ORE CONTROL OF KHIZOVAARA STRUCTURE DEPOSITS

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ABSTRACT

Ore-controlling factors determine the patterns of formation and localization of mineralization within ore regions and deposits. The need for this study arises from the importance of integrated assessment of mineral resources and improvement of metasomatic formation techniques. This is especially important for geological materials which are mined for their direct commercial value (industrial materials). This article is devoted to the study of the ore control of complex industrial minerals. The Khizovaara structure belongs to the Tikshozero greenstone belt. Within the structure, a multistage metamorphism and metasomatism processes are manifested. The totality of lithological, structural and petrologic ore control factors determines the existence within the structure of several deposits. These are deposits of industrial minerals, such as garnet, quartz, muscovite, kyanite, staurolite. In almost all cases, the ores are complex. The following objects were studied: Southern Lens (kyanite + quartz) deposit, Northern lens (kyanite + quartz) deposit, East Khizovaara (muscovite + quartz) deposit, Vysota-181 (garnet + staurolite + kyanite + muscovite + quartz) deposit, ore occurence Fuxit (decorative rocks). For the ores of each site, the processes of regional metamorphism of the amphibolite facies of kyanite-biotite and muscovite-chlorite-kyanite subfacies are important. Metamorphism, tectonic regime and geological connection with rocks has been studied as a ore control factor, based on this, data on the quantitative distribution of industrial minerals of metamorphic genesis have been obtained. Acidic and alkaline metasomatites of each site are considered. On the basis of these data, metasomatic processes that lead to the formation of complex ores are revealed. The process of superposition of metasomatosis products of the late stage on the products of early stage metasomatosis was studied. This process leads to the formation of complex ores of three or four minerals. The result of the work is a general scheme of metamorphic and metasomatic ores control for all studied objects.

Keywords: hizovaara structure, garnet, kyanite, muscovite, metasomatism, tectonic control.

INTRODUCTION

The transportation sector accounts for around 20% of the global energy consumption and is the biggest consumer of oil in the world. The growing energy demand in the transport sector and almost 95% cover the energy demand by fossil fuels increases the emission and facilitates global warming. The main alternatives to fossil fuel based liquid transport fuels are biofuels. The main biofuels currently in use around the world are biodiesel, bioethanol, and biomethane. The European Union remains the largest producer and user of biodiesel. Nevertheless, the future of biodiesel is threatened by the use of vegetable oil as a biodiesel feedstock and the low economic value of the by-product glycerol [1]. Biodiesel is mainly produced from plant-seed oils, i.e. rapeseed in Europe and soybean in the US, and conventionally production takes place by transesterification of triglycerides (TG) with methanol in the presence of basic catalysts. Another reaction used for the splitting of triglycerides is interesterification. Interesterification constitutes reaction with methyl acetate (MeAc) or another short chain monoester as a reactant. In the interesterification reaction (equation 1) with MeAc the same composition of FAME as in transesterification with methanol (equation 2) must to be synthesised, but another by-product TA appears:

$$TG + 3MeAc \rightleftarrows 3FAME + TA \qquad (1),$$

where TG – triglyceride, MeAc – methyl acetate, FAME – mixture of fatty acid methyl esters, TA – triacetin.

$$TG + 3MeOH \rightleftarrows 3FAME + G \qquad (2),$$

where MeOH – methanol, G – glycerol.

TA is compatible with FAME, it can be considered a fuel additive [2, 3] and included into biofuel composition, ensuring full conversion of oil to biofuel. By employing interesterification process for biodiesel production, instead of the more common transesterification process, it is possible to increase the yield of fuel and reduce production cost [4]. The interesterification is a relatively new and insufficiently investigated process for biofuel synthesis, yet it is widely known and industrially used for the modification of fat and oil mixtures for food [5, 6]. In the oil technology this process is frequently carried out using sodium hydroxide or sodium alkoxide as a catalyst at a relatively high temperature. Casas etc. had shown that in the interesterification reactions of oil with MeAc, proceeding at a boiling temperature of MeAc, only the alkoxide are active catalysts [7]. Since the process generated interest also from a practical point of view [8], activity of very different catalysts and circumstances has been investigated. Interesterification has been studied in the presence of enzymes and also without catalyst under supercritical conditions, but the drawbacks of these routes are significantly higher production costs [4]. Different chemical catalysts have also been investigated. For example, the interesterification with methyl acetate was performed in the presence of new niobium phosphate, γ-alumina zeolite heterogeneous catalysts at 250 °C [2]. Heterogeneous catalysts attract a great interest, as the removing of the homogeneous catalyst after neutralisation is a cumbersome stage. Regardless of the search for an active heterogeneous catalyst, the most successful realisation of reactions has been made in the presence of homogeneous catalysts [7], however, the high MeAc to oil molar ratio (higher than 18:1) is necessary. Only using potassium methoxide at concentration 1.0 % in the presence of ultrasonic radiation, 90% yield was observed at a molar ratio

