FAAE) from rapeseed oil that prevents formation of glycerol has been proposed. In interesterification reaction of rapeseed oil with carboxylate esters (methyl formate, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, tert-butyl acetate, methyl propionate, methyl butyrate and methyl isobutyrate) in presence of potassium *t*-butoxide/*t*-butanol catalytic system FAAE and triacylglycerols are formed. Triacylglycerols can be considered as valuable additives for biodiesel that do not need to be removed from the reaction mixture. The prolongation of unbranched alkyl group in alcohol moiety reduced the carboxylate ester reactivity while in acyl moiety – practically did not affect it.*

Key words: rapeseed oil, chemical interesterification, potassium *t*-butoxide, carboxylate esters

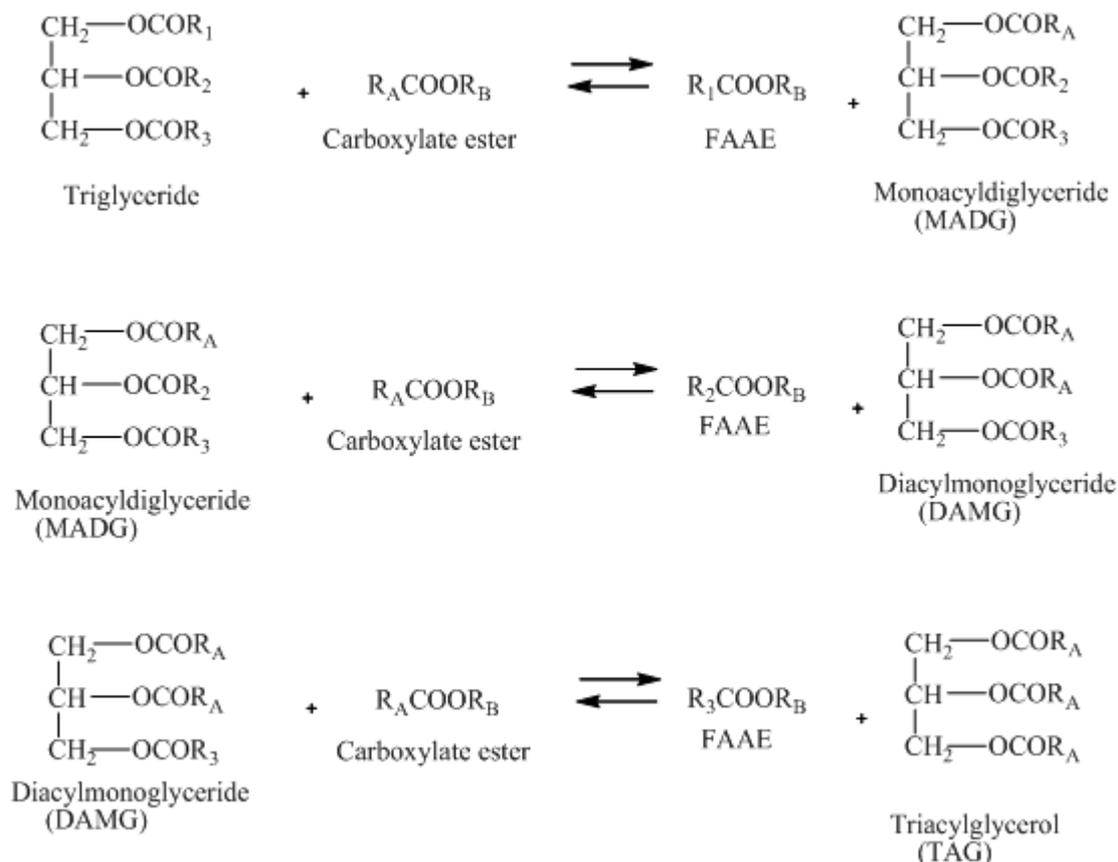
1. INTRODUCTION

Rising petroleum prices, increasing threat to the environment from exhaust emissions and global warming have generated intense international interest in developing alternative non-petroleum fuels for engines. Biofuel is one of the options to fulfil the need as transport fuel. It received attention as environmental friendly renewable substitutes fuel. Biodiesel has the potential to reduce the emissions from the transport industry, which is the largest producer of greenhouse gases (Salvi 2012). Biodiesel is chemically modified alternative fuel, derived from vegetable oils and animal fats. Conventionally, biodiesel was produced by transesterification of triglyceride (TG) with alcohols in the presence of an acidic or alkaline catalyst. The glycerol formed by this reaction is usually managed as a waste product (Voegelé 2008).

