

Chemical Interesterification of the Rapeseed Oil with Methyl Acetate in the Presence of Potassium *tert*-Butoxide in *tert*-Butanol

Z.Sustere¹, V.Kampars

Abstract - The chemical interesterification of the rapeseed oil is a promising alternative to transesterification in biodiesel production due to the fact that triacetin is formed instead of glycerol, which is usually considered as a waste product. Recent studies have shown that triacetin evolved as a valuable additive for biodiesel. Using commercially available sodium methoxide in methanol as a catalyst in interesterification does not allow to achieve the highest possible yield of triacetin, due to the side reactions place in methanol. The use of potassium *tert*-butoxide in *tert*-butanol as a catalyst increased the content of triacetin. The maximum content of fatty acid methyl esters and triacetin was 73.2 wt.% and 16.6 wt.%, respectively (the theoretically predicted was 81.1 wt.% and 18.9 wt.%). The optimal molar ratio of potassium *tert*-butoxide in *tert*-butanol to oil was 0.15 and molar ratio of methyl acetate to oil 36 was established.

Index Terms - Biodiesel, interesterification, methyl acetate, potassium *tert*-butoxide

I. INTRODUCTION

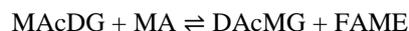
Biodiesel is a mixture of fatty acid methyl esters (FAME), produced from triglyceridic fats and oils using the transesterification with methanol, usually in presence of alkali or acid catalysts [1]-[4]. The main byproduct in this process is glycerol. To utilize this renewable feedstock the one of the possibilities currently being explored is the use of glycerol-based additives to improve petrol fuel properties [5]. Glycerol has also been esterified with acetic acid or transesterified with methyl acetate to yield glycerin triacetate (triacetin, TAc) [6], [7]. TAc has been introduced in biodiesel formulation, resulting in a final fuel having enhanced cold and viscosity properties [4]. Diacetyl glycerol (diacetin, DAc) and TAc have been shown to be valuable petrol fuel additives leading to either enhanced cold and viscosity properties when blended with diesel fuel or antiknocking properties when added to gasoline [5].

The other possibility is the interesterification of triglycerides (TG) with methyl acetate. It is a promising alternative to transesterification because TAc is formed instead of glycerol [8]-[12]. Furthermore, the interesterification method eliminates the risk of deactivation of enzyme by glycerol, when enzymatic biodiesel production were realized, as the triacetin has no negative effect on the lipase activity [8], [13]. When TAc is included in the formulation of biodiesel, the amount of biofuel obtained from TG increase [14]. A stoichiometric analysis indicates that theoretically predicted FAME and TAc content by full TG conversion into these two products will be 81.1 wt.% and 18.9 wt.%, respectively.

In contrast to the transesterification, in the interesterification reaction one ester exchanges its alcohol group with another. The absence or lower content of alcohol in the interesterification reaction mixture means that the reaction medium changes from polar to non-polar and the catalysts (usually alkaline methoxides) become insoluble [15]. Casas et al. [16] showed that the presence of the methanol in the commercial methanolic potassium methoxide increased the chemical interesterification reaction rate and improved the safety of the reaction process. However, if sodium or potassium methoxides in methanol are used as catalysts for interesterification reactions, simultaneously the transesterification reaction proceed and the system becomes more complicated. Also, in the presence of methanol, TAc can be converted into DAc, monoacetin (MAc) and glycerol (G). In order to facilitate the interesterification reaction the solvent of the catalyst must be deactivated. Potassium *tert*-butoxide is available in *tert*-butanol solution. The reactivity of the *tert*-butanol could be truncated in the interesterification reaction due to the steric reasons, the interesterification with methyl acetate should prevail. Therefore, the aim of this work was to compare the influence of two different alkoxide catalysts on the biodiesel synthesis. Reported earlier equations [11] of the interesterification reaction with methyl acetate includes possible side reactions with solvent of catalyst are shown in Scheme 1 following the abbreviation of compounds represented in Table I.

