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The effect of the acidity of rapeseed oil on its transesterification

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ABSTRACT

The aim of this work is to study the transesterification of vegetable oil with a high acid number at unchanged reaction conditions. Rapeseed oil was used as the raw material and its acid number was changed by the addition of oleic acid (from 0.89 to 12.25 mg KOH/g). Methanol was used for transesterification (molar ratio of oil to methanol 1:6) and potassium hydroxide was used as a catalyst. After the reaction time, the residue of the catalyst was neutralised by gaseous carbon dioxide and the methanol excess was removed. After the separation of two phases, each of them was analyzed (in the ester phase: yield, content of methyl ester and acid number; in the glycerol phase: yield, density, viscosity, content of glycerol, soaps, methyl ester, potassium carbonate and hydrogen carbonate). The obtained data was compared with theoretical material balances and the effect on the saponification of oil was discussed. The results show that the yield of methyl ester (biodiesel) is significantly affected by a higher acid number, as well as enhanced soap formation. On the other hand, the conversion of the oil and acid number of the ester phase remain at constant values in studied borders.

1. Introduction

Biodiesel is a renewable energy source for compression ignition engines with many benefits when compared with fossil diesel. It is a biodegradable substance; the contribution to the green-house effect is slow by its combustion. As shown in studies on contemporary motor types (Altın et al., 2001; Kegl, 2008), biodiesel is a direct substitute for fossil diesel.

The bases of raw materials are vegetable oils and animal fats. Vegetable oils such as rapeseed oil, sunflower oil, soybean oil, etc. are a good opportunity for agriculture, but the soil used for growing these plants cannot be used immediately for food production. Another way is the use of waste oils and fats.

In present technological processes, methanol as a reaction partner and the hydroxides of alkaline metals as catalysts are predominantly used (Vicente et al., 2004). This is probably the cheapest method for the conversion of oil to biodiesel. Typical reaction conditions are: molar ratio methanol:oil = 6:1, reaction temperature at 40–60 °C, reaction time 60–100 min, catalyst amount approximately 1 wt.% compared to the mass of oil. But these catalysts cause the saponification of oil and so it is sensitive to oil quality. Waste cooking oils with a high acid number even need the use of an acid catalyst to avoid the saponification. The using of acids as a catalyst is now under intensive investigation (Jacobson et al., 2008) as well as the transformation of fatty acids to methyl esters (Marchetti and Errazu, 2008), or the recovering of methyl esters from acidic esterification of FFA, obtained by acidifying of the glycerol phase, which contains soaps and methyl ester (Kocsisová et al., 2005). Other transesterification methods are based on heterogeneous catalysts (López et al., 2005) and enzymatic transformation (Iso et al., 2001). The reaction without a catalyst proceeds in a supercritical state, under high pressure and temperature (Demirbas, 2008).

The goal of this work is to study the effect of the acidity of rapeseed oil on base catalyst methanolysis.

The effect of free fatty acids content on the transesterification of beef tallow was previously studied (Ma et al., 1998) via analysis of variance with two factors in four levels. The first factor was the water content and the second was the free fatty acids content. Both factors had significant influence on the methyl ester yield, even the synergistic negative effect was revealed. Various FFA content was also studied by Vicente et al. (2006) on oils produced in Spain.

2. Theory

Various amounts of oleic acid were added to rapeseed oil to simulate the behaviour of natural plant oil with a higher acid number. Oleic acid is the most abundant acid (55–65 wt.%) in the oil composition (Mittelbach and Remschmidt, 2004).

Biodiesel was prepared by methanolysis (molar ratio of methanol to oil 6:1) and catalyzed by potassium hydroxide. The transesterification reaction proceeded in the heterogeneous mixture

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Nomenclature

AL	apolar layer
an	acid number
c_i	molar concentration of the *i*
EP	ester phase
FFA	free fatty acid
GP	glycerol phase
ME	methyl ester
$m_{\mathrm{EP}}^{t,\mathrm{id}}$	theoretical mass of the EP at ideal conditions, without saponification
$m_{\mathrm{FFA}}^{\mathrm{start}}$	mass of FFA present in the RO
$m_{\mathrm{GP}}^{\mathrm{sample1}}$	mass of the first sample of the GP
$m_{\mathrm{GP}}^{\mathrm{sample2}}$	mass of the second sample of the GP
M_i	molar weight of the *i*
m_i	mass of *i*
m_i^j	mass of *i* in the *j* phase
$m_{\mathrm{KOH}}^{\mathrm{neut.}}$	mass of KOH for neutralisation of the FFA
m_{ME}^t	theoretically calculated mass of the ME in the experiment
m_N	mass of the oil for transesterification
$m_\mathrm{S}^{\mathrm{start}}$	mass of soaps formed by neutralisation of the FFA
m_S^r	mass of soaps arised during the reaction
$m_{\mathrm{TG}}^{\mathrm{sap.}}$	mass of triglycerides being saponificated
p	atmospheric pressure
R	universal gas constant
RO	rapeseed oil
RRM	raw reaction mixture
S	soaps
T	absolute temperature
TG	triglyceride
V_1	the first volume of HCl at titration
V_2	the second volume of HCl at titration
V_i	volume of the *i*
ξ_i	mass fraction of the *i*
ξ_i^j	mass fraction of the *i* in the *j* phase

(RRM) after the mixing of the oil with a methanolic solution of potassium hydroxide. Before the surplus of methanol was removed, the catalyst was neutralised by gaseous carbon dioxide dosage not to reverse the reaction (Skopal et al., 2001). The carbon dioxide and KOH form carbonates. Besides catalytic function, the KOH allows the side saponification reaction of oil and methyl ester, and therefore, decreases the methyl ester yield.

