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Modelling of the Extent of Reaction Curve for the Transesterification Process between 2-Methylpropan-1-ol and Methyl Ethanoate

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Asymetric sigmoidal function is used to fit experimental data obtained from transesterification reaction involving 2-methylpropan-1-ol and methyl ethanoate at different conditions with good results.

1. Introduction

Polyvinyl alcohol is a water-soluble polymer non flammable, non toxic and biodegradable by several adapted microorganisms which is widely used for textile warp sizing, adhesive, paper sizing agent, ceramic binder and also used in cosmetics, emulsion stabilizer, construction, pharmacy and electronic industries. Unfortunately, in its industrial production an unavoidable residue is generated from the main reaction of vinyl alcohol with methanol. Recirculation of the non reacted methanol is difficult because it forms a side product with the residual methyl ethanoate, which is a binary azeotropic mixture.

Transesterification of methyl ethanoate with 2-methylpropan-1-ol has been proposed as one of the alternatives to revalue the residue of the industrial production of polyvinyl alcohol in order to obtain 2-methylpropyl ethanoate and methanol. This is a reversible reaction which it can be represented by the stoichiometric equation

$$CH_3COOCH_3 + (CH_3)_2CHCH_2OH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3COOCH_2CH(CH_3)_2 + CH_3OH$$

where k_1 and k_{-1} are the rate constants of forward and reverse second order reactions respectively.

Esterification and transesterification reactions are normally carried out under acid or base catalysis. Traditionally most of liquid phase organic reactions are catalysed by homogeneous acid catalysts – strong Brønsted acids and soluble Lewis acids – . These acids have many important advantages – they are cheap, readily available and very

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active – but they also suffer from some serious disadvantages – they are difficult to separate from the organic products and their use leads to large volumes of hazardous waste which they can generate environmental problems – . In this way it is well known that the use of heterogeneous acid catalysts for liquid phase organic reactions can give a lot of benefits from different points of view because they are safe-to-handle and store, environmentally benigns, recoverables and reusables.

Ester-interchange between methyl ethanoate and 2-methylpropan-1-ol is a very slow reaction in liquid phase which it can be catalysed in the presence of a small ammount of sodium hydrogen sulphate as an heterogeneous acid catalyst (Calvet-Tarragona et al., 2007). The high resolving power and extreme sensitivity of gas chromatography enables to estimate quantitatively low concentrations of reaction products, so the kinetics of this kind of reactions can be studied.

2. Materials and Methods

The chemical products used are provided by Fluka. The 2-methyl-1-propanol (reference 58450) has a purity higher of 99.5 % GC, the methanol (reference 65539) has a purity higher than 99.8 % GC, the isobutyl acetate (reference 45920) has a purity higher than 98.5% GC and the methyl acetate (reference 46000) has a purity higher than 99.0 % GC. The kinetic studies have been performed in a PPI Industries pressurized reactor of 300 mL of capacity. The reactor temperature is adjusted and maintained with a coiled heater connected to a U12 Lauda thermostatic bath and R400 Lauda temperature controller. The reactor is charged firstly with a stoichiometric mixture of 2-methylpropan-1-ol and methyl ethanoate from forward reaction and in a second charge with a stoichiometric mixture of 2-methylpropyl ethanoate and methanol from backward reaction containing in both cases the heterogeneous acid catalyst and it is let to evolve while samples are taken continuously for further analysis at definite time intervals. During each experiment, between 25 and 30 samples were taken. The samples are cooled to stop the reaction and are then analized by a Hewlett-Packard 5890 Series II Plus gas chromatograph. The gas chromatograph is equipped with a flame ionisation detector and electronic pressure control. The response peak signals were integrated by using Hewlett-Packard Chemstation software. Each time 1 μL of the reaction mixture was injected into the gas cromatograph column, the peaks were evaluated from a calibration curve performed with standard solutions prepared by gravimetry using a T214S Sartorius granatary.

3. Results

Sigmoidal models can be constructed with three parameters (Zwietering et al, 1990). Exponentiated exponential function (1) which contains mathematical parameters (B_0, B_1, and B_2) can be used to describe the extent of reaction through the entire set of experimental data and to estimate the parameters with chemical meaning (r_{max}, t_{lag}, and X_{max}) from the model. First derivative (2) and second derivative (3) of the exponentiated exponential function with respect to time are calculated.

$$y = B_0 \exp[-\exp(B_1 - B_2 t)] \qquad (1)$$

$$y' = B_0 B_2 \exp[-\exp(B_1 - B_2 t)] \exp(B_1 - B_2 t) \qquad (2)$$

$$y'' = B_0 B_2^2 \exp[-\exp(B_1 - B_2 t)] \exp(B_1 - B_2 t) [\exp(B_1 - B_2 t) - 1] \quad (3)$$

The extent of reaction, obtained from these experimental data, plotted against time shows a distribution, which it can be fitted by an asymetric sigmoidal function with a lag phase just after initial time followed by an exponential phase and then by a stationary phase (Easton et al, 1976). Results are illustrated in Figures 1 and 2.

