SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
12 (2006)

EFFECT OF RAPE SEED OIL QUALITY ON BIODIESEL COMPOSITION

František SKOPAL, Jaroslav MACHEK and Karel KOMERS[1]
Department of Physical Chemistry,
The University of Pardubice, CZ–532 10 Pardubice

Received September 30, 2006

The methanolysis of rape seed oil catalyzed by KOH has been studied from the standpoint of the dependences of the acid value (neutralisation number) and concentration of unreacted oil (as sum of glycerides) in the final mixture of methyl esters of fatty acids of the oil (biodiesel) on the initial KOH concentration in methanol and on the acid value and water content of the used oil.

Introduction

The new fuels for biodiesel engines would have the properties similar to the fossile diesel fuel. Therefore, at present a stress is put on the quality of alternative fuels, e.g. mixtures of methyl esters of higher fatty acids, produced from vegetable oils and animal fats, called biodiesel. The most part of biodiesel in Europe is produced by transesterification of rape seed oil with methanol (methanolysis) catalyzed by KOH.

---

[1] To whom correspondence should be addressed.

Theory

The alkaline methanolysis of vegetable oils and animal fats proceeds as a complicated system of simultaneous reactions [1], briefly

$$\text{Triglyceride} + 3\,CH_3OH \overset{(KOH)}{\rightleftarrows} 3\,RCOOCH_3 + \text{Glycerol} \quad (1)$$

$$\text{Triglyceride} + 3\,KOH \rightarrow 3\,RCOO^-K^+ + \text{Glycerol} \quad (2)$$

where R is the hydrophobic residue of some fatty acid. The first reaction (1) represents transesterification and all its steps are reversible; therefore a surplus of methanol must be used to shift the reaction to the final product – mixture of methylesters, biodiesel. The second reaction (2) — saponification, is irreversible, consumes the catalyst and changes the oil irreversibly to potassium soaps. It is, therefore, undesirable and is supported by the water present in the reaction mixture. After stoppage of the reaction by acidification, the undesirable soaps are converted to free fatty acids which are solved in methyl esters. Their concentration defines the acid value (neutralisation number) of biodiesel, expressed experimentally as the amount of KOH needed for their neutralisation (in mg KOH per 1 g biodiesel). The reversible methanolysis produces biodiesel and, according to the reaction conditions used, various amounts of residual unreacted oil (i.e. mixture of triglycerides of higher fatty acids), which also remains dissolved in the ester phase.

Experimental

The cold-pressed rape seed oil (firm ABC Bransouze, CZ), potassium hydroxide p.a. (ca. 85 % w/w), technical methanol, phosphoric acid p.a. conc. (85 % w/w), all Lachema Brno, CZ, were used.

An exact amount of rape oil was weighed into a glass vessel kept at constant temperature (20 °C). Then, with intensive stirring, the calculated amount of the solution of KOH in methanol was added as quickly as possible (reaction time t = 0). In various selected reaction times samples of the actual reaction mixture were taken and immediately acidified with phosphoric acid to pH = 2. The acidified samples were mixed 30 min, then the generated precipitate of KH_2PO_4 was filtered off, and methanol was distilled off from the filtrate. The resulting filtrate separated spontaneously by standing to give the ester phase (EP = biodiesel) and glycerol phase. The EP was then analyzed as follows [2]: Its acid value (AV_{EP}) was determined by alkalimetric titration with ethanolic analytic solution of 0.01 M

KOH in the milieu of ethanol : toluene = 3 : 1 (v/v) and indicated by phenolphtalein. The concentration of unreacted oil in EP (X_{RO}) was determined by HPLC isocratic method with refractometric indication, using the apparatus ECOM Praha, pump LCP 400 and refractometer RIDK 102, Laboratorní přístroje Prague, CZ. The mixture hexan : isopropanol = 97 : 3 (v/v) was used as the mobile phase. The water content in the used oil and ester phase were determined by the Karl-Fisher method [3].

Results and Discussion

The constant temperature kept in all the experiments was 20 °C. At first, the time dependences of AV_{EP} (and consequently the concentration of soaps created in EP) and of X_{RO} were measured for various initial KOH concentrations (P), both related to the initial mass of the oil. In all the experiments the constant molar ratio metha-

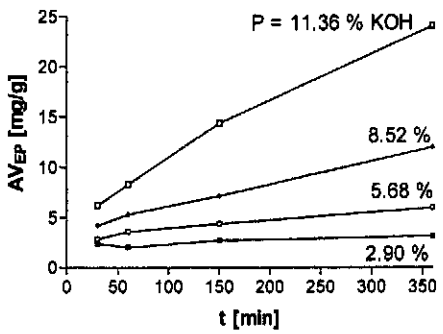

Fig. 1 Dependence of acid value in the ester phase (AV_{EP}) on reaction time t for various concentrations of the catalyst KOH in methanol (P)

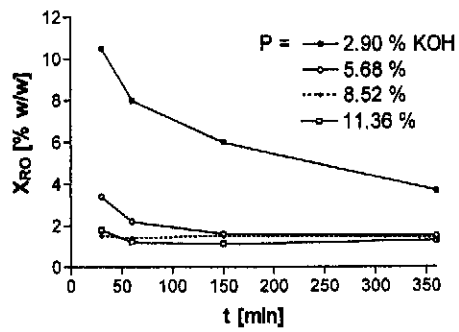

Fig. 2 Dependences of concentration of unreacted rape oil in the ester phase (X_{RO}) on reaction time t for various concentrations of the catalyst KOH in methanol (P)

nol : oil = 6 : 1 was used. In Figs 1 and 2 examples of the dependences AV_{EP} and X_{RO} vs. t are shown for initial AV of the rape oil AV_{RO} = 1.9 mg KOH g^{-1} and various P values.

