Research article

# Butanolysis: Comparison of potassium hydroxide and potassium *tert*-butoxide as catalyst for biodiesel preparing from rapeseed oil

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ABSTRACT

Biodiesel is a mixture of esters of fatty acids (most often palmitic, stearic and oleic) and lower alcohols (in our work butanol) produced by transesterification. It is a renewable source of energy, prepared from triacylglycerides, which are contained in vegetable oils and animal fats. This work focuses on alkaline catalyzed transesterification of rapeseed oil with butanol and comparison of two catalysts (potassium hydroxide and potassium *tert*-butoxide). In industry is usually transesterification of rapeseed oil carried out like reaction catalyzed by potassium hydroxide. Potassium hydroxide have high content of $K_2CO_3$, $KHCO_3$ and water. Moreover water is formed by neutralization of potassium hydroxide with free fatty acids contained in oil. In cause of *tert*-butoxide catalyzed reaction, it is not possible because *tert*-butoxide have not a $OH^-$ aniont, which is needed for water forming. The influence of various conditions (addition of water, temperature of separation, intensity of stirring and type of catalyst) on butanolysis process was studied for both catalysts. For both catalysts dependence of conversions on time were plotted. When *tert*-butoxide was used, satisfactory phase separation was not achieved. The only way was separation of hot crude reaction mixture without adding water. Ester formed by this method had high content of free glycerol and soaps, but reached higher conversion. The best results were obtained with KOH and subsequent separation of cold crude reaction mixture with the addition of water and slow stirring. The difference between reactions catalyzed by potassium hydroxide and potassium *tert*-butoxide was described.

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## 1. Introduction

Biodiesel is generally esters of higher fatty acid and low-molecular alcohol, usually methanol. Diesel engines may operate satisfactorily with fuels derived from fresh and waste vegetable oils and animal fats given the appropriate operating conditions. In many aspects, biodiesels result in engine performance that is essentially identical to that with diesel fuel. The utilization of non-esterified fresh and waste vegetable oils and animal fats requires higher injection pressures for better engine performance compared to diesel fuel (Tashtoush et al., 2007). The use of common abbreviation FAME (fatty acid methyl ester) is usually accepted in the industry especially because of the use of various oils. These esters are clear, yellow liquid with a viscosity slightly higher compared to petroleum-derived diesel. The European Standard EN 14214 indicates flash point of 101 °C, which is almost double compared to

55 °C for diesel. Petranović et al. presented numerical model, covers all of the physics relevant to the pollutant emission. Spray, the effect of the flow field on it, as well as the disintegration of liquid fuel were modelled. Further, the process of fuel evaporation, ignition and combustion are included. Finally, the formation of emissions, both nitrogen-containing pollutants and the soot is covered by the model. The model was validated by simulating the NO emissions over the range of operating conditions and comparing the data with experimental results. Furthermore, when biodiesel blend was used as a fuel, an average reduction in NO emissions of approximately 8% was found. This shows that a potential for the NO pollutant reduction in real IC engines exists, even with using biodiesel as fuel (Petranović et al., 2017).

The structure and composition of FAME indicates that biodiesel does not contain aromatic hydrocarbons. However, it contains more than 10 wt% of oxygen, which reduces fuel efficiency. This disadvantage can lead to a certain extent to suppress the exchange from methanol to butanol. The resulting butyl ester of higher fatty acids (FABE) with its calorific value is closer to diesel. Biodiesel is

produced industrially by transesterification of vegetable oils. The production of biodiesel is a system of three successive equilibrium reactions, however, use a large excess of butanol is in equilibrium considerably shifted towards the products.

It is possible to use three types of catalysis (homogeneous, heterogeneous and enzymatic) or carry out under supercritical condition. In this study, the waste shells were utilized for the synthesis of highlyactive heterogeneous calcium oxide (CaO) nanocatalyst to transesterify dry biomass into methyl esters (biodiesel). The CaO nanocatalyst was synthesised by calcination-hydratione-dehydration technique and fully characterized by accessible methods. The effect of nano CaO catalyst was investigated by direct transesterification of dry biomass into biodiesel along with other reaction parameters such as catalyst ratio, reaction time and stirring rate. The impact of the transesterification reaction parameters and microalgal biodiesel yield were analyzed by response surface methodology based on a full factorial, central composite design. The significance of the predicted mode was verified and 86.41% microalgal biodiesel yield was reported at optimal parameter conditions 1.7% (w/w), catalyst ratio, 3.6 h reaction time (Pandit and Fulekar, 2017). Aracil et al. studied enzymatic catalyst Novozym for transesterification of coconut oil with butanol. The proposed approach uses an integrated process for the production of two fractions, the first one LMWBE (low molecular weight) caprylate, caprate, laurate and myristate butyl esters which can be used as high values chemicals, the second remaining fraction HMWBE (high molecular weight) palmitate, stearate and oleate butyl esters (FABE). The influence of variables such as temperature, catalyst concentration and alcohol/oil molar ratio on the production of both fractions has been studied and optimized by means of factorial design and response surface methodology. From a technical point of view, the highest possible yield for the more valuable LMWBE fraction should be targeted, consequently a catalyst concentration of 5.8% an alcohol/oil molar ratio of 6.2:1 and an operation temperature of 65 C should be chosen. According to these conditions, conversion rates of 74% and 24% for LMWBE and HMWBE, respectively, could be obtained. (Bouaid et al., 2017).

