Research Article

The Unanticipated Catalytic Activity of Lithium tert-Butoxide/THF in the Interesterification of Rapeseed Oil with Methyl Acetate

Valdis Kampars, Zane Abelniece, and Sabine Blaua

Institute of Applied Chemistry, Riga Technical University, P. Valdena Str. 3/7, Riga LV-1048, Latvia

Correspondence should be addressed to Valdis Kampars; valdis.kampars@rtu.lv

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Conventionally, the biodiesel (mixture of fatty acid methyl esters, FAME) production proceeds by transesterification of triglycerides with methanol accordingly by the formation of glycerol as a by-product, which cannot be included in biofuel composition. Biodiesel could also be produced via interesterification ensuring full conversion of oil to biofuel, consisting of FAME and triacetin. The most effective catalysts for interesterification reactions are alkali metal alkoxides. The effectivity of alkoxide catalyst depends on its solubility determined by the structure of the alkyl chain. In our previous studies, we have shown that the branched chain catalyst tert-BuOK/THF is highly suitable for the realisation of interesterification reactions. Till now, in the scientific literature, very little is known about the influence of metal ions. In order to investigate the influence of counterion on the activity of alkoxide catalysts, in this work, we have investigated the proceeding of interesterification reactions of rapeseed oil with methyl acetate in the presence of lithium, sodium, and potassium tert-butoxides in THF. Experimentally obtained relationships for catalyst-to-oil molar ratio (COMR) influence rapeseed oil interesterifications with methyl acetate at 55°C for 1 h, with methyl acetate-to-oil molar ratio (MAOMR) 18 showing that the tert-BuONa/THF and tert-BuOK/THF have high and similar activity, but the tert-BuOLi/THF is fundamentally different. The low and diverse activity of lithium tert-butoxide can be explained by the association of ions and very low catalytic activity of ion pairs. Simulation of the influence of association on the FAME formation shows that at COMR 0.1 (sufficient for fast reaction proceeding in the presence of tert-BuONa/THF and tert-BuOK/THF, the concentration of tert-butoxide ions in the presence of tert-BuOLi/THF because of associations lowers from 28 mmol/L to 13 mmol/L, which is not sufficient for effective proceeding of reaction. Activity of alkoxides in this reaction is solely determined by the counterion.

1. 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% of the energy demand being covered by fossil fuels increases the emission and facilitates global warming. The main alternatives to fossil fuel-based liquid transport fuels are biofuels, with biodiesel being the most widely produced and used biofuel in Europe. Biodiesel is well known as a renewable, nontoxic, aromatic, sulphur-free, biodegradable, and environment-friendly fuel that can perfectly substitute petrodiesel. Biodiesel consists of fatty acid methyl esters (FAME) and can be produced from different sources of lipids: edible and nonedible vegetable oils, animal fats, algae, and waste oils [1], although in Europe, biodiesel is currently produced mainly from rape-seed oil. Biodiesel from edible vegetable oils belongs to the first-generation biofuels, and its production is restricted by food versus fuel pressures [2]. The EU still remains the world’s largest biodiesel producer, but, as a result of restricted raw materials, nearly two-thirds of the region’s installed production capacity is currently idle [3]. Conventionally, the biodiesel production proceeds by transesterification of triglycerides with methanol as shown in equation (1) in the presence of a basic catalyst by the formation of glycerol as a by-product that cannot be used in fuel formulations [4].
where MeOH is methanol and G is glycerol.

Highly active and most often used catalysts in the transesterification process are the homogeneous alkaline catalysts such as NaOH, KOH, CH3ONa, and CH3OK; however, the development of various heterogeneous catalysts is now on the increase [5, 6]. Biodiesel could also be produced via interesterification. In interesterification reaction with methyl acetate according to equation (2), the same composition of FAME as in transesterification with methanol (1) has to be synthesised, but another by-product is formed:

\[
\text{TG} + 3\text{MeOH} \rightleftharpoons 3\text{FAME} + \text{G}
\]

where MeOH is methanol and G is glycerol.

