BALANCE OF ONE-STEP REESTERIFICATION OF VEGETABLE OILS

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Theoretical relationships have been derived which are necessary for realization of reesterification of vegetable oils in production of biodiesel fuel on industrial scale. Using a model system of rapeseed oil–methanol, orientational calculations and their verification have been carried out.

Reports concerning utilization of vegetable oils as a fuel for Diesel engines first appeared in American patents[1 – 3]. Some sorts of oils were tested directly as fuels but the results were not good[4]. However, oils can be converted to more suitable products. Selective catalytic pyrolytic conversion of oils gives a mixture of liquid hydrocarbons[5]. A very much widespread modification consists in the reesterification of vegetable oils and animal fats with a suitable monoalcohol. Most papers and patents are focused on the reesterification with methanol[6,7] in the presence of esterification catalysts, both acidic and basic.

The present paper shows possibilities of calculation of the optimum procedure for selecting a practical reesterification method.

THEORETICAL

Let us presume an equilibrium reesterification reaction between an oil O and alcohol A giving ester E and glycerol G

$$O + 3A \longleftrightarrow 3E + G \tag{1}$$

with two liquid phases (1) and (2). Moreover, let us presume that the reaction described by Eq. (*1*) proceeds only in the phase (1), i.e. the oil O is not present in the phase (2). As the reaction (*1*) is not connected with any change in number of moles, it is possible – with the presumption of ideal behaviour – to write the expression (*2*) for the equilibrium constant K of reaction (*1*) in the phase (1)

$$K = n_{G(1)}\, n_{E(1)}^3 \big/ n_{O(1)}\, n_{A(1)}^3 \,, \tag{2}$$

where $n_{O(1)}$, $n_{A(1)}$, $n_{E(1)}$, and $n_{G(1)}$ are the equilibrium amounts of the reaction components O, A, E, and G, respectively, present in the phase (1). The amounts of the individual components of reaction (1) obey the following relationships at any reaction phase (i.e. in the equilibrium too)

$$n_O^0 - n_O = (n_A^0 - n_A)/3 = n_E/3 = n_G, \qquad (3)$$

where n_O^0 and n_A^0 are the initial amounts of the reactants.

When the phase and chemical equilibria are established, it is impossible to write the balance equations for the individual reaction components

$$n_O = n_{O(1)}$$

$$n_A = n_{A(1)} + n_{A(2)}$$

$$n_E = n_{E(1)} + n_{E(2)}$$

$$n_G = n_{G(1)} + n_{G(2)}, \qquad (4)$$

where $n_{A(2)}$, $n_{E(2)}$, and $n_{G(2)}$ are the equilibrium amounts of the reaction components A, E, and G, respectively, present in the phase (2).

For the individual distribution coefficients α_J (J = A, E, G) we can write

$$\alpha_J = \frac{n_{J(2)}}{V_{(2)}} \Big/ \frac{n_{J(1)}}{V_{(1)}} = \frac{n_{J(2)}}{n_{J(1)}} \frac{1}{v}, \qquad (5)$$

where $V_{(2)}$ and $V_{(1)}$ are volumes of phases (2) and (1), respectively, at the equilibrium, and

$$v = V_{(2)}/V_{(1)} \qquad (5a)$$

is the relative volume ratio of phases (2) and (1).

If the conversion degree (conversion) of reaction (1) denoted x and the parameter e are introduced according to Eqs (6) and (7), respectively

$$x = 1 - n_O/n_O^0 \qquad (6)$$

$$e = n_A^0/3\, n_O^0, \qquad (7)$$

the overall balance equations (4) can be rewritten into the form (8):

$$n_{O(1)} = n_O^0(1 - x)$$

$$n_{A(1)} = 3\, n_O^0\ (e - x)/(1 + \alpha_A v)$$

$$n_{E(1)} = 3\, n_O^0\ x/(1 + \alpha_E v)$$

$$n_{G(1)} = 3\, n_O^0\ x/(1 + \alpha_G v)\,. \tag{8}$$

The introduction of Eqs (8) into the expression (2) for the equilibrium constant and modification give Eq. (9).

$$K = \left(\frac{1 + \alpha_A v}{1 + \alpha_E v}\right)^3 \frac{1}{1 + \alpha_G v}\ \frac{x^4}{(1 - x)\,(e - x)^3}\,. \tag{9}$$

Note: If the reaction (1) proceeded without formation of phase (2), i.e. if all the distribution coefficients were zero, then for the parameter e and conversion x_0 the expression from Eq. (9) would apply

$$K = \frac{x_0^4}{(1 - x_0)\,(e - x_0)^3}\,. \tag{9a}$$

The comparison of Eqs (9) and (9a) provides a criterion of influence of the phase equilibrium upon the conversion of reaction. If the condition in Eq. (10) is fulfilled

$$\left(\frac{1 + \alpha_E v}{1 + \alpha_A v}\right)^3 (1 + \alpha_G v) < 1\,, \tag{10}$$

then the conversion x of reaction (1) with two phases will be smaller than the conversion x_0 with only one phase and vice versa.