of 12:1 and temperature of 40 °C [3]. The results of investigations of heterogeneous and homogeneous catalysts draw attention to the extraordinary importance of catalyst solubility. Partial solubility can remarkably lower the activity of homogeneous catalyst and extremely increase that of formally heterogeneous catalyst. The replacement of alcohol as a reactant in the transesterification reactions with the MeAc in the interesterification reactions lowered the polarity of reaction mixture, and transesterification catalysts used commonly become partially or fully insoluble. Solubility of the alkoxide catalyst depends on the cation and should increase with the prolongation and branching of the alkyl chain. In our previous work [5] we have established that the potassium tert-butoxide in tert-butanol (t-BuOK/t-BuOH) is an appropriate catalytic system for interesterification of rapeseed oil with methyl acetate, substantially increasing the yield of triacetin. This catalyst can also be dissolved in an aprotic solvent, and the aim of this work is to ascertain how the absence of hydroxyl group in solvent molecule affects the activity of t-BuOK and influences the composition and fuel characteristics of products.

2. MATERIALS AND METHODS

2.1. Materials

The refined rapeseed oil was purchased from a local producer *Iecavnieks*. Rapeseed oil characteristics are presented in *Table 1*. The methyl acetate (99 %), phosphoric acid (85 %) and potassium *tert*-butylate 1 M solutions in *tert*-butanol and THF were obtained from *Sigma-Aldrich*. Materials for GC analysis: methyl heptadecanoate (95%) was supplied from *Sigma-Aldrich*, 1,2,4-butanetriol (96%) and MSTFA (N-methyl-N-(trimethylsilyl)trifluo-

roacetamide, 97%) – from *Alfa Aesar*, tricaprin (>98%) – from *TCI Europe*, while heptane (>95%), and dichloromethane (pure) were supplied by *ROTH*.

Table 1. The main characteristics of refined rapeseed oil

Characteristic	Measured value
Average molecular weight (g/mol)	896
Saponification value (mg KOH/g)	190.7
Acid value (mg KOH/g)	0.16
Density at 20 °C (g/ml)	0.92
Fatty acid profile (wt%)	
Palmitic acid (C16:0)	5.3
Stearic acid (C18:0)	1.2
Oleic acid (C18:1)	63.6
Linoleic acid (C18:2)	21.8
Linolenic acid (C18:3)	6.7
Arachidic acid (C20:0)	0.4
Others	1.0
Triglyceride (wt%)	98.2
Diglicerides (wt%)	0.6
Monoglicerides (wt%)	0.3

1.2. Experimental procedure

The rapeseed oil and alkyl acetate were mixed and heated up to 55 °C in a 250-mL 3-neck round bottom 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 stoichiometric amount of phosphoric acid. Then excess of reagent was removed by rotary evaporation, and the sample was filtered and stored in refrigerator. To investigate a rate of reaction samples were collected at designed temperature after 3, 6, 10, 20, 60 min and immediately quenched with an equimolar amount of phosphoric acid to

remove the catalyst. Then after removing the excess of methyl acetate by rotary evaporation and the potassium phosphate by filtration, samples were stored in refrigerator until analysis. The concentration of catalyst was measured as a molar ratio to oil (COMR) and amount of reactant as a molar ratio of methyl acetate to oil (MAOMR).

