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KINETICS OF THE FISCHER ESTERIFICATION OF PALM FATTY ACIDS WITH ISOPROPANOL AND BUTYL-CELLOSOLVE

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Abstract

Fischer esterification of the mixture of palm fatty acids can be achieved in 80% conversion, under conditions of reactive distillation and methanesulphonic acid as catalyst. The volatility of the H_2O/alcohol azeotrope by-product confines the kinetic acceleration, relative to batch conditions.

Key words: Palm fatty esters, *Elaeis guineensis*, isopropyl fatty esters, butyl-cellosolve fatty esters, kinetics, reactive distillation.

Palabras claves: Ésteres grasos de palma, *Elaeis guineensis*, ésteres grasos de isopropilo, ésteres grasos del butil-cellosolve, cinética, destilación reactiva.

I. Introduction

Long-chain esters are useful industrial products. These compounds can be made by the usual Fischer reaction of acids with the desired alcohol under acidic catalytic conditions:

$$RCO_2H + \text{Alcohol} \rightleftharpoons H_2O + \text{Ester}$$

These esters are used as chemical intermediates, as well as final components of materials employed as fuel (*biodiesel*), lubricants, hydraulic fluids, plasticisers or pharmaceutical excipients and emollients [1, 2]. For example, isopropyl palmitate is a common emollient in shaving creams and alkoxy-alkyl fatty esters are potential emulsifiers.

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The processing of palm oil (*Elaeis guineensis*) yields a mixture of fatty acids as by-product, with the particular composition characteristic of the genetic make up of the plant. The raw material is purified to edible quality by stripping out free fatty acids, mono-acylglycerols and other relatively volatile components by a steam distillation process. The amount of palm RCO_2H currently produced in Costa Rica averages 200 ton/month (Rodolfo Vega, Compañía Numar. Personal communication). The composition of the mixture is: palmitic acid (50%), stearic acid (5%), oleic acid (33%) linoleic acid (9%), and 3% of other long-chain fatty acids.

Kinetic and thermodynamic data are necessary for scaling laboratory processes up to either pilot or industrial plant level. The Fischer reaction is nearly thermoneutral, as calculated from the enthalpies of formation of different esters, acids and alcohols [3]. The average value of $\Delta H°$ is - 3 ± 2 kJ/mol. This reaction is not expected to pose any engineering challenge for heat dissipation. A heat flux of only 0,8 kW would be generated, if these processes were designed to take place with a mean conversion rate of 1 kmol/h.

The van't Hoff equation allows the calculation of the effect of temperature on the degree of esterification:

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H^o}{RT^2} \tag{1a}$$

$$\left(\frac{d \ln K_{eq}}{dT}\right)_{300\,K} = \frac{-3\times 10^3}{300^2 R} = -\,0{,}004\,K^{-1} \tag{1b}$$

Thus around ambient temperatures, a mere 0,4 % decrease is expected in the equilibrium constant per one Kelvin increase. The matter seems to point exclusively to the kinetic features, since the thermodynamic behaviour of the reaction is rather insensitive to thermal changes.

The combination of chemical reaction and distillation in one unit operation is called *reactive distillation* [4]. This process allows greater efficiency not only in the degree of conversion of reactions which are limited equilibria (Le Chatelier-Braun principle), but also in decreasing costs of material handling and process design.

Therefore, we undertook the study of the kinetic features of the Fischer esterification of the mixture of palm acids (RCO_2H) as batch process and under reactive-distillation conditions, with isopropanol and butyl-cellosolve (2-butoxy-ethanol) in order to obtain basic data for further scaling of the process.

II. Materials and methods

Reagents: The mixture of palm fatty acids was obtained from Palmatica, Costa Rica. Isopropanol and butyl-cellosolve were technical grade and methanesulphonic acid was from Sigma.

Kinetic measurements and data treatment: The reaction mixtures were made by dissolving 10 mmol of RCO_2H in the alcohols, followed by $MeSO_3H$ also dissolved in the alcohols. All reaction mixtures were 0,5 *M* in $MeSO_3H$. The rates were measured by titration of remaining RCO_2H at suitable reaction times with NaOH/thymolphtalein, in aliquot portions taken from the reaction flask, immersed in a constant-temperature water bath. In all experiments, more than 10 measurements were collected (> 60% total extent of reaction).

The data were fitted to equation 5b (*vide infra*), by simple linear least-squares procedure. Error limits are standard deviations from at least three runs. The second-order rate constants for the esterification reactions were obtained by dividing the observed k_1 by the corresponding $MeSO_3H$ concentrations.

The experiments done under reactive distillation conditions were carried out in three-necked flasks immersed in water baths fitted with Dean-Stark distillation trap, sampling port and thermometer. The temperature of the reaction mixtures was kept at the boiling point of the azeotropes formed (77 °C for *i*-PrOH/H_2O and 95 °C for butyl-cellosolve/H_2O, both under 89 ± 1 kPa barometric pressure).