The expression (9) involves three variables: x, v, e. The parameter e can be chosen for the independent variable. For calculating the unknown x and v we must derive another relation between e, x, v. The volume balance of reaction (1) can serve for this purpose.

Let presume that the partial molar volumes of the individual reaction components in both phases are identical with the molar volumes. This means that the volumes of individual phases will equal the sum of volumes of the individual reaction components. The volume V_J of the J-th reaction component is given by the relationship $V_J = n_J M_J/\rho_J$,

where ρ_J is the density and M_J is the molecular weight of the J-th reaction component, and the relative volume ratio can be expressed as follows

$$v = \sum_J \frac{n_{J(2)} M_J}{\rho_J} \Big/ \sum_J \frac{n_{J(1)} M_J}{\rho_J}. \tag{11}$$

The introduction of Eqs (8) into Eq. (11) with the help of Eqs (5) and modification give Eq. (12) (the volume of catalyst is practically negligible).

$$\frac{3 M_A(\alpha_A - 1)(e - x)}{\rho_A(1 + \alpha_A v)} + \frac{3 M_E(\alpha_E - 1) x}{\rho_E(1 + \alpha_E v)} + \frac{M_G(\alpha_G - 1) x}{\rho_G(1 + \alpha_G v)} - \frac{M_O(1 - x)}{\rho_O} = 0 \tag{12}$$

The equations (9) and (12) form a set of nonlinear equations with two arbitrary unknowns. The most common case is the calculation of the unknowns x (the conversion of reaction) and v (relative volume ratio) for various chosen values of parameter e.

The analysis of the equation set (9) and (12) shows that both the conversion x and relative volume ratio v of phases increase with increasing e. The value of conversion of reaction asymptotically approaches unity. From the standpoint of the optimum results of reesterification it is necessary to choose a compromise value of parameter e, so as to obtain the highest possible yield of component E and to have this component in phase (1). Practically, this means to obtain the highest x value and, at the same time, the lowest v value. A suitable criterion, e.g., can be the rate of increase of the two quantities with changing e parameter. The numerical derivation of the calculated values x and v from the equation set (9) and (12) provides the values of derivatives dx/de, d^2x/de^2, and dv/de, d^2v/de^2 for various e parameters. The optimum parameter e then is that giving the greatest change dx/de and, at the same time, the smallest change dv/de.

The absolute volumes of the individual phases, $V_{(1)}$ and $V_{(2)}$, can be calculated from known e, x, and v values using Eq. (11).

$$V_{(1)} = V_O\left(1 - x + \frac{3 M_A \rho_O (e - x)}{M_O \rho_A(1 + \alpha_A v)} + \frac{3 M_E \rho_O x}{M_O \rho_E(1 + \alpha_E v)} + \frac{M_G \rho_O x}{M_O \rho_G(1 + \alpha_G v)}\right)$$

$$V_{(2)} = V_O\left(\frac{3 M_A \rho_O \alpha_A v (e - x)}{M_O \rho_A(1 + \alpha_A v)} + \frac{3 M_E \rho_O \alpha_E v x}{M_O \rho_E(1 + \alpha_E v)} + \frac{M_G \rho_O \alpha_G v x}{M_O \rho_G(1 + \alpha_G v)}\right) \tag{13}$$

The solution of the set (9) and (12) can also be used for calculating the weights of individual phases $m_{(1)}$ and $m_{(2)}$ using Eqs (5) and (8), since it must be

$$m_{(1)} = \sum_J n_{J(1)} M_J, \qquad m_{(2)} = \sum_J n_{J(2)} M_J. \qquad (14)$$

The calculation of weights of the individual phases must also take into account the weight of the catalyst used in the reesterification. In the case of an alkaline catalyst, its distribution favours the phase (2) (ca 90% of the catalyst is present therein).

EXPERIMENTAL

The theoretical relationships derived were verified on the industrially important reesterification of rapeseed oil (unfiltered, ZZN Chrudim, The Czech Republic) with methanol (pure, Lachema Brno, The Czech Republic). The rapeseed oil represents a mixture of triglycerides of higher fatty acids. The main features of realization of this reaction are represented schematically in Fig. 1. An example of reaction conditions is given in Table I. After mixing (ca 2 min) with methanol and alkaline catalyst