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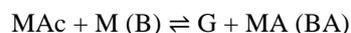
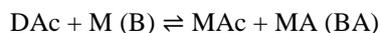
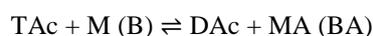
Interesterification of TG (main reaction) 1-3:



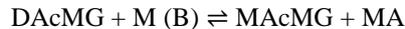
Transesterification of TG (side reaction) 4-6:



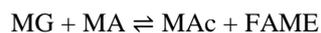
Transesterification of TAc (side reaction) 7-9:



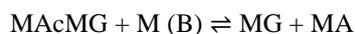
Transesterification of interesterification products (side reaction) 10-13:



Interesterification of transesterification products (side reaction) 14-15:



MAcMG transesterification and interesterification (side reaction) 16-19:



Scheme1. Scheme of triglyceride interesterification with methyl acetate.

Table I. Abbreviation of compounds.

Abbreviation	Compound
TG	fatty acid triglyceride
DG	fatty acid diglyceride
MG	fatty acid monoglyceride
FAME	fatty acid methyl esters
FABE	fatty acid tert butyl esters
TAc	triacetin
DAC	diacetin
MAc	monoacetin
MAcDG	monoacetindiglyceride
DACMG	diacetinmonoglyceride
MAcMG	monoacetinmonoglyceride
G	glycerol
MA	methyl acetate
BA	<i>tert</i> -butyl acetate
M	methanol
B	<i>tert</i> -butanol

II. MATERIALS AND METHODS

Materials

The refined rapeseed oil was purchased from a local producer Iecavnieks. The methyl acetate (99%) and phosphoric acid (85%) were obtained from Sigma-Aldrich and used as received. TAc (99%) was purchased from ACROS Organics and *tert*-butanol (99%) from ROTH. Catalysts 28.6% sodium metoxide solution in methanol (MeONa) was supplied from Latraps and 1.0 M potassium *tert*-butoxide solution in *tert*-butanol (t-BuOK) – 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 (pure) - were supplied from ROTH.

The main properties of the used rapeseed oil are given in Table II [17].

Table II. The main properties of rapeseed oil [17].

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

Experimental procedure

The rapeseed oil and methyl acetate were mixed and heated to the 55 °C in the 250-mL or 500-mL 3-neck flasks, 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 began. Reaction mixture was quenched after 60 minutes by adding the stoichiometric amount of phosphoric acid. Then excess of reagent was removed by rotary evaporation at 60 °C over 1 hour and the sample was filtered and stored in refrigerator.

Analytical methods

The analysis of all samples was carried out by using of an *Analytical Controls* biodiesel analyzer based on *Agilent Technologies* gas chromatograph 7890A, equipped with two 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 meters, an internal diameter of 0.25 mm and a film thickness of 0.25 μ m. Oven temperature was set to 200 °C.

Glycerol (G), monoglyceride (MG), diglyceride (DG) and TG, diacetinmonoglyceride (DACMG), monoacetindiglyceride (MAcDG), monoacetinmonoglyceride (MAcMG) were analysed using DB5-HT column (15 m, 0.32 mm, 0.10 μ m) under conditions prescribed in standard EN 14105 and quantified by the same linear regression coefficients as monoolein (for DACMG and MAcMG) and diolein (for MAcDG), similar Casas et al. [11]. Also MAc, DAC and TAc were analyzed using the same

column and quantified as in our previous work [18]. The mass of sample were approximate 20 mg. The oven temperature was set to 50 °C for 5 min and then temperature was first increased to 180 °C at a rate of 15 °C/min, then to 230 °C at 7 °C/min rate and finally to 370 °C at 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 standard deviations for determination of all compounds did not exceed $\pm 1.6\%$.

III. RESULTS AND DISCUSSION

Influence of the amount of catalyst

In order to determine the effect of the amount of catalyst on the reaction rate, set of experiments were carried out with molar ratio of methyl acetate to rapeseed oil equal to 18, temperature 55 °C and reaction time 1 hour. Reaction time for all experiments were set at 1 hour, because at least 30 minutes were required to reach the equilibrium of the reaction [11]. The influence of the MeONa amount on the investigated interesterification reaction (used range of catalyst to oil molar ratio was 0.05 - 0.41) is depicted in Fig.1.

