

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
8 (2002)

**TWO STEP METHANOLYSIS OF RAPESEED OIL
IN THE FEEDBACK CONTROLLED
CHEMICAL REACTOR**

Radim DVOŘÁK, Karel KOMERS¹ and František SKOPAL
Department of Physical Chemistry, The University of Pardubice,
CZ-532 10 Pardubice

Received September 10, 2002

The two step methanolysis of the rapeseed oil catalyzed by KOH has been studied in a feedback controlled chemical reactor (FCCR). The composition of the final methylester phase of both steps was determined. Advantages of this type of transesterification are the use of the optimum amount of the solution of KOH in methanol, shorter reaction time and the possibility to affect the quality of the product by simple alteration of the reaction conditions.

Introduction

At present many references are interested in preparation or production of biodiesel fuels. These alternative fuels substitute fossil fuels for diesel engines. Our laboratory has been engaged in the transesterification of vegetable oils by low

¹ To whom correspondence should be addressed.

molecular alcohols for several years [1–9]. This paper describes the methanolysis of rapeseed oil (RO) catalyzed by potassium hydroxide (KOH) realized in the feedback controlled chemical reactor (FCCR) with spectrophotometric indication [1,2].

Theoretical

The methanolysis of RO catalyzed by KOH proceeds in a heterogeneous liquid – liquid system (emulsion). Besides RO and main products - methylesters of fatty acids of RO (ME) and glycerol (G) - the reaction mixture also contains a small amount of potassium soaps (KA) due to neutralisation of free fatty acids (HA, always present in the used RO) and hydrolysis of ME by the present free KOH. The two side reactions are described in detail in Fig. 1.

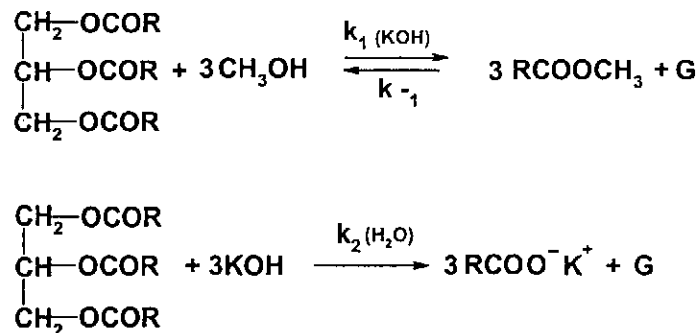


Fig. 1 Simplified reaction scheme: G – glycerol; R – rest of fatty acids; k_i – rate constant of the reaction i

The kinetics of these side reactions can be followed turbidimetrically in the visible region. Transmittance $I(\lambda)$ of the reaction mixture increases with increasing time. The change of $I(\lambda)$ is caused by the various mutual solubilities of the reaction components changing their concentrations during the reaction.

The main idea of FCCR is based on the feedback control of the injection of one or more reaction components into the reaction mixture. In our case the solution of KOH in methanol (M) is dosed into the reaction mixture under control of transmittance of this mixture. This transmittance is held at a constant selected value $I(\lambda)_0$ by means of the comparator and injector during the whole reaction time. The principle is shown in Fig. 2. The reaction is started by a fast dose of substoichiometric amount of KOH solution in M to the rapeseed oil in the glass cuvette by the injector A. After some reaction time the reaction mixture becomes

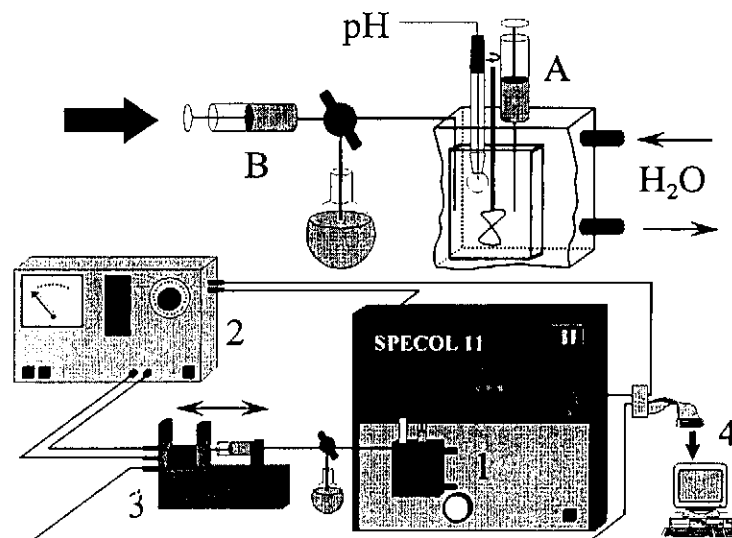


Fig. 2 Scheme of the used feedback apparatus with spectrophotometric indication: A – injector of chosen volume of KOH solution in M starting the reaction; B – feedback with injection of KOH solution in M (linear dosing machine); 1 – spectrometer with the thermostated glass cuvette; 2 – comparator comparing the actual density of transmitted light $I(\lambda)$ with the adjusted $I(\lambda)_0$ value; 3 – construction of the feedback dosage, syringe with the linear dosing machine; 4 – computer

less turbid and it is necessary to add more solution of KOH in M which is continuously dosed by means of the second injector B.

