



Ethanolysis of rapeseed oil by KOH as homogeneous and as heterogeneous catalyst supported on alumina and CaO

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ABSTRACT

The alkaline-catalyzed ethanolysis of rapeseed oil was studied. In the case of homogeneous catalysis (KOH), the effects of various reaction conditions on the quantity and quality of biodiesel (yield, purity, acid number, carbon residue, free glycerol, potassium content) and the glycerol phase (weight, soaps and ethyl esters content) were studied. The studied reaction conditions were: the reaction temperature and time, the catalyst concentration, the molar ratio of ethanol to oil, the revolutions of stirring, the temperature and time of deethanolisation and the initial temperature of the separation. Data was evaluated by linear regression on the statistical basis of multivariable systems. The final linear models were verified by independent experiments and they are able to predict the biodiesel quantity and quality in the range of the reaction conditions. Finally, the factor analysis of the ester phase variables was carried out. Moreover, ethanolysis was catalyzed by a heterogeneous catalytic system; attention was focused not only on catalyst activity but also on catalyst stability, which was determined by potassium leaching.

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1. Introduction

Biodiesel is the mixture of esters of higher fatty acids and a low molecular alcohol. It is produced by the transesterification of triglycerides included in vegetable oils and animal fats. Glycerol is formed as a by-product and it is present together with other materials in the glycerol phase. Homogeneous [1], heterogeneous and enzymatic [2] transesterification have been described. There is also developed a method without the use of the catalyst whereby alcohol reacts in a supercritical state [3].

Methanol is mostly used in transesterification; attention is also focused on ethanol utilization. The low toxicity and possibility of production from renewable resources are the advantages of ethanol in comparison with methanol. On the other hand, ethanol has a lower reactivity in comparison with methanol during transesterification [3], which is caused by a longer carbon chain [4].

Homogeneous transesterification: some authors tried to find out the kinetic model of transesterification [5,6] however statistical models are frequently used [7]. The kinetic models are based on the knowledge of natural patterns, which are in the case of transesterification very complicated and they are not completely known. Many chemical substances react and transesterification proceeds

on the interface between oil and alcohol (chemical and phase equilibrium). Since, the complete natural patterns describing transesterification are not known, the statistical models, which do not require knowledge of these laws, were used. The coefficients, in the statistical models, have no-physical significance. The factorial design matrix for linear models or central composite designs for non-linear models are frequent [8]. The effects of three independent variables – reaction conditions (the reaction temperature, the catalyst concentration and the molar ratio of ethanol to oil) on the yield or conversion of transesterification are the most intensely investigated [9,10].

This study is focused on the effect of a higher number of reaction conditions on the homogeneous ethanolysis process, i.e. the reaction temperature and time, the catalyst concentration, the molar ratio of ethanol to oil, the revolutions of stirring, the temperature and time of deethanolisation and the initial temperature of the separation. Reaction was carried out by KOH catalysis, stopped by CO₂ and the mixture was separated in the gravitational field after the evaporation of the ethanol excess. The ethanolysis process was monitored by various dependent variables describing the final ester and the glycerol phase (for the ester phase: yield, purity, concentration of free glycerol, concentration of potassium, Conradson carbon residue and acid number; for the glycerol phase: the weight of glycerol phase, the weight of soaps and the concentration of ethyl esters). Experiments were carried out on the basis of the Plackett-Burman statistic design and data were evaluated by linear

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Nomenclature

<i>AN</i>	acid number (mg g ⁻¹)
<i>CCR</i>	conradson carbon residue (wt.%)
<i>c</i>	catalyst concentration (rel. wt.%)
<i>m_{GP}</i>	weight of glycerol phase (g)
<i>m_S</i>	weight of soaps (g)
<i>MR</i>	molar ratio of ethanol to oil (-)
<i>rs</i>	revolutions of stirring (min ⁻¹)
<i>t</i>	reaction time (h)
<i>T</i>	reaction temperature (°C)
<i>T_{deet}</i>	temperature and time of deethanolisation (°C; min)
<i>T_{sep}</i>	initial temperature of the separation (°C)
<i>w_{fg}</i>	concentration of free glycerol (wt.%)
<i>w_e</i>	concentration of ethyl esters (wt.%)
<i>w_K</i>	concentration of potassium (wt.%)
<i>X</i>	conversion (wt.%)
<i>y_i</i>	dependent variables
<i>x_i</i>	independent variables
<i>Y_{fEP}</i>	the yield ester phase (wt.%)

regression. Heterogeneous transesterification: the main disadvantage of basic homogeneous catalyst is a side reaction (saponification), which consumes the catalyst and glycerides and formed soaps cause a problem during the separation of biodiesel. The other disadvantage is the impossibility to use the catalyst again. No heterogeneous catalysts have these disadvantages; therefore they are being researched nowadays. However, only a few papers are focused on heterogeneous catalytic systems dealing with ethanolysis [11–18]. For example, Liu et al. [19] described mixed oxides (reaction temperature 200 °C and 2.5 MPa pressures) with yield 97%. In this paper, the active species (potassium) was supported on two types of carriers (alumina and CaO) and their activity was tested in the ethanolysis. Moreover, this paper is also focused on catalyst stability during reaction, which was determined by potassium leaching.