1.3. Analytical methods

Average molecular mass was calculated from saponification value according to the following relation: average molecular mass = mass of oil / number of moles of base. Saponification value was determined according to the ASTM D5558, and acid value according to the EN 14104 standard. The elemental analysis was carried out on a EuroEA Elemental Analyser. Analysis of all components of each sample of interesterification products was carried out, using 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 an internal standard. The capillary column employed was a HP Innowax with a length of 30 m, an internal diameter of 0.25 mm and film thickness of 0.25 μm. Oven temperature was set at 200 °C. Glycerol (G), mono- (MG), di- (DG) and triglycerides (TG), diacetinmonoglyceride (DAMG), monoacetindiglyceride (MADG), monoacetinmonoglyceride (MAMG) and monoacetin (MA), diacetin (DA) and triacetin (TA) were analysed using DB5-HT column (15 m, 0.32 mm, 0.10 μm) under conditions prescribed in standard EN 14105, and mass percentage of reaction mixture was performed, as described in our previous work *[5]*. The oven temperature was set to 50 °C for 5 min,

and then it was increased to 180 °C at a rate of 15 °C/min, then to 230 °C at a rate of 7 °C/min, and finally to 370 °C at a rate of 10 °C/min. Helium was used as carrier gas, and detector temperature was set at 390 °C in both methods. Each measurement was made in doubles, and the average value was calculated. The same procedure but without silylation was used for characterisation of fatty acid composition in mass % of total FAME. Percentage by mass (% m/m) of the obtained biofuel was calculated, multiplying its mass fraction to oil by 100. Higher heating value (HHV) was determined using Parr oxygen bomb calorimeter 6100, density (15 °C) was determined with the use of Anton Paar DMA 4500 density meter according to the standard method EN ISO 12185. Kinematic viscosity (40 °C) was determined with the use of Anton Paar SVM 3000 viscosity meter according to the standard method EN ISO 3104. The measurements of cold filter plugging point (CFPP) were performed on the basis of DIN EN 116 standard method with the use of ISL FPP 5Gs equipment. Carbon residue (from 100 % sample) was determined using Alcor MCRT- 160 tester according to the standard method ASTM D 4530. Each experiment was carried out two times, and the average value was calculated. The biodiesel vacuum distillation procedure was performed according to ASTM D 1160.

2. RESULTS AND DISCUSSION

On the basis of the previous investigation [5, 7] it can be considered that the main variables in interesterification reaction with methyl acetate (MA) should be as follows: catalyst composition, molar ratio of catalyst to oil (COMR), molar ratio of MA to oil (MAOMR), reaction temperature and time. Reaction temperature and time are interconnected, and they were

usually harmonised with those of transesterification. Therefore, the temperature of 55 °C and the time of 1h were maintained invariably in this work for the investigation of COMR and MAOMR influence on the reaction proceeding.

3.1. Catalyst to oil molar ratio

Investigation of the influence of COMR variation has been conducted at the fixed MAOMR 18, determining the content of TA and FAME in the obtained reaction mixtures. As shown in *Figure 1*, irrespective of the catalyst composition, reaction only begins when some critical value of COMR is reached. Subsequently a steep and almost linear shape follows with the reaching of a plateau. The apparent critical COMR for reaching plateau is near to 0.09 in both cases.

Both catalytic systems demonstrated similar influence on the interesterification reaction proceeding, however, catalytic system BuOK/THF seems to be a slightly more active than the other one – BuOK/BuOH, as the steep rising part is shifted to a lower COMR region by approximately 0.005. Either THF or BuOH can be considered an inactive solvent because its influence on the content of the most sensitive compound TA is practically identical.