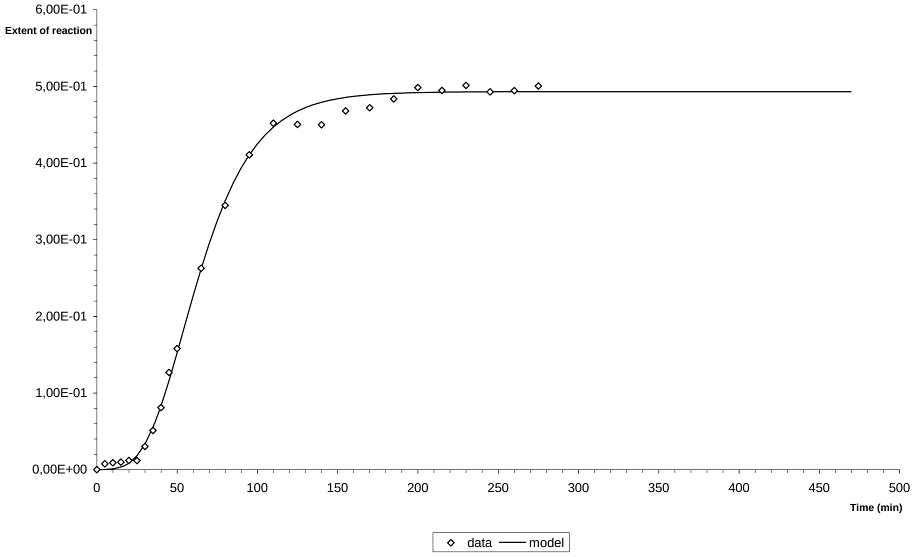

Figure 1: Extent of forward reaction curve versus time at 363 K from an equimolar mixture of 2-methylpropan-1-ol and methyl ethanoate fitted with the model.

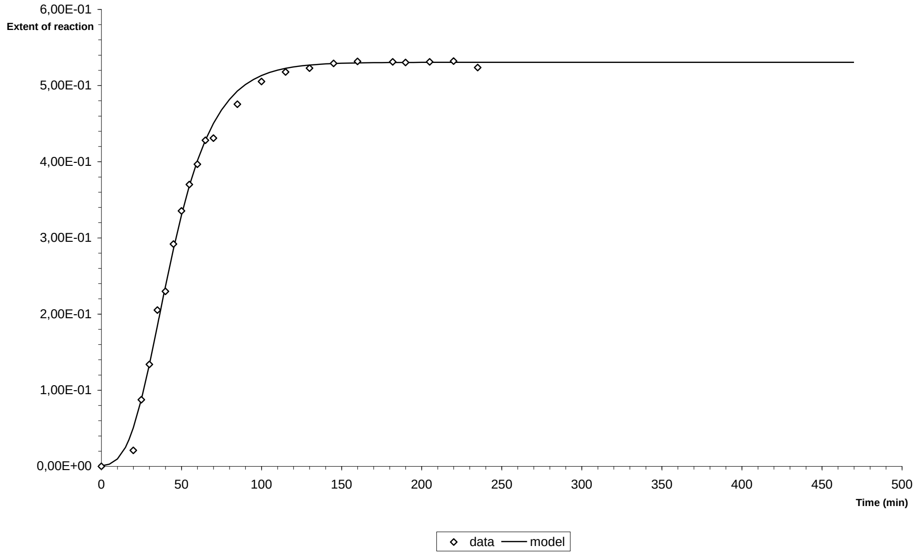

Figure 2: Extent of reverse reaction curve versus time at 363 K from an equimolar mixture of 2-methylpropyl ethanoate and methanol fitted with the model.

The three phases of the extent of reaction curve can be described by: the maximum reaction rate (r_{max}), which is defined as the tangent in the inflection point; the lag time (t_{lag}), which is defined as the x-axis intercept of this tangent and besides these values, another valuable parameter of the curve is the asymptote, which is the maximal value of the extent of reaction (X_{max}) reached.

