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Catalytic reaction performed in the liquid–liquid system: comparison of conventional and neural networks modelling methods

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Abstract

A comparative analysis of two modelling methods has been performed for the hydrolysis of propionic anhydrite catalysed with sulphuric acid. The first modelling method is based on a theory of mass transfer with simultaneous catalytic reaction; in the second method the reaction kinetics and mass transfer phenomena are approximated with the neural network.

Keywords: Catalytic reaction; Hydrolysis of propionic anhydrite; Liquid–liquid reaction; Modelling of reaction kinetics; Neural networks

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1. Introduction

In our previous paper [1] the results of experimental studies on hydrolysis of the propionic anhydrite performed at batch and semibatch operating conditions have been reported and discussed. An influence of process parameters such as: the reaction temperature, the concentration of the catalyst and the initial volume of the organic phase on the overall reaction rate as well as on the heat generation rate have been investigated. All reported experiments have been carried out in the RC1 Mettler Toledo reaction calorimeter.

Despite of a simple stoichiometric equation, $A + H_2O \xrightarrow{H^+} 2C$, the mechanism for the considered reaction is quite complex and uncertain [1]. Due to a limited solubility of the propionic anhydrite in the aqueous phase, consisting here of water and propionic acid, the process is usually carried out in the heterogeneous liquid–liquid system. In such a system the chemical reaction and mass transfer phenomena occur simultaneously affecting the overall reaction rate. An observation of the obtained results [1] indicates that in the batch reactor the overall rate of the hydrolysis increases during the reaction progress. This may indicate that the autocatalytic effect should be taken into account. The performed analysis as well as independent solubility measurements have led us to the conclusion that the increase of the anhydrite solubility in the aqueous phase, caused by an increase of the concentration of propionic acid in this phase, may be partially responsible for this effect. Since during the reaction progress also the interfacial contact surface area changes (the anhydrite making up the organic phase is converted into the propionic acid, which remains in the aqueous phase) as well as simultaneously the concentration of the catalyst (the H^+ ions) is changed, therefore the conclusions related to the reaction kinetics drawn from the overall reaction rate measurements are uncertain. Therefore additional kinetic studies carried out in a stirred cell with

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Nomenclature

A	experimental constants ($m^3/(mol\,s)$, $m^6/(mol^2\,s)$)
c	molar concentration (mol/m^3)
E	activation energy (J/mol)
F	interfacial area (m^2)
H_0	Hammet's acidity function
ΔH_A	enthalpy of reaction (J/mol)
J_A	mass flux through the interface ($mol/(m^2\,s)$)
k_1	pseudo-first order kinetic constant (1/s)
k_{eff}	effective kinetic constant ($m^3/(mol\,s)$)
k_L	mass transfer coefficient (m/s)
m_A	solubility coefficient
m_{H_0}	Hammet's coefficient
n	number of moles (mol)
q	molar addition rate (mol/s)
$Q_D = \dot{m}c_p(T_R - T_o)$	power needed to heat up the added substrate (W)
$Q_F = UA(T_R - T_J)$	heat withdraw rate due to cooling (W)
$Q_L = (UA)_o(T_R - T_o)$	heat withdraw rate due to losses (W)
$Q_R = R_A \Delta H_A$	power generated due to the reaction progress (W)
r	reaction rate ($mol/(m^3\,s)$)
R	overall conversion rate (mol/s)
$R' = R/R_{max}$	dimensionless conversion rate
t	time (s)
T	temperature (K)
$T' = T/T_{max}$	dimensionless temperature
V	volume (m^3)
X	molar fraction

Greek letters

θ	dimensionless time
Φ	volumetric fraction
σ	activity function

Subscripts

A	anhydrite
C	propionic acid
L1, L2	organic and aqueous phases, respectively
S	sulphuric acid
W	water

well-defined interfacial area have been postulated as a conclusion from discussion of the paper [1].