The solutions of tertiary alkoxides in the corresponding alcohols are known to have generated a great practical interest as catalysts and condensation agents because due to the high steric hindrance they are less prone to different side reactions than primary or secondary alkoxides [9]. At concentrations above 0.1 M the secondary and tertiary alkoxides in corresponding alcohol solutions form ion pairs or ion pair aggregates [9]. In non-alcoholic solvents, for example, in DMS even at a concentration of 0.01 M, *tert*-butoxides exist in a form of ion pairs which can be dissociated by adding *tert*-butanol
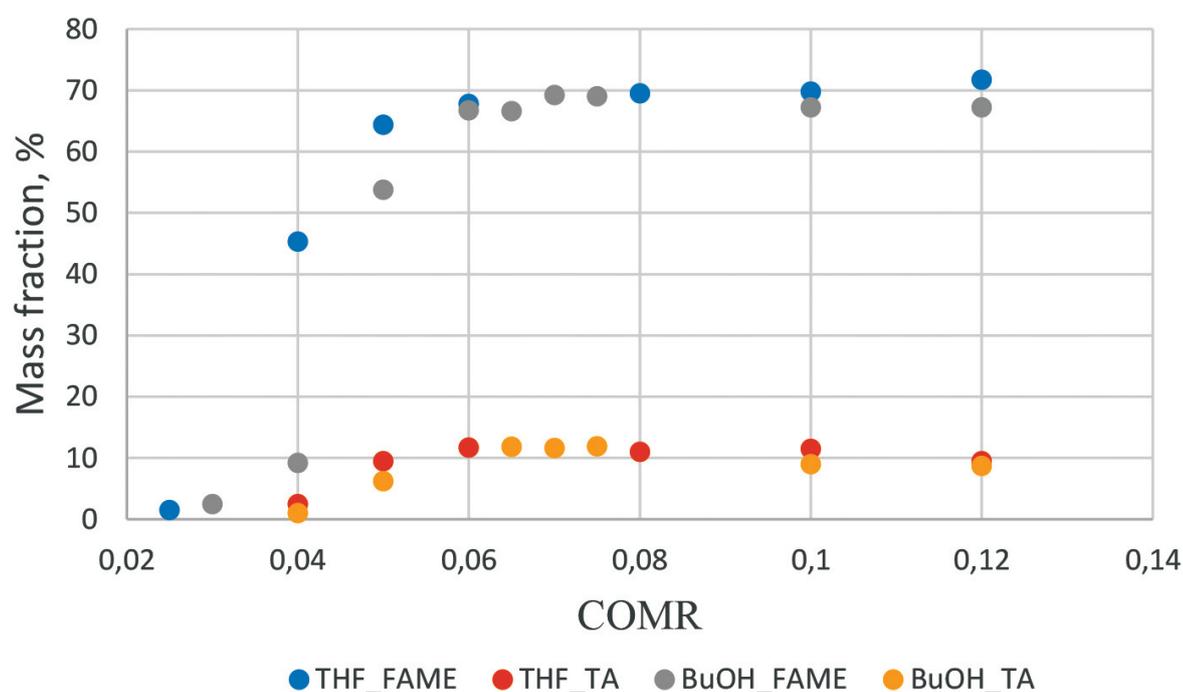

Figure 1. Influence of COMR on FAME and TA content in reaction mixtures. Two different catalytic systems BuOK/THF and BuOK/BuOH were used.

[10]. In ethereal solutions, including THF, alkoxide could exist in a form of ion pair monomers, dimers, or tetramers. Higher aggregates are usually less reactive than ion pairs, while ion-pairs are less reactive than solvated anions. This order of activity of alkoxides can be changed in reactions with requirement for desolvation before nucleophilic attack [11]. A slightly higher activity of BuOK/THF catalytic system than that of BuOK/BuOH can be caused by the formation of hydrogen bond and more effective solvation in the presence of BuOH which cumbers the desolvation during the transesterification reaction. From the influence of COMR of both catalytic systems under investigation on the occurrence of the interesterification it can be concluded that the structures of t-BuOK in 1M solutions in BuOH and THF are similar and cannot be remarkably diverged by the degree of aggregation. THF, which is more suitable by polarity to that of reaction mixture, facilitates the desolvation of *tert*-butoxide anion and slightly accelerates the reaction.

3.2. Methyl acetate to oil molar ratio

An increase of methyl acetate to oil molar ratio (MAOMR) should shift the equilibrium (1) to the formation of FAME and TA. In order to obtain experimental evidence of the influence of MAOMR on proceeding of the reaction of interesterification in the presence of catalytic system of BuOK/THF, reactions at 55 °C, reaction time 1h and slightly rising COMR have been made with MAOMR 18, 21, 24 and 27. As can be seen from *Table 2*, the content of intermediates decreased, while the content of target products increased with the increase of MAOMR.