Three samples of oil with AV_{RO} = 0.3, 0.6 and 1.9 mg KOH g^{-1} and with practically identical water content V_{RO} = ca 0.15 % w/w were used for the study of the influence of AV_{RO} on the quality of the ester phase.

The influence of V_{RO} on the biodiesel quality was studied using the rape oil with AV_{RO} = 0.3 mg KOH g^{-1}, to which known amounts of water were added. Examples of the dependences AV_{EP} and X_{RO} on AV_{RO} are presented in Fig. 3. An example of the dependence AV_{EP} vs. V_{mix} (concentration of water in the reaction

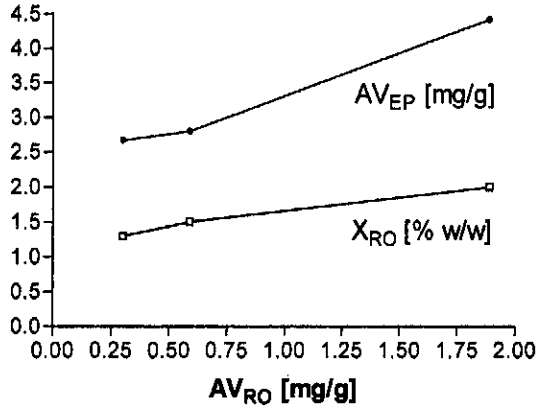

Fig. 3 Dependences of AV_{EP} and X_{RO} vs. AV_{RO} (acid value of the used oil)

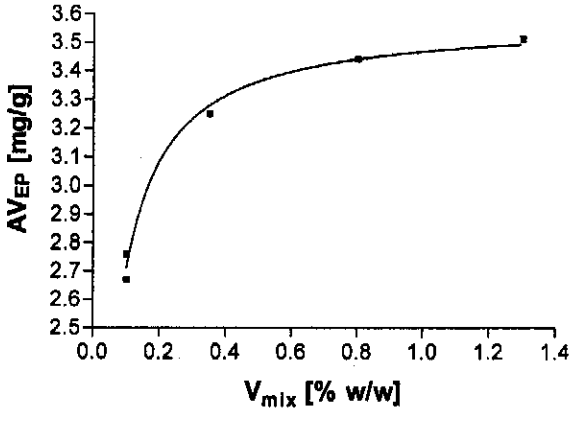

Fig. 4 Dependence of AV_{EP} on V_{mix} (concentration of water in the reaction mixture)

mixture) for experimental conditions $AV_{RO} = 0.3$ mg KOH g^{-1}, $t = 150$ min, $P = 2.63$ % w/w and $X_{RO} = 1.4 \pm 0.1$ % w/w is given in Fig. 4.

From the results in Figs 1 and 2 it is obvious that with increasing t, AV_{EP} increases markedly with the concentration of the catalyst KOH in methanol, while the X_{RO} value decreases, both in accord with the expectation following from Eqs (1) and (2). From the comparison of both graphs it follows that AV_{EP} increases much faster than X_{RO} decreases. It signifies that, on one hand, the amount of the unreacted oil X_{RO} decreases but, on the other hand, the concentration of the soaps in *EP* and, therefore, also AV_{EP} substantially increases. Therefore, it is advantageous to choose a mildly concentrated solution of KOH in methanol as the reaction partner of the oil and prefer prolonging the reaction time.

The main goal of the experiments in Figs 3 and 4 is to check whether the chosen parameters of the used rape oil affect its methanolysis and thus also the *EP* — biodiesel quality. From Fig. 3 the increase of the acid value of the produced biodiesel AV_{EP} with increasing acid value of the used oil AV_{RO} is evident, as expected. According to Fig. 4 the amount of water in the reaction mixture has a substantial effect on AV_{EP}. Concentration of the unreacted oil in biodiesel X_{RO} increases with its increasing AV_{RO} (see Fig. 3), but it is practically independent of the water concentration in the reaction mixture V_{mix}.

Conclusion

The acid value (neutralisation number) and the water content of the oil used for its methanolysis to biodiesel should be as low as possible.

Acknowledgements

This work was financially supported by the Ministry of Education, Youth and Sport, research project MSM0021627502.

References

[1] Komers K., Skopal F., Stloukal R., Machek J.: Eur. J. Lipid Sci. Technol. **104,** 728 (2002).

[2] Komers K., Stloukal R., Machek J., Skopal F., Komersová A.: Fett/Lipid **100,** 507 (1998).

[3] Komers K., Stloukal R., Machek J., Skopal F.: Eur. J. Lipid Sci. Technol. **103,** 363 (2001).