III. Results and discussion

Batch conditions. All reactions followed the well-established kinetic rate law, under the initial alcohol/RCO_2H molar ratio = 100/1 [5a]:

$$RCO_2H + \text{Alcohol} \rightleftharpoons H_2O + \text{Ester}$$

$$-\frac{d[RCO_2H]}{d\,t} = k_2[RCO_2H][MeSO_3H] - k_{-3}[MeSO_3H][Ester][H_2O] \tag{2}$$

This rate equation can be transformed into the form:

$$\frac{dx}{dt} = k_1(A - x) - k_{-2}\,x^2 \tag{3}$$

where x = [Ester] = [H_2O], $A = [RCO_2H]_o$, $k_1 = k_2$ [$MeSO_3H$] and$k_{-2} = k_{-3}$ [$MeSO_3H$]. Integration yields:

$$\int dx\,/\,(A - x - Bx^2) = k_1\,t + constant \tag{4}$$

with $B = (A\text{-}x_\infty)/x_\infty^2 = k_{-2}/k_1$. The final result is

$$\int dx \,/\, (A - x - Bx^2) = Int\,(x)$$

$$Int(x) = \frac{-2}{\sqrt{-q}} \tanh^{-1}\left(\frac{-2Bx - 1}{\sqrt{-q}} \right) + C \qquad (5b)$$

$-q = 1 + 4AB$. Thus linear fitting of the *Int(x)* – time data pairs should yield k_1. The corresponding k_2 results are given in Table 1, and includes some MeOH reactions for comparison.

The rate constants for esterification of pure palmitic and stearic acids with MeOH are practically the same as for the mixture of palm RCO_2H. The reason is doubtlessly due to the fact that structural differences in the RCO_2H are located far from the reacting carboxylic moiety.

The data also indicate that methanol reacts faster than either butyl-cellosolve or *i*-PrOH. The reason is attributed to the intrinsically greater steric hindrance exerted by primary and secondary alcohol moieties. This steric effect appears in the values of Arrhenius E_{act}. The energy of activation for the Fischer esterification of RCO_2H with MeOH is 42 kJ/mol, and 53 kJ/mol for other alcohols [6]. Camacho-Leandro [7] found a value of 53 ± 3 kJ/mol for the esterification of caprylic acid with ethylene glycol. The acid-catalysed 1-propanolysis of β-naphtyl acetate is 16 times faster than the 2-propanolysis, at 25 °C [5b, 8]. This difference in reactivity corresponds to a difference in $E_{act} \approx 7$ kJ/mol.

The two values of k_2 obtained for the esterification of palm RCO_2H with *i*-PrOH allow the estimation of Arrhenius $E_{act} = 64$ kJ/mol, a value just the right magnitude as expected from the above data (53 kJ/mol + 7 kJ/mol = 60 kJ/mol).

TABLE 1.

PSEUDO SECOND-ORDER RATE CONSTANTS FOR THE BATCH ESTERIFICATION OF FATTY ACIDS CATALYSED BY METHANESULPHONIC ACID. INITIAL ALCOHOL/RCO_2H MOLAR RATIO = 100/1.

RCO_2H + Alcohol	Temperature	10^3 k_2 / s^{-1} M^{-1}
Palm RCO_2H + MeOH	30,0 °C	11 ± 2
Palm RCO_2H + Butyl-cellosolve	30,0 °C	0,119 ± 0,006
Palm RCO_2H + i-PrOH	25,0 °C	0,078 ± 0,008
Palm RCO_2H + i-PrOH	45,0 °C	0,40 ± 0,02
Palmitic acid + MeOH	30,0 °C	14 ± 1
Palmitic acid + i-PrOH	30,0 °C	0,084±0,003
Stearic acid + MeOH	30,0 °C	13,9 ± 0,9

Reactive distillation conditions. All experiments were carried out under ambient barometric conditions of 89 ± 1 kPa. The degree of esterification of palm RCO_2H in the batch experiments is 63%, due to the competing back hydrolysis reaction. Under reactive distillation conditions, the degree of esterification increases to 80%. Despite the small negative temperature effect on the equilibrium constant, the observed increase in degree of conversion must be solely due to the continuous removal of water from the reaction medium.

Figure 1 shows the time evolution of the fractional conversion data for the *i*-PrOH reaction. It must be kept in mind that the reverse reaction operates to a very small extent in this situation.

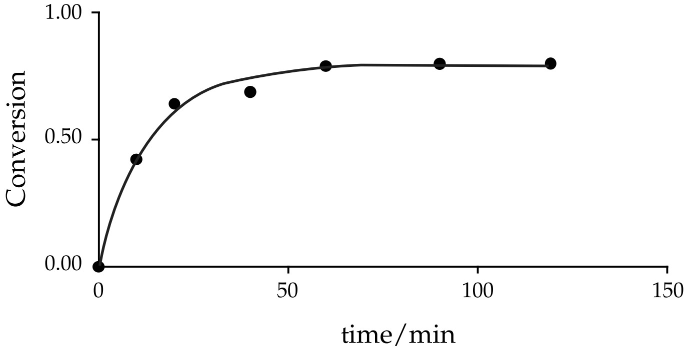

Figure 1. Esterification of palm fatty acids with isopropanol, under reactive distillation conditions. $[MeSO_3H] = 0,5$ *M*, 77 °C, 89 ± 1 kPa.