Intesterification process of biofuel synthesis is an alternative process to transesterification, because the triacetin has obtained instead by-product glycerol. The replacement of methanol with methyl acetate in the production of biodiesel has been studied previously to solve problems related to methanol use, although only of the context of enzymatic (Du 2004, Xu 2005) or supercritical (Saka 2009). Triacetin has considered as a valuable additive and do not have to be removed from the reaction mixture (Casas 2010). When the triacetin is included in the formulation of biodiesel, the yield of biofuel obtained from TG noticeably increases.

Usually potassium and sodium methoxide solutions in methanol were used as catalysts in chemical interesterification. Casas et al. discovered that the presence of methanol in the case of potassium methoxide solution in methanol increased the reaction rate of interesterification (Casas 2013). Unfortunately using methanolic solution, not only interesterification but simultaneously also the TG transesterification proceeds and fatty acid methyl esters (FAME) are produced. Therefore to determine the influence of acyl and alcohol moieties of carboxylate esters, in this study potassium *tert*-butoxide solution in *tert*-butanol were used because the reactivity of *tert*-butanol is low, and only interesterification reactions could proceed. It is known that the structure of carboxylate ester influenced the proceeding of interesterification reactions. For example, 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 (Goembira 2012). Structure effects quantitative characteristics of acyl and alcohol moieties of carboxylate esters in interesterification reactions have not been yet determined or analysed in literature.

The TG interesterification reaction with carboxylate esters is represented in Fig. 1. The intermediates are monoacyldiglyceride (MADG) and diacylmonoglyceride (DAMG). The main products are fatty acid alkyl esters (FAAE) and triacylglycerols (TAG) - triformin, triacetin, tripropionin, tributyrin – formed in interesterification with methyl formate, methyl acetate, methyl propionate, methyl butyrate (and methyl isobutyrate), respectively. In interesterification with methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate and *tert*-butyl acetate the main products are FAAE and triacetin.



R₁, R₂, R₃ – hydrocarbon residues; R_A – Alkyl residue in acyl moiety; R_B – Alkyl residue in alcohol moiety.

Fig. 1. TG interesterification reaction with carboxylate esters

2. MATERIALS AND METHODS

2.1. Materials

The refined rapeseed oil was purchased from a local producer *Iecavnieks*. The main properties of the used rapeseed oil are given in Table 1(Sustere 2016). The methyl acetate (99%) and ethyl acetate (99%) were obtained from *ROTH*, propyl, isopropyl and *tert*-butylacetate (99%) were obtained from *Alfa Aesar*. Methyl formate (97%) was obtained from ACROS ORGANICS, methyl propionate (98%) from *Sigma-Aldrich*, methyl butyrate, methyl isobutyrate (99%) were obtained from *TCI*. Phosphoric acid (85 %) was obtained from *Sigma-Aldrich*. Potassium *tert*-butoxide (BuOK) was obtained from *Sigma-Aldrich* and *tert*-butanol was obtained from *ROTH*. 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 (pure) - were supplied by *ROTH*.

Table 1. The main properties of rapeseed oil

Property	Value
Monoglycerides, wt.%	0.3
Diglycerides, wt.%	0.7
Triglycerides (TG), wt.%	97.7
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. Experimental procedure

The rapeseed oil and carboxylate monoester were mixed and heated up to 27°C or 55°C temperature in the 250 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 salt was filtered. In the kinetics experiments 5 mL sample from reaction mixture was removed after defined time and also stoichiometric amount of phosphoric acid was added. Then excess of reagent was removed by rotary evaporation and the sample was filtered and stored in refrigerator. Each experiment was carried out two times and the average value was calculated.