The requested parameters of the final reaction mixture can be reached by proper choice of the reaction conditions (e.g. ratio KOH : M, $I(\lambda)_0$, temperature) or by the use of FCCR in more steps. This paper describes the methanolysis in the FCCR in two steps. In the first step pure RO and low concentrated solution of KOH in M were used. From the resulting final reaction mixture the glycerol phase (GP) was separated. The remaining methylester phase (MP, with about 10 % unreacted RO) was again introduced into the reactor and the second step of methanolysis was carried out.

Experimental

Chemicals used

Rapeseed oil (RO), firm ELSA-EKO Ziebiker, Lužany by Jičín (acid value 1.3 mg KOH per gram of RO). Potassium hydroxide, solid (min 83 % w/w, the rest is water), phosphoric acid (85 % w/w), HCl (min 25 % w/w), hexane (p.a.), 2-

propanol (p.a.), potassium carbonate, waterless (p.a.), toluene (99 %), ethanol denatured (benzene or pyridine), methanol (p.a.), all Lachema, Brno, CZ.

Apparatus

Figure 2 shows the detailed scheme of the apparatus used.

Experimental Conditions

All measurements were realized at 20 °C, transmittance was measured at 570 nm (absorbance of RO and other products is nearly zero at this wavelength). In every experiment we used a glass cuvette (30 cm³, optical path 2 cm). The cuvette was charged with exactly about 18 cm³ (17.3 g) RO and brought to the desired temperature.

First Step

Into the cuvette with RO the defined substoichiometric initial amount m_{KOH}^s [g] of solution of KOH in M was added with the initial concentration c_{KOH}^s [g KOH 100 % / g M]. On the comparator the constant value of transmittance ($I(\lambda)_0 = 57.8$ %) was adjusted. Concentration of the KOH solution in M in the injector of the feedback 3 (see Fig. 2) had a constant value c_{KOH}^j . Further portions of the solution were added by means of the feedback up to the moment when any next portion was practically not required. For faster and more quantitative separation this reaction mixture was centrifuged 10 min at 5000 min⁻¹ and the alkaline MP-I (methyl ester phase of the first step) was isolated. This product (mixture of oil, methyl esters, methanol, KOH and soaps) was used as the feed for the second step of the methanolysis. To check the composition of MP-I, the whole phase was analyzed from time to time [2,3].

Second Step

The glass cuvette was charged with the MP-I from the first step, mixed and brought to the desired temperature. On the comparator the value of transmittance was adjusted. The further course of the reaction was similar to that of the first step. From the moment when any next portion of the solution of KOH in M was not required we proceeded as described above. The obtained methyl ester phase MP-II was separated and analyzed.

Analysis of MP

In MP-I and/or II the concentration of the unreacted RO, free fatty acids and potassium ions were determined. All the analytical methods used are described in detail in Refs [3,4]. Determination of RO by isocratic HPLC see [3], Chap. 2.3.1, of potassium ions see [3], Chap. 2.3.1, of acid value (concentration of free fatty acids of RO in MP) see Ref. [4].

Results and Discussion

The individual measurements were repeated three times and the obtained experimental data were statistically evaluated (Horn's technique [10]).

First Step

The measured variables were: mass of both phases (m_{MP}^I , m_{GP}^I), reaction time of the first step t_R^I , consumption of solution of KOH in M in the first step, concentrations of fatty acids and acylglycerols in MP-I.

Inputs of the First Step

$m_{ol} = 17.3$ g (mass of rapeseed oil); $m_{KOH}^S = 1.76 \pm 0.02$ (initial mass of starting solution); $c_{KOH}^S = 0.106 \pm 0.005$ [g KOH 100 % / g M] – concentration of starting solution; 20 °C; $I(\lambda)_0 = 57.8$ % (transmittance adjusted on comparator); $c_{KOH}^S = 0.102 \pm 0.005$ [g KOH 100 % / g M] – concentration of solution in injector B.

Outputs of the First Step

$m_{MP}^I = 17.05 \pm 0.1$ g (mass of MP-I); $m_{GP}^I = 2.70 \pm 0.05$ g (mass of GP-I); $t_R^I = 37.9 \pm 1.1$ (min, reaction time); $m_{MeOH}^I = 2.38 \pm 0.15$ g (total mass of M for the first step); $m_{KOH}^I = 0.25 \pm 0.01$ g (total mass of KOH for the first step); $AV^I = 1.1 \pm 0.1$ mg g⁻¹ (acid value of MP-I (mg KOH per gram of MP-I)); $RO^I = 7.8 \pm 0.2$ % (amount of the unreacted oil in MP-I (% w/w)).