The lower effective concentration of the catalyst depends on the acidity of reaction mixture. Since the acid value of methyl acetate is insignificant (<0.1 mg KOH/g), amount of 0.08 equivalents of MeONa catalyst was enough to carry out the interesterification process with the methyl acetate to oil molar ratio equal 18. As it can be seen in Figure 1.a, neutralization of acids requires approximately 0.04 equivalents of MeONa catalyst. The influence of the *tert*-BuOK amount on the investigated interesterification reaction (used range of catalyst to oil molar ratio was 0.05 - 0.31)

is shown in Figure 1.b. In *tert*-BuOK-catalyzed reactions the amount of catalyst required for neutralization also is close to 0.05. Increase of the amount of both catalysts caused rapid decrease of TG content in product. Amount of catalyst necessary for full conversion of TG is 0.12 equivalents for both catalysts (see Fig. 1). With catalyst to oil molar ratio equal to 0.10 the content of FAME reached the value of 67.7%, thus providing approximately the same result that in the synthesis with MeONa. The obtained curves (Fig. 1) show that the activity of catalysts is practically identical and the slopes of linear parts of curves are practically identical - for MeONa it is equal to 1950 and for *tert*-BuOK it is 2000.

To eliminate the possibility of fatty acid *tert*-butyl esters (FABE) formation during the interesterification in presence of *tert*-BuOK catalyst (TG transesterification with *tert*-butanol, side reactions 4–6 in Scheme 1) IR spectra for the reaction mixtures were registered. Absorption near 3000 cm^{-1} , representing fundamental vibrations of C-H bonds, were almost identical for all reaction mixtures, indicating that TG transesterification with *tert*-butanol in sufficient amount for registration did not occur. Additional experiment of TG transesterification reaction with *tert*-butanol in presence of *tert*-BuOK and MeONa also shows, that TG reaction with *tert*-butanol practically does not occur. Running the experiment with molar ratio of *tert*-butanol to oil of 18 and the catalyst to oil molar ratio of 0.15 over the period of one hour at 55 °C the TG conversion was lower than 1%.

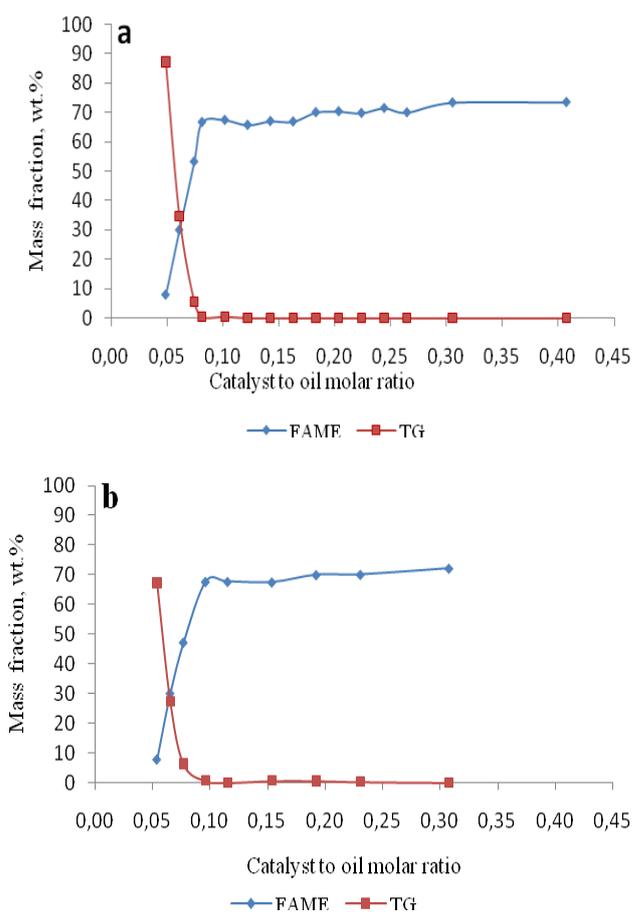


Figure 1. The effect of the amount of catalyst on the interesterification. (a) FAME and TG (wt.%) content in product using MeONa. (b) FAME and TG (wt.%) content in product using *tert*-BuO

Presuming that the optimal amount of catalyst using MA to oil molar ratio 18:1 is the amount producing the maximum total content of FAME and TA, it was determined that for MeONa catalyst the optimal amount was 0.08 and for *tert*-BuOK it was 0.10. Under these conditions in MeONa-catalyzed reaction the content of FAME and TA was 66.7% and 8.1%, but in *tert*-BuOK-catalyzed reaction 67.7% and 14.0%, respectively (see, Fig. 1 and 2).

The yield of FAME for both reactions was identical, however the yield of TA in *tert*-BuOK-catalyzed reaction was almost two times higher. It can be explained by the more facile side reactions of triacetin with methanol than with *tert*-butanol. Results of investigation of TA reaction with methanol were reported earlier [19].