2.3. Analytical methods

The analysis of all components of each sample was carried out by using of an *Analytical Controls* biodiesel analyser based on *Agilent Technologies* gas chromatograph 7890A, equipped with 2 columns. Ester content was determined according to modified standard method EN 14103, using a methyl heptadecanoate as internal standard. 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 μ m. Oven temperature was set at 200 °C.

Glycerol, monoglyceride, diglyceride (DG) and triglyceride (TG), – diaacylmonoglyceride (DAMG), monoacyldiglyceride (MADG), monoacylmonoglyceride (MAMG) and triacylglycerol (TAG – triformin, triacetin, tripopionin, tributyrin) were analysed using DB5-HT column (15 m, 0.32 mm, 0.10 μ m) under conditions prescribed in standard EN 14105 and quantified as in our previous work (Sustere 2014). The oven temperature was set to 50 °C for 5 min and then temperature was first increased to 180 °C at the rate of 15 °C/min, then to 230 °C at the rate of 7 °C/min and finally to 370 °C at the rate of 10 °C/min. Helium was used as carrier gas and detector temperature was set to 390 °C in both methods. Each measurement was carried out twice and the average value was calculated.

The theoretically predicted content of FAME in reactions with methyl formate, methyl acetate, methyl propionate and methyl butyrate (and methyl isobutyrate) by full triglyceride conversion accordingly to

the Fig.1. are 84.0 wt.%, 80.9 wt.%, 78.0 wt.% and 75.3 wt.%, and the theoretically predicted content of triacylglycerols are 16.0 wt.%, 19.1 wt.%, 22.0 wt.% and 24.7 wt.%, respectively. The theoretically predicted content of FAEE, FAPE (and FAiPE) and FAtBE in reaction mixture by full TG conversion accordingly to the Fig.1. is 81.6 wt.%, 82.2 wt.% and 82.8 wt.%, and the theoretically predicted content of triacetin is 18.4 wt.%, 17.8 wt.% and 17.2 wt.%, respectively. The FAAE percentage yield (FAAE yield %) was calculated as percentage of experimentally obtained mass contents from the theoretically predicted ones.

3. RESULTS AND DISCUSSIONS

3.1. Structure effect on interesterification equilibria

To determine the influence of different acyl and alcohol moieties of carboxylate esters on the composition of interesterification mixture, experiments were carried out under such selected conditions - 55 °C temperature, carboxylate ester to oil molar ratio (CEOMR) 18:1, catalyst molar ratio to oil (COMR) 0.16, reaction time 1 hour. Percentage compositions of reaction mixtures obtained are shown in Table 2. As the boiling point of methyl formate is only 32 °C, reactions with methyl formate and methyl acetate also at 27 °C temperature were done (see the 3.2. section).

Table 2. Percentage compositions of reaction mixtures obtained with carboxylate esters at 55 °C temperature and COMR 0.16

Carboxylate ester	Content, m/m%						FAAE, yield %
	DAMG	MADG	TG	DG	TAG	FAAE	
Methyl acetate	5.8	1.8	0	0.4	8.4	68.5	84.7
Ethyl acetate	7.6	2.4	0	0.2	9.1	65.9	80.7
Propyl acetate	5.6	1.3	0	0.1	8.4	62.6	76.1
Isopropyl acetate	7.1	3.0	0.8	0.6	8.3	61.5	74.8
tert-Butyl acetate	0	14.3	67.2	1.1	0	3.9	4.7
Methyl propionate	0	0	89	7.3	0	1.5	1.9
Methyl butyrate	7.7	1.5	0	0	12.9	63.3	84.1
Methyl isobutyrate	0	0	81.3	14.7	0	3.1	4.1

As can be seen in Table 1, the prolongation and branching of alcohol moiety in alkyl acetate molecule causes decrease of alkyl acetate reactivity in order methyl>ethyl>propyl>isopropyl>tert-butyl. In tert-butyl reaction this effect reached maximum, as only 4.7% yield of FAAE was obtained.

Very low conversion of rapeseed oil and FAAE yield in reactions with methyl propionate (1.9%) and methyl isobutyrate (4.1%) is connected with the dissolving problem of catalyst in the reaction mixture. In both reactions adding a catalyst forms a cloudy appearance of the reaction mixture.