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\[
\text{TG} + 3\text{MeAc} \rightleftharpoons 3\text{FAME} + \text{TA}
\]

where TG is triglycerides, MeAc is methyl acetate, FAME is a mixture of fatty acid methyl esters, and TA is triacetin. TA is compatible with FAME and can be included into biofuel composition, thus ensuring full conversion of oil to biofuel with the biofuel yield higher than 115% [7, 8]. In interesterification reactions, alkali metal hydroxides were inactive, whereas alkoxide, for example, potassium methoxide, shows a very high activity [9]. Nevertheless, the homogeneous alkali metal alkoxide catalyst in the form of a solution in the corresponding alcohol cannot be used for the realisation of pure interesterification reaction because the solvent has initiated a parallel transesterification reaction [10]. Despite the data published about the fast kinetics of the interesterification reaction in the presence of potassium methoxide in methanol [11], through the investigation and comparison of different interesterification reactions, a fixed reaction time usually 1 h is selected as a characteristic time for the industrial biodiesel synthesis stage [12–14]. Interestesterification reactions, as well as transesterification one, also proceed under supercritical conditions or in the presence of enzymatic catalysts. The supercritical and enzymatic methods of interesterification reactions have their advantages and disadvantages, but they are not as productive as the chemical ones in the presence of appropriate alkoxide catalyst. The effectivity of alkoxide catalyst depends on its solubility into the reaction mixture. The interesterification reaction mixture is less polar than that of transesterification, and poor solubility of a highly polar catalytic system can cause the lowering of reaction rate by including the mass transfer stage. The solubility of alkoxides and their reactivity depends on the alkali metal cation and the structure of the alkyl chain. It has been noted that alkali metal alkoxides in solutions often exist as ion pairs and oligomeric or polymeric compounds, especially when the R group is small (Me, Et) [15]. The solubility of tertiary alkoxides is higher, and its solutions have caused a great interest as catalysts and condensation agents because tertiary alkoxides, due to higher steric hindrance, are less prone to different side reactions than primary or secondary alkoxides [16]. In our previous research, we have shown that tert-BuOK/tert-BuOH and tert-BuOK/THF catalysts [10, 12, 14, 17] have high levels of activity and are very suitable for realisation of interesterification reactions, thanks to the influence of the tert-butyl moiety on the solubility. Till now, very little is known about the influence of metal cation in the scientific literature. According to [18], except for certain compounds of lithium, alkali metals are assumed to form predominantly electrovalent compounds; however, a study of the crystal structure of lithium methoxide has provided evidence that lithium-oxygen bond in this compound is approaching covalency. In solutions, interaction with counterion often occurs, and the nature of the solution must be considered in any description of ion-pairing behaviour [16]. It is known that lithium alkoxide usually differs from other alkali metal alkoxides. For example, the ion-pairing constant [19] for the solution of lithium tert-butoxide in dimethylsulfoxide is much higher than ion-pairing constants for sodium, potassium, and caesium tert-butoxides (for tert-BuO Li 10³; Na 10⁶; K 270, Cs 200 M⁻¹). The reactivity levels of "free" alkoxide ions usually are higher than that of ion pairs [19], and the ion pair formation can initiate a remarkable lowering of the reaction rate in case of lithium alkoxides. Since reactions with a different catalytic activity of t-BuOK and t-BuONa also are known [20], the effect of the counterion could be very complex and depends not only on the solubility and association but also on the interaction of metal cation with reaction centre. In order to examine the influence of counterion on the activity of alkoxide catalysts, in this work, we have investigated the proceeding of interesterification reactions of rapeseed oil with methyl acetate in the presence of lithium, sodium, and potassium tert-butoxides. The proceedings of the interesterification reactions as well as transesterification reactions depends not only on the structure and properties of the catalyst, but also on the catalyst-to-oil molar ratio (COMR), methyl acetate-to-oil molar ratio (MAOMR), reaction temperature, and reaction time, whereas stirrer speed is the least significant factor [21]. This investigation aims to determine how the changing of counterion in the line lithium, sodium, and potassium changed the proceeding of interesterification reactions.

2. Materials and Methods

2.1. Materials. The refined rapeseed oil was purchased from a local producer Iecavnieks. The average molecular weight of the oil was 896 Da, density 25°C 0.91 g/ml, viscosity 40°C 34.1 mm²/s, HHV 39.86 MJ/kg, element composition C 77.736% and H 11.551%, saponification value 186.7, and acid value 0.32 mg-KOH/g. The percentage of fatty acids of the oil: palmitic 4; stearic 2; oleic 64; linoleic 22; and linolenic 8. The methyl acetate (99%); phosphoric acid (85%); and 1 M lithium, sodium, and potassium tert-butoxide solutions in THF were obtained 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%) were obtained from Alfa Aesar:tricaprin (>98%) was obtained from TCI Europe; heptane (>95%) and dichloromethane (pure) were supplied by ROTH.
2.2. 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, the 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 reagent was removed by rotary evaporation, and the sample was filtered and stored in a refrigerator. The concentration of catalyst is measured as a molar ratio to oil (COMR) and amount of reactant as the molar ratio of methyl acetate to oil (MAOMR).