The RRM separates spontaneously after demethanolisation into the polar (glycerol phase – GP) and apolar phase (ester phase – EP) – biodiesel. Besides glycerol, the GP consists of water, soaps, salts, methyl ester and methanol. The EP is formed mainly by methyl esters of fatty acids and the residue of acylglycerols, water and soaps.

2.1. Material balances

For a better understanding of the studied system, some material balances can be made. Input amounts of raw materials and their quality as well as output product analysis are described.

2.1.1. Balances of soaps

The free fatty acids (FFA) present in raw oil consume the catalyst. The content of FFAs is characterised by the acid number (*an*, mg KOH/g of oil). To simplify the calculations, the mean molar weight of free fatty acids is considered the same as the molar weight of oleic acid.

The amount of the soaps $m_\mathrm{S}^{\mathrm{start}}$ originated from the FFAs is:

$$m_\mathrm{S}^{\mathrm{start}} = \frac{an}{1000} \cdot \frac{M_\mathrm{S}}{M_{\mathrm{KOH}}} \cdot m_\mathrm{N}, \tag{1}$$

which needs extra KOH for their neutralisation:

$$m_{\mathrm{KOH}}^{\mathrm{neut.}} = m_\mathrm{S}^{\mathrm{start}} \cdot \frac{M_{\mathrm{KOH}}}{M_\mathrm{S}}, \tag{2}$$

where *an* (mg KOH/g) stands for the acid number of the oil, M_S is the molar weight of soaps, M_{KOH} represents the molar weight of KOH and m_N (g) is the batched amount of oil.

The entire amount of soaps m_S, determined experimentally, can be calculated from GP analysis (3)

$$m_\mathrm{S} = \xi_\mathrm{S} \cdot m_{\mathrm{GP}}, \tag{3}$$

where ξ_S is the mass fraction of soaps in GP and m_{GP} (g) is the total mass of GP.

The mass of soaps formed by the saponification of oil and methyl esters m_S^r must be the difference between entire experimentally determined amount of soaps m_S and soaps originated from the FFA, $m_\mathrm{S}^{\mathrm{start}}$ (1).

$$m_\mathrm{S}^\mathrm{r} = m_\mathrm{S} - m_\mathrm{S}^{\mathrm{start}} = \xi_\mathrm{S} \cdot m_{\mathrm{GP}} - \frac{an}{1000} \cdot \frac{M_\mathrm{S}}{M_{\mathrm{KOH}}} \cdot m_\mathrm{N}, \tag{4}$$

2.1.2. Balances of oil, theoretical yield of methyl ester

Let us assume that the rapeseed oil (RO) consists only of triglycerides (TG), free fatty acids and water.

It is possible to calculate the mass of FFAs from the acid number as

$$m_{\mathrm{FFA}}^{\mathrm{start}} = \frac{an}{1000} \cdot \frac{M_{\mathrm{FFA}}}{M_{\mathrm{KOH}}} \cdot m_\mathrm{N}. \tag{5}$$

Water mass fraction $\xi_{\mathrm{H_2O}}^{\mathrm{RO}}$ was determined by the titration, see Section 3.2.

Then, Eq. (6) for the mass of triglycerides m_{TG} in the batch can be written

$$m_{\mathrm{TG}} = m_\mathrm{N} - m_{\mathrm{FFA}}^{\mathrm{start}} - m_{\mathrm{H_2O}}^{\mathrm{RO}} = \left(1 - \frac{an}{1000} \cdot \frac{M_{\mathrm{FFA}}}{M_{\mathrm{KOH}}} - \xi_{\mathrm{H_2O}}^{\mathrm{RO}}\right) \cdot m_\mathrm{N}. \tag{6}$$

m_{TG} means the amount of TG capable for transesterification in the batch.

Assuming no glycerides and methyl ester saponification and the stoichiometric transesterification reaction (ideal): TG + $3CH_3OH$ → 3 ME + glycerol, the theoretical mass of the ester phase $m_{\mathrm{EP}}^{t,\mathrm{id}}$ at complete conversion is given by the relation

$$m_{\mathrm{EP}}^{t,\mathrm{id}} = m_{\mathrm{TG}} \cdot \frac{3M_{\mathrm{ME}}}{M_{\mathrm{TG}}}. \tag{7}$$

The mass of the EP calculated according (7) is the maximum obtainable one and our experimental results were compared with it.

The experimental mass of the EP is always smaller, because the saponification reaction takes place and some methyl ester dissolves in the GP. This mass of methyl ester in the GP ($m_{\mathrm{GP}}^{\mathrm{ME}}$) can be estimated by analysis of GP. The mass of TG saponificated by the side reaction is