Comparing the FAAE yield in reactions with methyl acetate and methyl butyrate, we can conclude that the prolongation of alkyl chain in acyl moiety of carboxylate ester practically does not affect its reactivity.

To extend the structures of acyl moieties of carboxylate esters, some experiments were carried out also at 27 °C temperature (as the boiling point of methyl formate is 32 °C) and COMR 0.12, keeping other reaction circumstances without variation. Percentage composition of reaction mixtures obtained is shown in Table 3.

Table 3. Percentage composition of reaction mixtures obtained with carboxylate esters at 27 °C temperature and COMR 0.12

	wt. %						FAME yield, %
	DAMG	MADG	TG	DG	TAG	FAME	
Methyl formate	5.3*	1.3*	0 *	0.2*	2.0*	74.2*	88.3
Methyl acetate	8	3.2	0.6	0.4	15.6	71	87.8

*calculated using mass of layers

In reaction with methyl formate two layers were formed. The upper layer has high FAME content, but the lower layer accordingly to GC and H NMR analysis consists of mono-, di- and triformin and glycerol. The FAME content given in table was calculated by multiplication of the measured FAME content in upper layer with mass ratio of upper layer to mass of both layers.

As can be seen in Table 2 the yield of FAME is practically the same (88%) in both – methyl acetate and methyl formate reactions, what confirmed that the prolongation of alkyl chain in acyl moiety of carboxylate ester practically does not affect its reactivity.

3.2. Quantitative characteristics of structure effects

To obtain quantitative characteristics of the structure effects in the form of substituent at carboxyl group C and O atoms effects, the relation

$$\text{Yield(FAAE)/yield(FAME)} = E_i \text{ (for alkyl group)}$$

was used. Obtained E_i represented relative formal effect of alkyl group in alcohol moiety and E_{i^*} - relative formal effect of alkyl group in acyl moiety. In this system the E_i and E_{i^*} values for the methyl group is assumed to be 1. Considering the results in Table 3, also the E_{i^*} value of hydrogen atom also is 1, see Table 4.

Table 4. Substituent effects on FAAE yield

Substitute R	E_i (in alcohol moiety)	E_{i^*} (in acyl moiety)
H	-	1.0
CH ₃	1.0	1.0
CH ₃ CH ₂	0.95	-
CH ₃ CH ₂ CH ₂	0.9	0.99
(CH ₃) ₂ CH	0.88	-
(CH ₃) ₃ C	0.06	-

It can be concluded, that the introduction of the same substitutes in acyl and alcohol moieties of carboxylate esters affects its reactivity differently. Prolongation of unbranched alkyl groups in alcohol moiety reduced the reactivity of carboxylate esters, while prolongation of unbranched alkyl groups in acyl moiety do not affect the reactivity practically. Most feasible the obtained substituent effects are related to its steric influence, therefore it is interesting to compare these effects with known steric (σ_s) constants of the same substituents (Ploom 2006). As can be seen in Fig.2., between σ_s and E_i exists a complex interconnection, in which the isopropyl group does not incorporate. Nevertheless the tendency – increasing steric effect of alkyl group decrease the FAAE yield – is typical and allow to conclude that steric effects of substituents in alcohol moiety of carboxylate esters has significant impact on interesterification reaction.