2.3. Analytical Methods. The average molecular weight was calculated from saponification value according to the following relation: average molecular mass = mass of oil/number of moles of base. The 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. 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, equipped with two columns. The ester content was determined according to the modified standard method EN 14103, using a methyl heptadecanoate as an internal standard. The capillary column employed was an HP Innowax with a length of 30m, an internal diameter of 0.25 mm, and a film thickness of 0.25 μm. The oven temperature was set at 200°C.

Glycerol (G), monoglycerides (MG), diglycerides (DG), triglycerides (TG), diacetinmonoglyceride (DAMG), monoacetindiglyceride (MADG), monoacetinmonoglyceride (MAMG), monoacetinmonoglyceride (MAG), diacetin (DA) and triacetin (TA) were analysed using DB5-HT column (15m, 0.32mm, and 0.10 μm) under conditions prescribed in standard EN 14105, and the mass percentage of reaction mixture was performed as in our previous work [5]. The oven temperature was set to 50°C for 5 min and then was 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 at 390°C in both methods. Each measurement was made twice, and the average value was calculated.

3. Results and Discussion

3.1. Catalyst-to-Oil Molar Ratio. From the extensive empirical material of the investigation of transesterification and interesterification reactions in the presence of a different catalyst, it is clear that for the realisation of the reaction under defined circumstances, some critical concentration of the catalyst in the reaction mixture is necessary. Below this critical concentration of catalyst, usually expressed in COMR units, the reaction does not proceed or does not proceed with the necessary rate for achieving equilibrium in an acceptable time frame. Usually, the influence of COMR is represented as a plot of experimentally determined percentage of the mass of the target product FAME versus COMR, obtained at other fixed variables. Experimentally obtained relationships for the COMR influence on inter-esterification of rapeseed oil with methyl acetate at 55°C during 1 h with MAOMR 18 for investigated catalytic systems are shown in Figure 1. All FAME curves are “C” type curves. The curves for tert-BuONa/THF and tert-BuOK/THF are steep and agree to one another within experimental error. The shape of the curve for tert-BuOLi/THF is fundamentally different. It is shallow, approaching 70% level after COMR 0.2. The TG curves are as different as the FAME curves and doubtless. Figure 1 represents two different catalytic systems in which the tert-BuONa/THF and tert-BuOK/THF are the one and the tert-BuOLi/THF is the other.

As it is seen in Table 1, the compositions of the reaction mixtures obtained in the presence of tert-BuONa/THF and tert-BuOK/THF agree to one another within the experimental error, while the composition of the reaction mixture obtained in the presence of tert-BuOLi/THF is remarkably different.

The polarising power of lithium-ion is higher than those of sodium and potassium, and specific activity of lithium tert-butoxide could be caused by the association of ions [16] in the reaction mixture which can be represented by the simplified equation and characterised by the corresponding equilibrium constant:

$$K_{a} = [(RO^-)s + (M^+)s] \leftrightarrow (RO^-M^+)$$  \hspace{1cm} (3)

$$K_{a} = [((RO^-M^+)s) + [(RO^-)s]] [(M^+)s],$$

where (X)s is the solvated ion or ion pair, respectively.

There can be three types of ion pairs: familiar solvent-separated, solvent-shared, and contact ion-pairs, but for the interpretation, the majority of experimental results use equations more complex than (3), which are not necessary [16]. It is known that the association constants $K_{a}$ for common alkyl chain lithium alkoxides are higher than those for sodium and potassium ones. It is also known that in medium polar solvents such as propanols, the association constants are so large that 0.1 M alkoxide solutions of more than 90% can be in the form of ion pairs [16], and formation of more complex aggregates (RO·M+)n with lower activity is not excluded.

If a simple association according to equation (3) takes place, reaction mixture must contain two forms of the catalyst with different activity levels, and the experimentally determined activity depends on the concentration of the solvated alkoxide ions and solvated ion pairs. The concentration of alkoxide ions depends on the degree of dissociation of ion pairs. The degree of dissociation in its turn relates to constant $K_{a}$ and for weak electrolytes can remarkably decrease with the increase of concentration. If solvated ions are the most active form of catalyst, the concentration of the active form always will be lower than COMR and not proportional to COMR.