Homogeneous catalysis can be divided to acidic and alkalic. Acid catalysis is very slow and isn't used in industry. In the case of homogeneous alkaline catalysis, it occurs in each step of reaction as side reactions with the catalyst, so-called saponification. The resulting crude heterogeneous reaction mixture is composed of the ester and glycerol phase. Komers et al. was investigated mechanism and kinetics of the transesterification of rapeseed oil by methanolic KOH solution. At given time intervals, the samples, which were analyzed immediately, were taken from reaction mixture. From the obtained data, the dependence of concentration on time for each component was constructed. Furthermore, these depending interspersed with theoretical models and their parameters were optimized by program Gepasi. In given circumstances, the resulting models showed that the overall reaction is only controlled by kinetics independent from the mass transport. It is decided to express model by using seven transesterification reactions and equilibrium model for the hydrolysis with four irreversible reactions. For each reaction, rate constant was counted (Komers et al., 2002). This article is similar to study presented by Okullo and Temu, which also uses simplified kinetic model transesterification. The model was expressed by three equilibrium reactions; however, the saponification was not taken into account. Rate constants were calculated in Matlab (Temu and Apita, 2015). Saponification is studied by Dias et al., which carried out the transesterification of wasted cooking oil and virgin oil like cold-pressed oil. For virgin oil conversion, it was, on average, 5% higher than wasted cooking oil (Dias et al., 2008).

The actual transesterification with butanol is homogeneous. Unlike in heterogenous methanolysis, the miscibility of the oil and

methanol is considerably limited. In heterogeneous transesterification is remaining alkali catalyst dissolved only in the methanol phase. Thus, the reaction proceeds only in the oil dissolved in methanol and on the methanol-oil interface. The reaction is governed by second order kinetics, and hence a low concentration of oil results in the low reaction rate. Therefore, it increases mixing effect, or the effect of dispersion of oil in methanol (Černoch et al., 2010). In contrast to heterogenous, a homogeneous transesterification is both reactants in the same phase, therefore, begins to maximum concentration (i.e. the highest reaction rate). Homogenity of butanolysis is achieved by less polar character of butanol. To increase the miscibility of oil and methanol phase with dissolved catalyst, co-solvent such as tetrahydrofuran or methyl *tert*-butyl ether is used (Boocock et al., 1998).

Shahbazi et al. show that the reaction yield was higher in case of KOH than NaOH, which compensates higher price KOH. It can be considered as an advantage of it. Reactions were carried out at degummed oil that was a food grade. If the commonly used KOH was replaced by an alkali metal alkoxide, there would be no release of water from the neutralization of the catalyst with a free fatty acid. In practice, this idea was tested by Vincente et al. (Vicente et al., 2004) with the parameters 1.6 wt% potassium methoxide at 50 °C and the molar ratio of methanol to oil 4.5:1. This experiment achieved the yield of 95.8% containing 0.75% soap (Shahbazi et al., 2012).

Labor (Hájek et al., 2017) focused on butanolysis of vegetable oil in an alkaline environment. The influence of conditions such as the molar ratio, amount of catalyst, reaction temperature, duration of reaction, duration of debutanolisation, the temperature of separation process and duration of separation were observed. The molar ratio of butanol to oil 15:1, was achieved even separation of crude reaction mixture to ester phase and crude glycerol phase. Experiments with a molar ratio of 6:1 remained homogeneous and inseparable. It was also demonstrated that the higher temperature takes place to get increased saponification. Furthermore, the influences of the addition of demineralized water to separation rate and the potassium content in the ester phase were examined. When the addition of 0.35 ml of water to 20 g of crude reaction mixture was separated quickly, the resultant ester had a potassium content of 100 times lower than sample without addition of water.

Determination of optimal water amount added to crude reaction mixture was described by Machek et al. The transmittance was measured in dependence on time in a thermostatically controlled extension of spectrofotometer in 30 ml cell with 2 cm optical path. Water was dosed into the crude reaction mixture with microburet. The wavelength was set as 570 nm. Transmittance declined rapidly just after each addition of water to the crude reaction mixture, and then rised rapidly to a steady state. It increased with each addition until the point of the maximum transmittance reached, ie. the equivalence point. After this point, all subsequent additions have only decreased transmittance. The fastest separation was achieved by the addition of water corresponding to equivalence point (Machek et al., 2008). Similarly, Cernoch et al. studied the effect of adding water to the crude reaction mixture after ethanolysis. The monitored variables were dependent from potassium content and free glycerol in the ester phase and the yield of the ester phase. The addition of water significantly reduced the potassium content and free glycerol in the ester phase. The optimum addition of water ethanolysis was 0.054 ml/g of crude reaction mixture (Černoch et al., 2009).

Freedman et al., were performed experiments with 0.5% and 1% of a catalyst butoxide, at 20–60 °C and the ratio of butanol to soybean oil was 30:1. Due to large excess of BuOH reactions governed by kinetics and the pseudo-first order, the reaction rate was