As displayed in Fig. 2, increase of the amount of catalyst over optimal value caused the decrease of content of TA. In MeONa-catalyzed reaction simultaneously the MAG and DAG content increased to 1.02% and 5.7%, respectively (side reactions 7– 9, Scheme 1). In the *tert*-BuOK catalyzed reaction the decrease of TA begins at higher catalyst concentration, but the final increase of MAG and DAG content was similar (0.7% and 5.4%, respectively) indicating that the TA react with *tert*-butanol (side reactions 7– 9, Scheme 1).

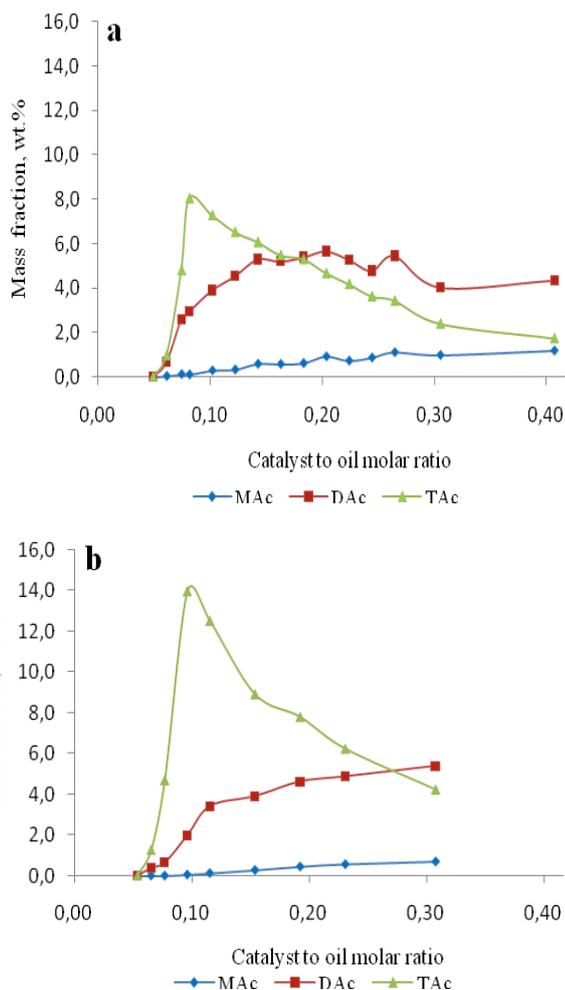


Figure 2. The effect of the amount of catalyst on the interesterification. (a) MAc, DAc and TAc (wt.%) content in product using MeONa. (b) MAc, DAc and TAc (wt.%) content in product using *tert*-BuOK.

To corroborate the possibility of such reaction, comparative investigation of transesterification reaction of TA with *tert*-butanol in presence of both catalysts were performed.

Table IV. Influence of the molar ratio of methyl acetate to oil on the composition of the reaction mixture by MeONa catalysis.

Catalyst to oil molar ratio	Methyl acetate to oil molar ratio	wt.%							
		DAcMG	MAcDG	TG	MAc	DAc	TAc	FAME	
0.08	3	5.8	16.0	11.8	0.0	2.1	0.9	43.6	
0.08	9	8.0	6.8	1.6	0.1	2.4	5.2	61.8	
0.08	18	6.4	2.2	0.4	0.1	3.0	8.1	66.7	
0.08	27	7.7	6.5	2.6	0.1	2.3	5.5	60.6	
0.08	36	1.5	6.6	63.8	0	0	0	17.4	

Table IV shows that the molar ratio above 18 in MeONa-catalyzed reactions decreased the content of FAME.

The reaction conditions were as follows: a molar ratio of *tert*-butanol to TA of 10, catalyst to TA molar ratio of 0.1, temperature 55 °C and duration 1 hour. The reaction mixtures were analyzed using GC in the same way as the TG interesterification products. Results are showed in Table III.

Table III. Composition of samples obtained by TA reaction with *tert*-butanol using MeONa and *tert*-BuOK catalysts.

catalyst	wt.%			
	G	MAc	DAc	TAc
MeONa	2.4	64.3	24.4	8.9
<i>tert</i> -BuOK	0.8	58.4	10.5	30.4

The TA reaction with *tert*-butanol were investigated using both catalysts. After 1 hour in reaction mixture obtained using *tert*-BuOK 30.4% of TAc remained unconverted, but in reaction mixture using MeONa only 8.9%. This indicated that MeONa is more active catalyst than *tert*-BuOK.