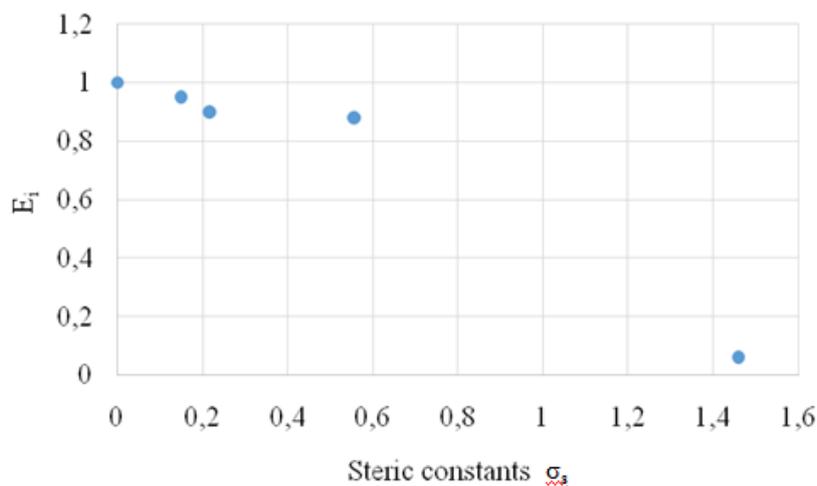


Fig. 2. Substituent effects E_i versus steric constants σ_s

3.3. Structure effect on reaction kinetics

As can be seen in Fig.3., the kinetics of interesterification depends on substituents in carboxylate ester structure. Interesterification with methyl and ethyl acetates proceeds similarly, the high yield of FAAE (70 wt. %) are obtained after 10 minutes.

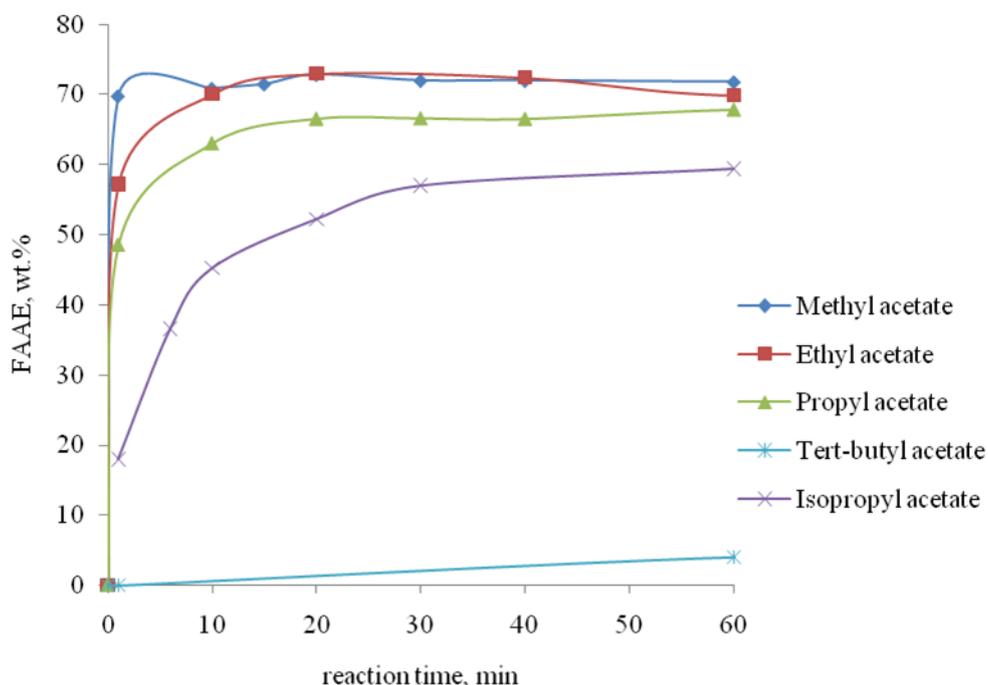


Fig. 3. Plot of FAAE content versus time. The reaction conditions: 55 °C temperature, CEOMR 18:1, COMR 0.15

The reaction with isopropyl acetate proceeds slower, and the maximal yield of FAAE after 60 minutes was not reached. The shape of the FAAE curve in the case of isopropyl acetate is more complicated and requires additional investigation.

CONCLUSIONS

The rapeseed oil interesterification process is alternative to transesterification process for biodiesel production because triacylglycerols are formed instead of glycerol. The introduction of the same substitutes in acyl and alcohol moieties of carboxylate esters affects its reactivity differently. Prolongation of unbranched alkyl groups in alcohol moiety reduced the reactivity of carboxylate esters, while prolongation of unbranched alkyl groups in acyl moiety do not affect the reactivity practically. The highest FAME yield were obtained with methyl acetate and methyl butyrate, 84.7 % and 84.1 %, respectively, by 55 °C temperature, carboxylate ester to oil molar ratio 18:1, catalyst molar ratio to oil 0.16 and reaction time 1 hour.

ACKNOWLEDGMENTS

This work was supported by the Programme 1.1.1.1/16/A/078 “Biodiesel synthesis in rapeseed oil interesterification”.

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