Table 2. Composition of reaction mixtures of interesterification with rising MAOMR

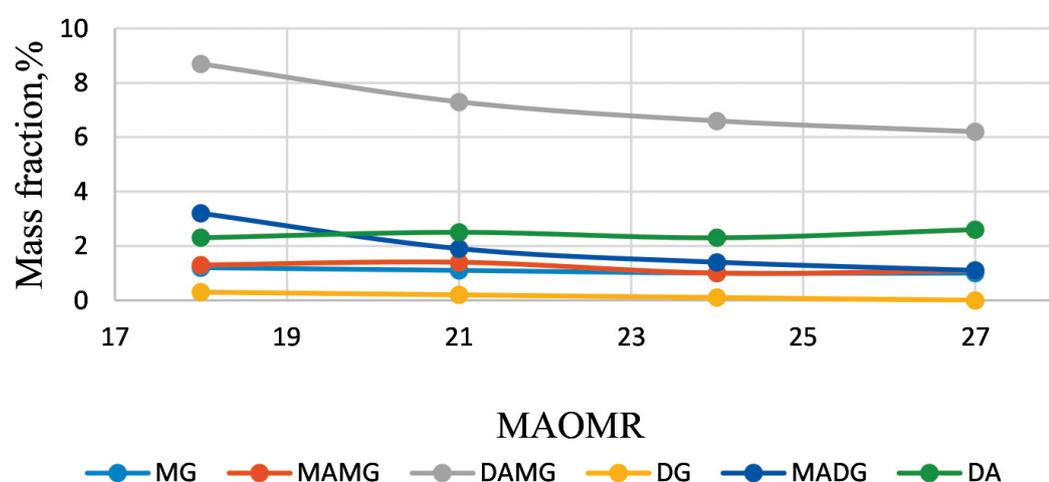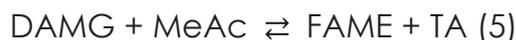| MAO	CO	Content in mass %							
MR	MR	MG	MAMG	DAMG	DG	MADG	DA	TA	FAME
18	0.1	1.2	1.3	8.7	0.3	3.2	2.3	11.5	69.5
21	0.11	1.1	1.4	7.3	0.2	1.9	2.5	11.9	71.7
24	0.11	1	1	6.6	0.1	1.4	2.3	12.9	72.2
27	0.12	1	1.1	6.2	0	1.1	2.6	13.1	74

Figure 2. *Influence of MAOMR on the content of intermediates in final reaction mixtures.*

Nevertheless, the content of intermediates remained high up to MAOMR 27, and the positive influence of the increase of MAOMR was partially quenched by stabilisation tendencies for MG and MAMG and increase of DA (**Figure 2**).

3.3. Rate of reaction and its stepwise character

Characteristic reaction time 1h has been usually selected for the investigation of biodiesel synthesis via inter- or transesterification of oils. Actually reaction of rapeseed oil with MeAC in presence of BuO/THF at the desired temperature 55 °C proceeds so fast that approximately after 5 min the chemical equilibrium has been reached. This time is too short for the investigation of starting phase of reaction using conventional methods of sample collection and analysis. Therefore, we decided to lower the temperature to 25 °C. As it is seen from the **Figure 3** the temperature lowering extended the time for the reaching of chemical equilibrium till 30 min, what gives the possibility to analyse the formation of intermediates.

It is known that the realisation of summary reaction proceeds stepwise via reactions (3-5):