To summarize the obtained results we can conclude that the theoretically predicted content of FAME and TA by full TG conversion into these two products was 81.1 wt.% and 18.9 wt.%, respectively, were not reached neither by use the MeONa, nor the *tert*-BuOK catalyst. In both sets of reactions the interesterification is the dominant process, however the content of intermediates is quite high, therefore in order to increase the yield of desired products the excess of methyl acetate have to be increased.

The influence of excess of methyl acetate

The influence of excess of methyl acetate on the interesterification process was analyzed by determination of content of all products and intermediates in mixtures; obtained using optimal amount of catalysts (MeONa - 0.08, *tert*-BuOK - 0.10). The excess of methyl acetate was increased to 36 (molar ratio of methyl acetate to oil).

The decrease of the FAME content was caused by the increase of the reactant by lowering the catalyst concentration through neutralization reaction. It is known that the amount

0.04 equivalents of MeONa (of optimal 0.08) is required for neutralization using molar ratio 18, hence residual 0.04 were necessary for catalysis. Then optimal amount of catalyst (OC) can be calculated using following equation (eq. 1):

$$OC = 0.04 * p / 18 + 0.04 \quad (1)$$

where p is methyl acetate to oil molar ratio
The optimal amounts of catalysts were calculated using equation 1 and results obtained by using these amounts were summarized in Table V.

Table V. Content of reaction mixtures obtained by the increase of molar ratio of methyl acetate to oil.

Catalyst to oil molar ratio	Methyl acetate to oil molar ratio	wt. %						
		DACMG	MAcDG	TG	MAc	DAC	TAc	FAME
MeONa								
0.05	3	4.6	17.5	19.9	0.1	0.8	0.6	35.7
0.06	9	6.2	16.2	17.3	0.1	1.4	1.8	39.6
0.08	18	6.4	2.2	0.4	0.1	3.0	8.1	66.7
0.10	27	5.5	1.7	0.6	0.2	4.7	9.9	71.4
0.12	36	3.7	0.5	0.0	0.4	6.5	11.8	75.1
<i>t</i>-BuOK								
0.06	3	8.1	19.9	13.5	0.1	0.7	1.9	38.4
0.08	9	11.5	14.0	4.9	0.0	0.9	5.8	54.0
0.10	18	7.7	2.5	0.6	0.1	2.0	14.0	67.7
0.13	27	5.9	1.1	0.0	0.1	3.3	15.4	73.0
0.15	36	4.7	0.5	0.0	0.1	2.8	16.6	73.2

As it is shown in Table V in MeONa-catalyzed reactions, the increase of methyl acetate caused the increase of the content of FAME and TAc, up to 75.1% and 11.8%, respectively. While intermediates of interesterification decrease, however there are still 3.7% of DACMG and 0.5% of MAcDG remained in reaction mixture with molar ratio being equal to 36. Using molar ratio of 48, similar data were obtained by Casas et al. [16] - DACMG content decreased to 4%. As the result of the TAc reaction with methanol (reactions 7-9, Scheme 1) the content of DAC increase suddenly and reached 6.5% at molar ratio of 36.

Using molar ratio of 36 in *tert*-BuOK catalyzed reactions the content of FAME and TAc in reaction mixture reached - 73.2 and 16.6%, respectively, the content of DAC did not exceed 2.8%, some MG remained (0.8%) and DG was not observed in reaction mixture. The content of DACMG and MAcDG were similar to those in MeONa-catalyzed reactions - 4.7% and 0.5%, respectively.

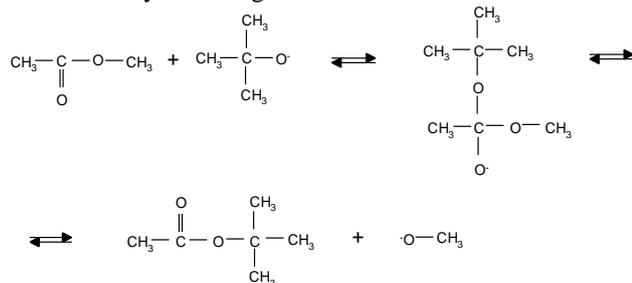
These results allow to conclude, that large excess of reactants provided fewest side products in reaction mixture, besides employment of *tert*-BuOK catalyst practically lets to avoid the TG transesterification (reaction 4-6, Scheme 1). The highest values of FAME and TAc - 73.2 and 16.6%, respectively, were obtained using *tert*-BuOK catalyst (0.15 molar ratio to oil) and methyl acetate to oil molar ratio of 36 (or the yields of FAME and triacetin were 90.3% and 87.8%, respectively). The content of TAc obtained in

tert-BuOK-catalyzed reactions was remarkably higher than in the reactions with MeONa catalyst.