In this work the results of these supporting kinetic studies have been reported and two methods of kinetic modelling have been proposed, discussed and tested. In the first modelling method the reaction rate is expressed with the conventional kinetic expressions. Then the kinetic constants have been determined and a general theory of mass transfer with simultaneous chemical reaction has been applied to model the reactor. In the second approach instead of kinetic expressions the neural network is employed to approximate the overall reaction rates without any a priori assumptions related to the reaction mechanism. Such a neural network approach has provided very promising results, when applied to model the reactions performed in the liquid–liquid systems [2,3].

2. Experimental

A series of the kinetic measurements have been carried out in the stirred cell reactor, where the interfacial surface area is well defined see Fig. 1. During performance of experiments the aqueous phase has been intensively mixed, however the stability of the interfacial contact area between the aqueous and organic phases has been always maintained, due to a specific design of the Teflon ring (2). The reaction progress has been followed by taking samples of the aqueous phase (each of 1 μl in volume). Then, after extracting of the propionic acid from the aqueous sample into hexane, a content of the propionic acid in the stirred cell has been determined with a gas chromatography. An extraction of the propionic acid into the hexane has applied to avoid addition of sulphuric acid into a chromatographic column.

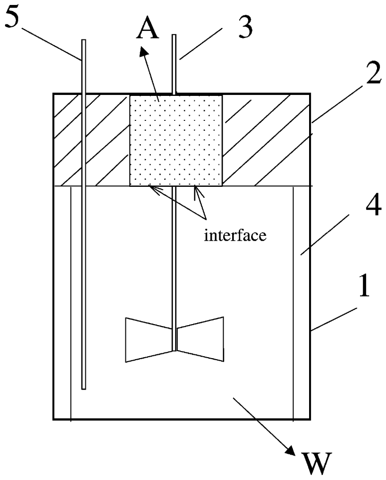

Fig. 1. Stirred cell reactor for kinetic measurements. Volume of the aqueous phase: $V = 0.8\,\mathrm{dm}^3$, interfacial contact surface area $F = 6.87\ 10^{-3}\,\mathrm{m}^2$: 1, thermostated glass vessel; 2, Teflon ring; 3, stirrer; 4, baffles; 5, sampling tube; A, anhydrite; W, water and H_2SO_4.

The concentration versus time plots, obtained for different contributions of the catalyst, are shown in Fig. 2. From the obtained data, the flux of the propionic anhydrite through the interface, J_A, has been estimated as a function of time, following the relationship:

$$J_A = \frac{V}{2F}\frac{dc_C}{dt} \qquad (1)$$

Since at the same time the concentration of the propionic acid in the bulk of the aqueous phase was known, the solubility of the anhydrite in those phase could be calculated following the previously elaborated relationship [1]. Also the mass transfer coefficient in the aqueous phase, $k_L = 0.6 \times 10^{-4}$ (m/s), has been estimated. From the obtained results and according to the general theory of mass transfer accompanied with the chemical reaction [4] the following conclusions have been drawn:

- mass transfer resistances in the organic phase can be neglected (this phase consists of pure propionic anhydrite only);
- no depletion of water in the film is observed (because of its great excess);
- the reaction can be considered as a pseudo-first-order with respect to the anhydrite (because of a molar excess of water);
- maximal value of the Hatta number (defined with the pseudo-first order kinetic constant k_1 as $\mathrm{Ha} = \sqrt{k_1 D_A}/k_L$) calculated at the highest applied temperature and the catalyst concentration never exceeded the value of 0.18. So, the criterion for the slow reaction regime $\mathrm{Ha} < 0.3$ is always fulfilled. This is a correction of a conclusion obtained directly from the RC1 measurements [1], where due to uncertainties in estimation of the interfacial area