The esterification with *i*-PrOH was carried out with $[MeSO_3H] = 0,5$ *M*, at the azeotrope boiling temperature of 77 °C. The observed $t_{1/2}$ is 8,4 min, whereas the expected value for the batch process would be 19 min. For the esterification with butyl-cellosolve with $[MeSO_3H] = 0,5$ *M* at the azeotrope boiling temperature of 95 °C, $t_{1/2} = 15$ min compared to 24 min expected for the batch process.

It strikes at first glance, that the *i*-PrOH reaction proceeds faster than the reaction with butyl-cellosolve, despite the fact that the latter occurs at a higher temperature and the intrinsic greater steric hindrance of the *i*-Pr group, relative to $BuO\text{-}CH_2\text{-}CH_2$.

Figure 2 shows the time course of the rate of fractional conversion (*dy/dt*). The rate of reaction decreases as the reaction proceeds, due to consumption of the reacting fatty acids. The *i*-PrOH reaction indeed proceeds faster towards completion ($dy/dt \rightarrow 0$).

A mole balance of the process dynamics explains the observations. Neither the catalyst, RCO_2H nor the esters formed are practically volatile. In these experiments $[Alcohol]_o > [RCO_2H]_o$, and it also follows that $[Alcohol]_o > [H_2O]$. For the sake of mass balance, one can consider that H_2O-alcohol azeotrope mixture would be the "product" distilled off from the reaction pot. Thus for H_2O:

$$\text{Accumulation} = \text{In} - \text{Out} + \text{Generation} \qquad (6)$$

$$\text{Accumulation} = 0 - F_{H_2O} + V\, d[H_2O]/dt \qquad (7)$$

where F_{H_2O} is the water output (as the azeotropic H_2O-alcohol mixture) and V is the volume of the reaction mixture. Under steady-state conditions, no accumulation of water occurs and equation (7) results as:

$$V\, d[H_2O]/dt = F_{H_2O} \qquad (8)$$

Azeotropes are constant-composition mixtures resulting from the interplay of intermolecular forces in solution. The value of F_{H_2O} at the boiling point of the azeotropic mixture is a function of the apparent "volatility" of water in the mixture.

The qualitative expectation is that the H_2O/*i*-PrOH azeotrope is more volatile than the higher boiling analogue H_2O/butyl-cellosolve. Thus, the reaction takes place faster with *i*-PrOH than with butyl-cellosolve, because the rate of conversion evolves along reaction time as fast as the rate of water removal (equation 8).

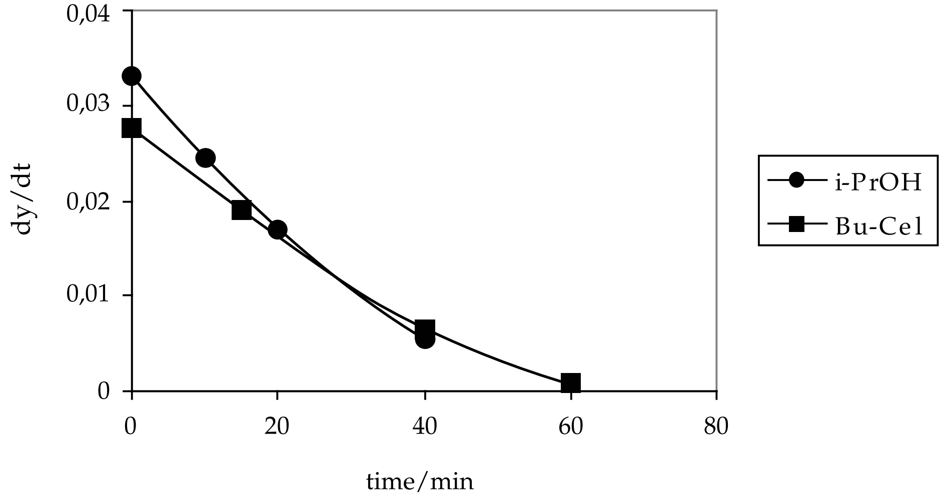

Figure 2. Variation of the rate of conversion in the esterification of palm fatty acids with isopropanol and with butyl-cellosolve, under reactive distillation conditions. $[MeSO_3H] = 0{,}5$ *M*, 89 ± 1 kPa.

IV. Conclusion

The fatty-acid mixture from palm can be transformed into the esters of isopropanol and butyl-cellosolve with 80% conversion, under reactive-distillation conditions. This yield is higher than the observed 63% degree of conversion, observed in batch process. The rate of H_2O removal (as the corresponding azeotrope) confines a maximum value of the reaction rate, by elimination of the effect of the back hydrolysis reaction.

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