The mechanism of transesterification reaction

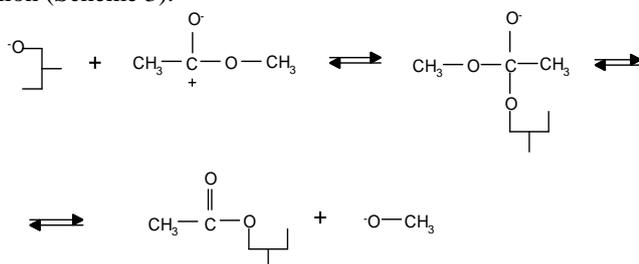
Obtained results show that both catalysts accelerate the interesterification reaction at the some extent in spite of its different chemical structure. It is known that two different mechanisms are proposed for the reactions of carboxylic acid esters in the presence of alkoxide ions. Reactions can begin by the formation of enolate [20] and/or by a nucleophile attack [21]. The rate of formation of the enolate should be not susceptibly affected by the chemical structure of alkoxide anion and obtained results formally support the importance of enolate mechanism. If the interesterification begins with the alkoxide nucleophile attack a carbonyl carbon, the rate of the formation of tetrahedral intermediate shall depend on steric hindrance caused by the structure of alkoxide. One can anticipate that the formation of tetrahedral intermediate in case of *tert*-butoxide should be slower than in the case of methoxide. Since the interesterification consists of complicated interconnected reversible reactions it isn't clear whether the slower stage of tetrahedral intermediate formation in the case of *tert*-butoxide can influence the equilibrium of the overall process or not. The nucleophile can attack either the triglyceride or the methyl acetate carbonyl carbon. Considering the excess of the methyl acetate in the reaction mixture the attack at carbonyl carbon of methyl acetate should be critical. According to the reaction in

Scheme 2 the attack of *tert*-butoxide anion on carbonyl carbon of methyl acetate generates the methoxide anion.



Scheme 2. Reaction scheme of methyl acetate and *tert*-butoxide anion.

After the generation of the essential transesterification reaction intermediate – the glycerolate anion, the following reactions also proceed with the regeneration of methoxide anion (Scheme 3).



Scheme 3. Reaction scheme of methyl acetate and the glycerolate anion.

The equations demonstrated in Scheme 2 and Scheme 3 show that the transesterification reaction in presence of *tert*-butoxide anion proceeds with its consumption and generation of methoxide anion what can lead to the same overall process characteristics than in the case of methoxide anion catalyst. If this assumption is right the characteristics of processes, where the generation of methoxide is excluded, will be different. In order to corroborate this idea we investigated the transesterification reaction of oil with isopropanol in presence of methoxide and *tert*-butoxide and established that methoxide is more active than *tert*-butoxide. Conversion of TA during the transesterification reaction with *tert*-butanol in presence of methoxide was 91% and in presence of *tert*-butoxide was 69 % confirming the higher activity of the former catalyst.

IV. CONCLUSIONS

The activity of the two investigated alkoxide catalysts and its optimal amount for the obtaining the highest content of FAME and triacetin in the reaction mixture were almost equal, but the composition of products obtained were different. The use of potassium *tert*-butoxide in *tert*-butanol gave the reaction product with much higher triacetin content. The increase of catalyst to oil molar ratio over optimal value caused the drop of triacetin formation, due to the fact that triacetin reacted with the both alcohols used as solvents for catalysts, also regardless of oil practically did not react with *tert*-butanol. Large molar ratio of methyl acetate to oil was necessary for the suppression of side reactions. Varying the

molar ratio of reactant to oil the optimal amount of catalyst was not constant, however it mostly depends on the amount of methyl acetate used. The best conditions for the synthesis of biodiesel and triacetin were employing *tert*-butoxide catalyst to oil molar ratio of 0.15 and methyl acetate to oil molar ratio of 36 (73.2 wt.% of fatty acid methyl esters and 16.6 wt.% of triacetin content were obtained).

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