TABLE I
Starting materials and conditions

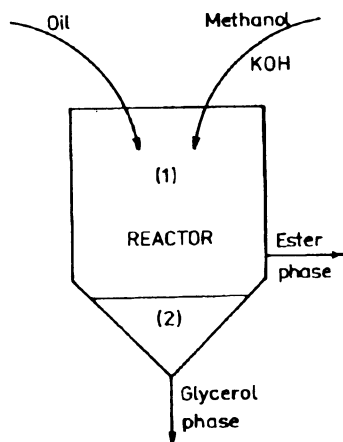| Substance	V_J, cm^3	m_J, g	Parameter e
Rapeseed oil, (O)	20	18.28	
Methanol, (A)	3.6	2.85	1.43
KOH		0.275	
$\sum$	23.6	21.405	

FIG. 1
Schematic representation of the reesterification with formation of two phases

and ca 4 h reaction, two liquid phases are formed. The upper one mainly contains a mixture of methyl esters of the higher fatty acids, the residual rapeseed oil, a part of unreacted methanol, a small amount of catalyst, and a practically immesurable amount of glycerol. After removing the methanol and catalyst, one directly obtains the fuel for Diesel engines – biodiesel fuel. The lower phase predominantly contains glycerol and catalyst with dissolved methanol and esters and/or salts of the higher fatty acids. Table II gives all resulting data from the experiment specified in Table I.

First we measured the distribution coefficient of methanol between the esters and glycerol. Both phases were analyzed by gas chromatography (Chrom 5). The other distribution coefficients were calculated from the reesterifications after analyzing both phases by means of the methods of gas and liquid chromatographies (Hewlett–Packard). The equilibrium constant was calculated from an estimate of the Gibbs energy change. The other data were taken from tables[8]. All necessary parameters for the balance calculations are summarized in Table III. The measurements were carried out at 20 °C with the alkaline catalyst KOH (pure, Lachema Brno, The Czech Republic) of 1.5% concentration (by wt. with respect to the rapeseed oil according to patents[6,7]).

RESULTS AND DISCUSSION

Theoretical courses of the dependences of x and v on e are presented in Fig. 2. The circles denote the experimental points from chromatographical analyses. For a comparison with a real system, this figure gives the dependence of x_0 on e according to Eq. (9a). The values of the first and the second derivatives of x and v with respect to e were calculated by the numerical five-point derivation[9]. The analysis of the derivatives in

TABLE II
The equilibrium values of reesterification

Phase	$V_{(i)}$, cm^3	$\rho_{(i)}$, g cm^{-3}	$m_{(i)}$, g	wt.%		x	v
				methanol	glycerol		
(1)	20 S	0.88	17.6	1	0	0.976	0.18
(2)	3.6	1.06	3.82	20	42		
Σ	23.6		21.42				

TABLE III
The data for calculations

Substance	M, g mol^{-1}	ρ, g cm^{-3}	α	K
Rapeseed oil	879.1	0.914	0	
Methanol	32.04	0.791	25	
Methyl ester	294.4	0.875	0.35	4 000
Glycerol	92.1	1.262	100	

Fig. 3 gave the value of parameter $e = 1.14$ which is connected with the greatest increase in the conversion x. On the other hand, from this value the increase in the relative volume v is diminished.

Let denote the general relative volumes of the J-th reaction component in the i-th phase with the symbol $\varphi_{J(i)}$, the relative volume of the i-th phase with the symbol $\varphi_{(1)}$ defined as follows:

$$\varphi_{J(i)} = V_{J(i)}/V_O, \qquad \varphi_{(i)} = V_{(i)}/V_O, \qquad (15)$$

where V_O means the volume of oil. These values were calculated from Eqs (11) and (13) and are represented in Figs 4 and 5 for the phases (1) and (2), respectively. At the reaction conditions given a very good agreement with the measured values $\varphi_{(1)}$ and $\varphi_{(2)}$ was obtained for the e parameter in the interval from 1.0 to 1.6. From Fig. 4 it follows that the curve 3 (i.e. dependence of $\varphi_{E(1)}$ on e) goes through a maximum and the curve 2 (i.e. $\varphi_{A(1)}$ vs e) has a point of inflexion. From numerical derivations of these curves one obtains the values of e parameter for the maximum $e_{max} = 1.48$ and point of inflexion $e_{inf} = 1.29$. From Fig. 5 it follows that the relative volumes $\varphi_{A(2)}$ and $\varphi_{E(2)}$ depend practically linearly upon e for $e > 1.2$. Beginning from this value, $\varphi_{G(2)}$ almost does not
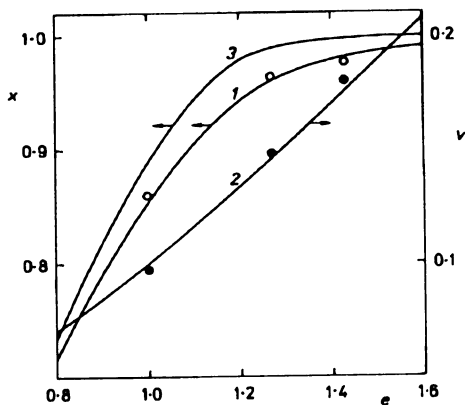