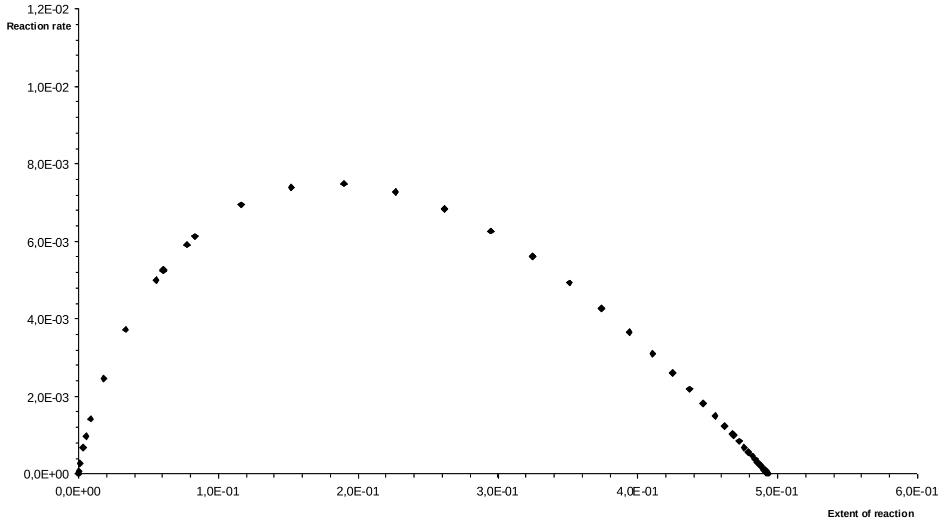

Figure 3: Forward reaction rate versus extent of reaction at 363 K

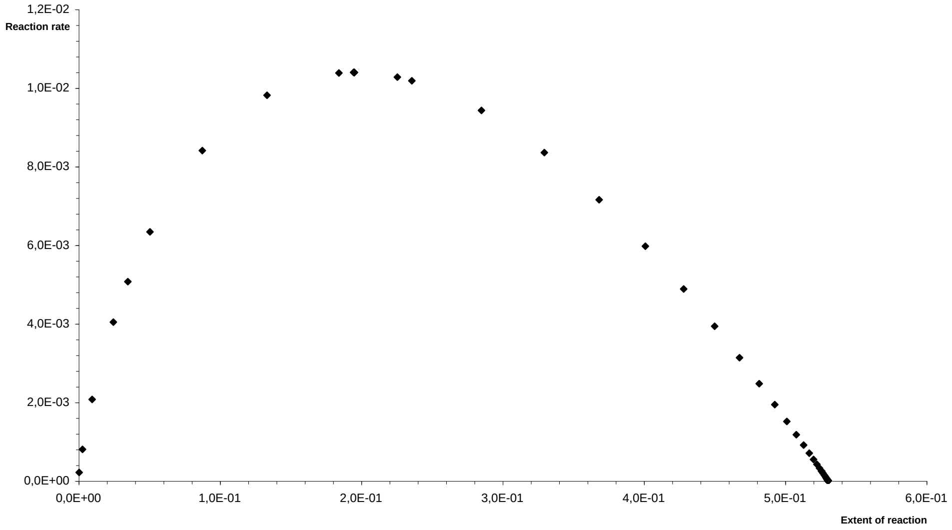

Figure 4: Reverse reaction rate versus extent of reaction at 363 K

Sigmoidal curve of the extent of reaction shows a phase in which the rate of reaction starts at a value of zero and then accelerates to a maximal value in a certain period of time, resulting in a lag phase. In addition, the curve contains a final phase in which the rate of reaction decreases and finally reaches zero, so that an asymptote is reached as shown in Figures 3 and 4. In chemical equilibrium, the reaction rate is equal to zero.

This asymetric sigmoid function is a type of mathematical model for a time series, where growth is slowest at the start and end of time period (Easton, 1978). The lower left-hand value asymptote of the function can be approached much more gradually by the curve than the upper right-hand value asymptote.

Relationship between mathematical parameters B_0 (4), B_1 (5), B_2 (6) and r_{max}, t_{lag}, X_{max} are as follows:

$$B_0 = X_{max} \quad (4)$$

$$B_1 = (r_{max}\, e / X_{max})\, t_{lag} + 1 \quad (5)$$

$$B_2 = (r_{max}\, e / X_{max}) \quad (6)$$

where e is Euler’s number. Values obtained are shown in Table 1.

Table 1 Parameters at 363 K

Reaction	B_0	B_1	B_2	t_{lag}	X_{max}	r_{max}
Forward	0.4930	2.230	0.041	29.73	0.49	0.0075
Backwad	0.5305	1.919	0.053	17.26	0.53	0.0104

With increasing of temperature, the reaction rate increases, but nearly the same equilibrium conversion is obtained along the temperature range. The reason is that the heat of reaction for esterification and transesterification reactions is small, i.e., the equilibrium constant depends only the slightly on temperature (Simons, 1983). Some alternative reactions available in the literature are the transesterification with n-butanol (Steinigeweg and Gmehling, 2004) or ethanol (Bonet-Ruiz et al, 2010).

4. Discussion and Conclusions

Transesterification reactions are known to be reversible second order reactions. Several kinetic experiments for the heterogeneous catalyzed transesterification of 2-methylpropan-1-ol and methyl ethanoate, as well as the reverse reaction, were carried out. The experimental results are in good agreement with the adjusted model, wich proves the validity of the sigmoidal models for this kind of reaction. The mathematics of exponentiated exponentials functions may be the simplest way to handle those otherwise often intractable asymetric sigmoid relationships. Exponentiated exponential formulation can describe the full course of a process from exponential start to exponential conclusion, and give a simplicity of expression that allows easy description of process that may otherwise require formidable complexities of ordinary kinetics. Then it appears to have as good or better predictive capabilities than ordinary kinectics, and with less trouble. Therefore we can conclude that all the extent of reaction curves which are presented here are better fitted with the exponentiated exponential model than any other kind of mathematical model.

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