3.2. Simulation of the Reaction Proceeding in the Presence of tert-BuOLi/THF. Similarly, the FAME content dependence on the COMR in the presence of the catalytic systems
BuONa/THF and BuOK/TH can be explained with the same active substance that can be the solvated tert-butoxide anions \( \text{RO}^- \). We can assume that the solvated anion is much more active than the ion pair and that the catalytic activity in all cases is determined by the concentration of anion in the reaction mixtures. For sodium and potassium salts, full dissociation of ion pairs proceed, and the ion concentrations are always equal to the COMR, while for the lithium tert-butoxide, the dissociation is partial and the concentration of tert-butoxide anion is lower than COMR and depends on the constant \( 1/K_{\text{as}} \). If the concentration of tert-butoxide anion in the reaction mixture is known, we can determine the FAME value from the idealised FAME-COMR curve.

If anion is the only active substance, we can calculate its concentration on the basis of equation (3):

\[
K_{\text{dis}} = \frac{1}{K_{\text{as}}} = \frac{[\text{BuO}^-]^2}{[\text{BuOLi}]} \tag{4}
\]

where \([\text{BuO}^-]\) and \([\text{BuOLi}]\) are the equilibrium concentrations of anion and ion pair.

If the magnitude of the equilibrium constant \(K\) is known, the actual concentration of the active catalyst \([\text{BuO}^-]\) can be calculated by solving the following quadratic equation:

\[
[\text{BuO}^-]^2 + K \times [\text{BuO}^-] - K \times \text{COMR} = 0 \tag{5}
\]

where COMR is the total concentration of catalyst in COMR units.

For example, we can select a set of constant \(K_{\text{dis}}\) calculate the actual concentration of anion for every \(K_{\text{dis}}\) and used COMR, and find the FAME value from the idealised FAME-COMR curve.

To get the specified region of \(K\) values, we assumed three different degrees of dissociation for BuOLi at the lowest value of nominal COMR (0.03): 50, 70, and 90%, and calculated three adequate values of equilibrium constant (Table 2). Using these constants, we calculated the possible concentration of the tert-butoxide anion. In all of the cases, the concentration of the active part of the catalyst decreased quickly with the increase of COMR (Table 2) that changed the shape of the COMR-FAME curve.

As seen in Figure 3, the decrease of the degree of dissociation in the line 90%, 70%, and 50% considerably lowered the slope of the linear part of the curve and shifted the curve to a higher COMR region. The effect of ion pair building on the shape of COMR-FAME curve is significant and much larger than the possible effect of catalyst concentration variation caused by experimental error, but does

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**Table 1:** The main components of reaction mixtures by using different COMR values of catalysts.

| COMR  | MADG | DAMG | TA  |
|-------|------|------|-----|
| Li    | Na   | K    | Li  | Na | K | Li | Na | K |
| 0.03  | 0.7  | 2    | 0.3 | 0.7 | 1.2 | 0.0 | 1.0 | 1 |
| 0.04  | 0.5  | 15.5 | 19.4 | 9.7 | 11.8 | 10.5 | 3.0 | 6.0 | 2.5 |
| 0.06  | 15.7 | 1.0 | 3.2 | 11.6 | 8.3 | 8.9 | 5.1 | 12.6 | 11.7 |
| 0.08  | 13.9 | 0.8 | 3.6 | 12.11 | 8.2 | 9.1 | 6.3 | 11.9 | 10.5 |
| 0.1   | 13.0 | 0.8 | 3.2 | 11.4 | 8.1 | 8.7 | 7.2 | 12.0 | 11.5 |
| 0.12  | 11.6 | 0.7 | 3.4 | 11.5 | 7.8 | 9.0 | 6.9 | 11.7 | 6.9 |
| 0.14  | 10.4 | 0.8 | 2.3 | 11.1 | 7.5 | 8.9 | 7.3 | 10.6 | 7.7 |
| 0.16  | 9.4  | 0.7 | 1.9 | 10.7 | 7.2 | 7.5 | 7.5 | 10.3 | 7.5 |
Table 2: The dependence of the degree of ion pair dissociation on the COMR.