Table I Inputs for the second step: m_{MP}^I – initial amounts of MP-I; $I(\lambda)_0^{II}$ – transmittance adjusted on the comparator for the second step; X_{KOH} – concentration of KOH in MeOH in the feedback injector

Name	m_{MP}^I , g	$I(\lambda)_0^{II}$, %	X_{KOH} , g KOH/g M
1A	16.3 ± 0.1	7.3	0.025 ± 0.005
2A	16.3 ± 0.1	12.4	0.069 ± 0.005

Second Step

Inputs of the Second Step

Four various experiments were carried out using the same MP-I feed. The concentrations of the used solution of KOH in M in the feedback injector and the transmittance adjusted on the comparator are given in Table I. The temperature was constant 20 °C.

Outputs of the Second Step

The mass of both phases (MP-II and GP-II), total reaction time t_R^T , total consumption of solution of KOH in M (in the first and second step), concentrations of fatty acids and acylglycerols (expressed by the acid value AV^{II} and the value of RO^{II}) in MP-II are shown in Table II.

Table II Outputs of the first step: m_{MP}^{II} – mass of MP-II (with unreacted M); m_{GP}^{II} – mass of GP-II (with unreacted M); e – equivalence (the total M consumed in both steps); KOH^T – total KOH consumed in both steps; AV^{II} – acid value of MP-II; RO^{II} – amount of unreacted oil in MP-II; K^+ – concentration of potassium ions, t_R^T – total reaction time (sum of times of first and second step); η – ration of treated MP-II and used rape seed oil

Name	m_{MP}^{II} , g	m_{GP}^{II} , g	e, mol M/mol oil	KOH^T , g KOH/g oil	
1A	15.7 ± 0.2	0.63 ± 0.05	1.49 ± 0.05	0.0156 ± 0.002	
2A	15.8 ± 0.1	0.63 ± 0.02	1.46 ± 0.05	0.0173 ± 0.002	
Name	AV^{II} , mg ml ⁻¹	RO^{II} , %	K^+ , mg ml ⁻¹	t_R^T , min	η , %
1A	1.28 ± 0.15	2.4 ± 0.3	0	50 ± 2.0	85.2
2A	1.62 ± 0.10	1.3 ± 0.2	0	53 ± 1.4	86.6

Conclusion

From the results obtained it follows that:

- 1) The use of two step FCCR leads to higher conversion of RO to ME in comparison with the one step apparatus under the same conditions.
- 2) The advantages of FCCR in comparison with the batch reactor are:
 - the optimum amount of the solution of KOH in M with the given composition.
 - shorter reaction time.
 - simpler control of the biodiesel quality by the choice of the initial conditions (mainly $I(\lambda)_0$) and even also by the change of the experimental conditions during the reaction process.
- 3) The initial reaction conditions were selected in this work aside from the desired quality of the main product ME as biodiesel. More experiments will be needed to reach the normed biodiesel quality with regards to the effect of the change of the individual mutually interfering parameters.

The main disadvantage of the used apparatus is the too small volume of the reactor and therefore also of the reaction mixture. The relatively great number of operations leads to great loss of this mixture. This factor affected the precision of the final mass balances.

List of Abbreviations

AV – acid value; *FA* – fatty acids; *FCCR* – feedback controlled chemical reactor; *G* – glycerol; *GP* – glycerol phase; $I(\lambda)$ – transmittance of sample at wavelength λ ; *KA* – potassium salts (soaps) of *FA* of *RO*; *M* – methanol; *ME* – methylesters of *FA* of *RO* – biodiesel; *MP-I, II* – *ME* phase in the step *I, II*; $m_i^{I,II}$ – mass of the phase or substance *i* in the step *I, II*; *RO* – rape seed oil.

Acknowledgements

This work was financially supported by the Czech Ministry of Education, Health and Sport, research project CZ 310008/2010/3340.

References

- [1] Skopal F.: *React. Kinet. Catal. Lett.* **46**, 65 (1992).
- [2] Dvořák R., Skopal F., Komers K.: *Eur. J. Lipid. Sci. Technol.* **103**, 742

- (2001).
- [3] Stloukal R., Komers K., Machek J.: *Fett/Lipid* **100**, 507 (1998).
 - [4] Komers K., Skopal F., Stloukal R.: *Fett/Lipid* **99**, 52 (1997)
 - [5] Skopal F., Komers K.: *J. Prakt. Chem.* **338**, 83 (1996).
 - [6] Komers K., Stloukal R., Machek J., Skopal J.: *Fett/Lipid* **100**, 507 (1998).
 - [7] Komers K., Machek J., Stloukal R.: *Eur. J. Lipid Sci. Technol.* **103**, 359 (2001).
 - [8] Komers K., Stloukal R., Machek J., Skopal J.: *Eur. J. Lipid. Sci. Technol.* **103**, 363 (2001).
 - [9] Komers K., Skopal F., Stloukal R., Machek J.: *Eur. J. Lipid. Sci. Technol.* **104** (2002) – in press.
 - [10] Meloun M., Militký J.: *Statistical Processing of Experimental Data* (in Czech), PULS, Prague, 1994.