FIG. 2
The dependences of conversion x (1), relative volume ratio v (2) and conversion x_0 (3) upon parameter e
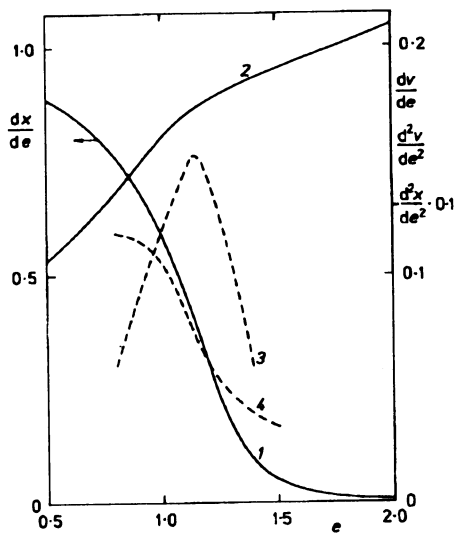
FIG. 3
Courses of the first (1 and 2) and the second derivatives (3 and 4) of x and v, respectively, with respect to parameter e

change either. Hence for e above 1.2 one encounters a loss of ester E (the desirable product) in phase (1).

The basic idea of the present work is the balance of reesterification of vegetable oils to give biodiesel fuel. This is a reaction with two liquid phases in equilibrium. The results depend on the choice of reaction conditions. The present paper shows the possibilities of theoretical calculations according to the choice of concrete procedures and requirements of technology. At the same time one must also respect nonchemical factors (economical, ecological, time, space etc.). All presumptions for the balance are valid for the thermodynamic (both phase and chemical) equilibrium. This paper does not deal with the time course of reaction. Concrete conditions can more or less differ from the equilibrium due either to objective reasons or intervention of man. Therefore, the procedure chosen by an user must be proved experimentally.

The varying of conditions of reesterification course (reaction temperature, type and amount of catalyst) can significantly affect the results of calculations. On the other hand, on the basis of final requirements one can predict the effect of input parameters and try to change them so as to obtain satisfactory results.
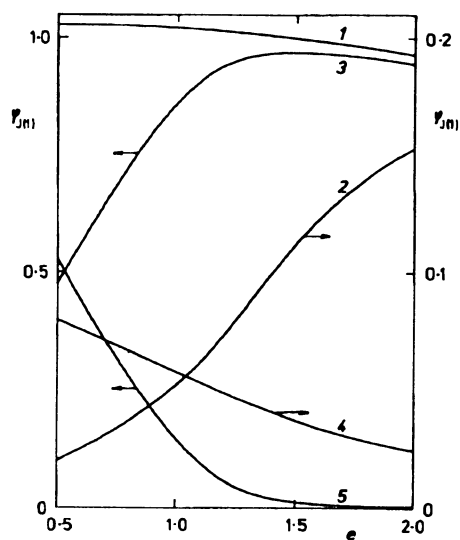

FIG. 4
Dependences of relative volume of phase (1) (*1*) and relative volumes of methanol (*2*), esters (*3*), glycerol (*4*), and oil (*5*) in phase (1) upon parameter e
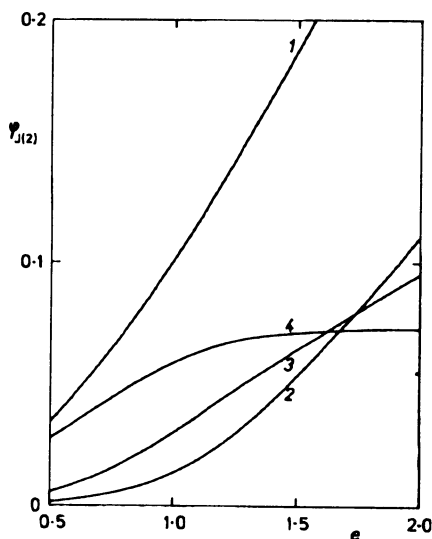
FIG. 5
Dependences of relative volume of phase (2) (*1*) and relative volumes of methanol (*2*), esters (*3*), and glycerol (*4*) in phase (2) upon parameter e

SYMBOLS

e	parameter (notion of equivalence)
K	equilibrium constant of reesterification
$m_{(i)}$	weight of the i-th phase, g
M_J	molecular weight of the J-th reaction component, g mol^{-1}
v, φ	relative volume
$V_{J(i)}$	volume of the J-th reaction component in the i-th phase, cm^3
x	degree of conversion in the reaction (conversion degree)
$n_{J(i)}$	amount of the J-th reaction component in the i-th phase, mol
α_J	distribution coefficient of the J-th reaction component
ρ_J	density of the J-th reaction component, g cm^{-3}

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