| COMR (mol/mol) | Equilibrium constants and degree of ion pair dissociation | $K = 0.015$ | $K = 0.049$ | $K = 0.243$ |
|----------------|----------------------------------------------------------|-------------|-------------|-------------|
| 0.03           | 50.0                                                     | 70.0        | 90.0        |
| 0.04           | 45.3                                                     | 65.3        | 87.4        |
| 0.05           | 41.8                                                     | 61.5        | 85.1        |
| 0.06           | 39.0                                                     | 58.3        | 83.0        |
| 0.07           | 36.8                                                     | 55.7        | 81.1        |
| 0.08           | 34.9                                                     | 53.4        | 79.3        |
| 0.10           | 32.0                                                     | 49.7        | 76.1        |
| 0.12           | 29.7                                                     | 46.7        | 73.4        |
| 0.15           | 27.0                                                     | 43.1        | 69.9        |

![Figure 3](image-url)  
**Figure 3:** Plots of FAME percentage by mass, obtained by the simulation of the tert-butoxide ion pair formation versus COMR.

Table 3: The dependence of the degree of ion pair dissociation on the COMRR.

| COMR (COMRR) | Equilibrium constants and degree of ion pair dissociation | $K = 0.002$ | $K = 0.0036$ | $K = 0.004829$ |
|--------------|----------------------------------------------------------|-------------|-------------|-------------|
| 0.03 (0.004) | 50.0                                                     | 60.0        | 65.0        |
| 0.04 (0.014) | 31.3                                                     | 39.5        | 44.0        |
| 0.05 (0.024) | 25.0                                                     | 32.0        | 35.9        |
| 0.06 (0.034) | 21.5                                                     | 27.7        | 31.3        |
| 0.07 (0.044) | 19.2                                                     | 24.8        | 28.1        |
| 0.08 (0.054) | 17.5                                                     | 22.7        | 25.8        |
| 0.10 (0.074) | 15.1                                                     | 19.8        | 22.5        |
| 0.12 (0.094) | 13.5                                                     | 17.8        | 20.2        |
| 0.15 (0.124) | 11.9                                                     | 15.7        | 17.9        |

\[
\text{RCOOCH}_3 + \text{BuO}^- \rightleftharpoons [\text{RCO(OCH}_3]_2 (\text{OBu})^- \tag{8}
\]

If the MAOMR is constant and the same oil and methyl acetate is used, the loss of the concentration of catalyst has to be independent from COMR. Considering that the real COMR of catalyst (COMRR) can be calculated as \( \text{COMRR} = \text{COMR} - 0.026 \), we have made the next step of the simulation. The finding of the $K_{\text{dis}}$ values has been made in the previous way by assuming 50, 60, and 65% dissociation degrees for the ion pairs in the case of the lowest COMRR. The results obtained are represented in Table 3.

As illustrated in Table 3, the variation of COMR in this variant of simulation caused reduction of the degree of ion pair dissociation that was approximately two times larger than that within the previous model. Such sharp reduction of the degree of dissociation created the sloped shape of the experimental curve and with $K_{\text{dis}} = 0.005608$, a good level of conformity of calculated data has been achieved (Figure 4).

The low concentration of the catalyst in the reaction mixture was pointed out by Casas et al. [9]. They calculated the possible lowering of the catalyst concentration in the real interesterification mixture due to irreversible reaction with water, present in reactants, and concluded that the catalyst concentration by MAOMR of 12 and COMR 0.05 is approximately 5 mmol/L. Our simulation shows that at COMR 0.1, the concentration of tert-butoxide anion in case of sodium and potassium butoxide in the presence of tert-BuONa/THF and tert-BuOK/THF catalytic systems under selected experimental variables is 28 mmol/L, which is sufficient for the active proceeding the interesterification, but in the presence of tert-BuONa/THF, the concentration of tert-butoxide is only 13 mmol/L, which is insufficient.

4. Conclusion

The interesterification reaction of rapeseed oil with methyl acetate at MAOMR 18 in the presence of catalytic system tert-BuOLi/THF proceeds radically different from that in the presence of tert-BuONa/THF and tert-BuOK/THF. This distinction has been caused by the association of ions and very low catalytic activity of ion pairs in case of tert-BuOLi/THF, while the lowering of tert-butoxide concentration in
case of tert-BuONa/THF and tert-BuOK/THF proceed only through reaction with water and acidic compounds, present in the reaction mixture. As a result, the concentration of tert-butoxide ions in the presence of tert-BuONa/THF and tert-BuOK/THF at COMR 0.1 is 28 mmol/L, which is sufficient for the fast proceeding of the reaction, but in the presence of tert-BuOLi/THF, the concentration of tert-butoxide ions is only 13 mmol/L, which is not sufficient.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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