$$TG + MeAc \rightleftarrows FAME + MADG \quad (3),$$

$$MADG + MeAc \rightleftarrows FAME + DAMG \quad (4) \text{ and}$$

$$DAMG + MeAc \rightleftarrows FAME + TA \quad (5)$$

Reactions (3) and (4) produced FAME but failed to produce TA. If all reactions don't proceed practically simultaneously, the maximal mass percentage of FAME in reaction mixture (see **Figure 3**) should appear earlier than the maximal mass percentage of TA, what isn't observed experimentally. From the other hand, step-by-step proceeding will cause the fast disappearance of TG with passing MADG and DAMG through maxima and contemporaneous formation of TA. As it is seen from **Figure 4** experimental results confirm such order. Obtained results show, that interesterification really proceeds as step-by-step process, but the summary mass percentage of TA, probably, depends not only on formation but also on destroying via side-reactions.
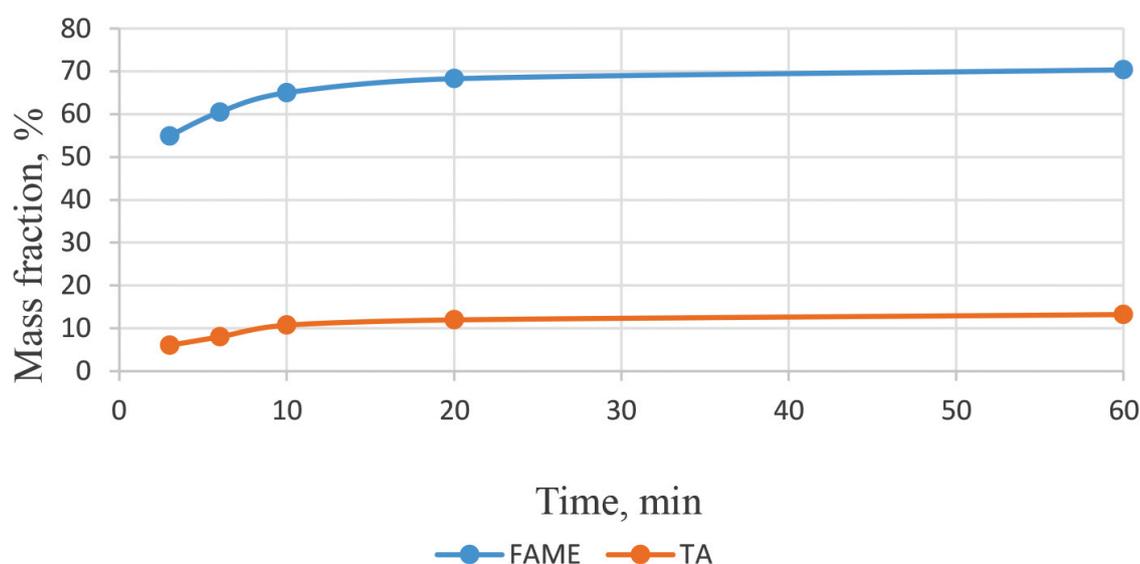

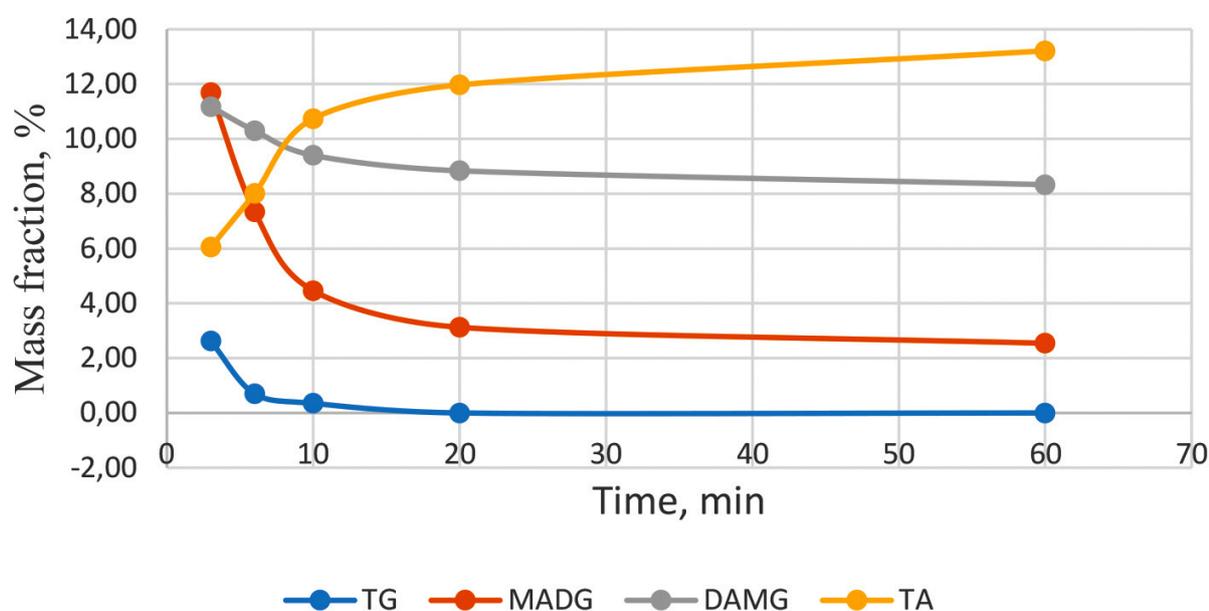**Figure 3.** *Formation of target products during interesterification at 25 oC.*