2. Materials and methods

2.1. Chemicals

Cold-pressed, filtrated rapeseed oil, free of erucic acid (acid number 0.95 mg KOH g⁻¹, water content 600 ppm and density 0.920 g cm⁻³ (20 °C) produced by the company ABC Brancouze Trebíč, absolute ethanol (water content 0.12%), potassium hydroxide (purity 86%, Lachema Brno) and Carbon dioxide (Linde Gas) were used. The carries alumina (≥275 m²/g) and CaO (≥10 m²/g) were purchase from NanoScale.

2.2. Homogeneous catalysis

2.2.1. Variables, design of experiments and evaluation

The independent variables (*x_i*) substantially affecting biodiesel production were selected (on the basis of preliminary experiments): the reaction temperature (*T*), the reaction time (*t*), the catalyst concentration (*c*, relative weight percentage of catalyst to oil), the molar ratio of ethanol to oil (*MR*), the revolutions of stirring (*rs*), the temperature and time of deethanolisation (*T_{deet}*, logic variable, the combination of temperature and time of evaporation of the excess ethanol) and the initial temperature of the separation (*T_{sep}*, then cooling down spontaneously to laboratory temperature 25 °C) were selected as the independent variables (Table 1).

Table 1

Investigated intervals of independent variables.

<i>x_i</i>	Bottom limit (-1)	Top limit (+1)
<i>T</i> (°C)	25	45
<i>t</i> (h)	3	5
<i>c</i> (rel. wt.%)	0.89	1.33
<i>MR</i> (-)	6:1	7.5:1
<i>rs</i> (min ⁻¹)	700	1000
<i>T_{deet}</i> (°C; min)	25; 180	75; 45
<i>T_{sep}</i> (°C)	25	75

The following dependent variables (*y_i*) in the ester phase were selected: the yield of biodiesel – ester phase (*Y_{EP}*, calculated as a ratio of measured weight and theoretical weight of the ester phase – 1.052 g of ethyl esters may be theoretically formed from 1 g of rapeseed oil), the purity of the ester phase (*X*, calculated as the ratio of the sample peak area and ethyl esters standard peak area), the concentration of free glycerol (*w_{fg}*), the concentration of potassium (*w_K*), the Conradson carbon residue (*CCR*) and the acid number (*AN*). The dependent variables (*y_i*) in the glycerol phase were: the weight of the glycerol phase (*m_{GP}*), the weight of soaps (*m_S*) and the concentration of ethyl esters (*w_e*). The following linear model was presumed:

$$y_i = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_5x_5 + a_6x_6 + a_7x_7 \quad (1)$$

The Plackett–Burman design of experiments is suitable to be applied for linear models with many independent variables [20]. Eight experiments planned by the Plackett–Burman design and four other additional experiments (because of better statistical data evaluation) were carried out. The investigated intervals of the values of the independent variables (bottom and top limit) are depicted in Table 1. The values were standardized into the interval from -1 (bottom limit) to +1 (top limit), because the comparison among effects is simpler and more evident. The experimental conditions (standardized values of the independent variables) of all experiments are stated in Table 2.

The parameters *a_i* of the linear statistical model (1) were determined by multidimensional linear regression using PC software QC Expert 2.5 (method of the least squares, significance level 0.05). The statistical tests (heteroskedasticity, normality, influence points) were also calculated. Insignificant variables and outliers were removed on the basis of the statistical testing.

2.2.2. Transesterification

For the homogeneous catalyst, the reaction processed in a spherical flask (1000 ml volume) equipped with orifices for a paddle-shaped stirrer (2 paddles 3 × 1 cm), a pH-electrode, a cooling/heating attachment and a thermometer were used as the reactor. The

Table 2

Experimental conditions of all experiments (standardized values of independent variables).

Run	<i>T</i>	<i>t</i>	<i>c</i>	<i>MR</i>	<i>rs</i>	<i>T_{deet}</i>	<i>T_{sep}</i>
1	+1	+1	+1	-1	+1	-1	-1
2	+1	+1	-1	+1	-1	-1	+1
3	+1	-1	+1	-1	-1	+1	+1
4	-1	+1	-1	-1	+1	+1	+1
5	+1	-1	-1	+1	+1	+1	-1
6	-1	-1	+1	+1	+1	-1	+1
7	-1	+1	+1	+1	-1	+1	-1
8	-1	-1	-1	-1	-1	-1	-1
9	0	-1	-1	-0.11	+1	+1	-1
10	-1	-1	0	-0.11	+1	-1	+1
11	0	+1	-1	-0.11	0	-1	+1
12	0	0	0	-0.11	-1	+1	-1

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