Figure 4. *Consumption of TG and formation of intermediates and TA*

Table 3. Fuel properties of interesterification products

Sample	Characteristics						
	Flash point, °C	Density, kg/m³	Viscosity, mm²/s	Carbon residue, %	CP, °C	CFPP, °C	PP, °C
TG	285	910	34.1	0.3			
FAME	>200	882	4.0861	< 0.01	-12	-10	-13
Th*	>150	922.8	4.1176	< 0.01	-11	-11	-14
MAOMR							
18	114	904.1	5.4054	0.22	-7	-9	-10
21	>200	923.8	5.0341	0.19	-8	-8	-11
24	120	925.1	4.8215	0.20	-9	-9	-12
27	>200	924	4.8328	0.18	-6	-8	-13

3.4. Fuel properties

It is characteristic of biodiesel fuel to be sensitive to the composition of FAME and different ingredients. Biodiesel must contain at least 96.5% m/m of FAME and meet the fuel quality standard known as EN 14214. Reaction mixtures obtained after interesterification of rapeseed oil consist of intermediates, TA and FAME. Moreover, as can be seen from **Table 2**, the FAME content is up to 74 % m/m, and therefore the obtained biofuel cannot meet all the re-

quirements of the said standard. The main fuel characteristics of obtained mixtures (**Table 3**), excluding density and carbon residue, complied to the requirements of EN14214 when MAOMR exceeded 21, however, they were worse than those for 100 % pure biodiesel, specially synthesised from the same oil by transesterification with methanol and refined by vacuum distillation.

The artificial mixture of pure biodiesel and TA also retains excellent characteristics

(excluding density), confirming the possibility to use the interesterification reaction for synthesis of biodiesel. The obtained results acknowledged that the quality of biofuel improves with an increase of MAOMR and a decrease of content of intermediates in the obtained final reaction mixtures.

CONCLUSION

The absence of alcoholic hydroxyl groups in the catalytic system *tert*-butoxide/THF ensures a slightly higher activity in interesterification reaction of rapeseed oil than that of catalytic system *tert*-butoxide/*t*-butanol, however, it does not change the yield of FAME and TA. A similar yield of the target products excludes the possible participation of BuOH in transesterification of TA. Whereas the similar shape of COMR influence for both catalytic systems points to the similar degree of aggregation and alkoxide structures in 1M solution in both THF and BuOH. THF as being more suitable by polarity to that of reaction mixture therefore facilitates the desolvation of *tert*-butoxide anion and somewhat accelerates the interesterification reaction. The content of TA, as well as the content of FAME can only be increased by increasing the MAOMR from 18 to 27. During this alteration in MAOMR the content of intermediates decreased but remained relatively high also at MAOMR 27, and the positive influence of the increase of MAOMR was partially quenched by stabilisation tendencies for MG and MAMG content and increase of DA. At 55 °C chemical equilibrium is reached after 5-10 minutes, while at 25 °C after 30 minutes. Kinetics of intermediate formation at 25 °C confirms the step-by-step proceeding of the reaction.

Fuel properties of the obtained interesterification mixtures become more conformable with the requirements for biodiesel standard as a result of an increase of MAOMR. The main fuel characteristics of the obtained mixtures, excluding the density and carbon residue, complied to the requirements of EN14214 when MAOMR exceeded 21, however, they were not so excellent than those for 100 % pure biodiesel and its mixture with pure TA. Further enhancement of fuel properties of interesterification reaction mixtures is only possible by lowering the content of intermediates.

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