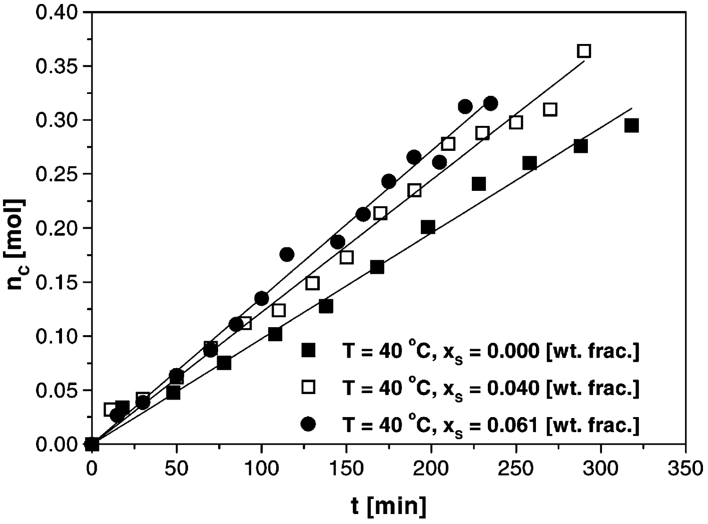

Fig. 2. Typical results obtained in the stirred cell reactor at $T_R = 40\,^\circ\mathrm{C}$.

all inaccuracies have been lumped into the kinetic term;

- kinetic constant k_1 contains the contribution of the catalyst, so in fact it should be considered as the apparent (or effective) experimental kinetic constants: $k_1 = k_{\mathrm{eff}} c_{\mathrm{W,L2}}$.

The obtained results of additional experiments performed in the stirred cell reactor has helped us to indicate uniquely the regime of the investigated hydrolysis reaction as well as to develop the kinetic expressions.

3. Conventional model of the reactor (CMR)

For the considered case (reaction slow in comparison to mass transfer, so mass transfer resistances has been neglected), according to the general theory of mass transfer accompanied with chemical reaction [4] and employing the above listed conclusions, the reaction rate in the investigated system per unit volume of the reaction mixture has been expressed as follows (see also Fig. 3):

$$\begin{aligned} r_{\mathrm{A}} &= k_{\mathrm{eff}} m_{\mathrm{A}} c_{\mathrm{A,L1}} c_{\mathrm{W,L2}} (1-\Phi) \\ &= k_{\mathrm{eff}} c^{i}_{\mathrm{A,L2}} c_{\mathrm{W,L2}} (1-\Phi) \end{aligned} \tag{2}$$

where the solubility of the anhydrite in the aqueous phase, m_{A}, is expressed as a function of the temperature and the concentration of the propionic acid in this phase [1].

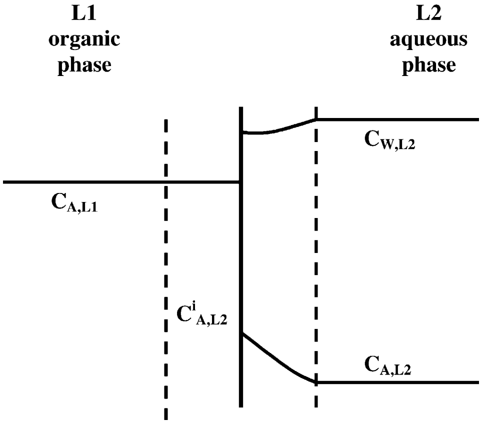

Fig. 3. Concentration profiles of the reactants close to the liquid–liquid interface.

For the detected regime; mass transfer with a slow chemical reaction, the concentration of anhydrite in the bulk of the aqueous phase is almost equal to the concentration at the interface, so the relationship $c_{\mathrm{A,L2}}/c^{i}_{\mathrm{A,L2}} \geq 0.95$ holds [5]. Therefore Eq. (2) can further be simplified giving

$$r_{\mathrm{A}} = k_{\mathrm{eff}} c_{\mathrm{A,L2}} c_{\mathrm{W,L2}} (1-\Phi) \tag{3}$$

This is equivalent to the corroboration that the reaction takes place mainly in the bulk of the aqueous phase, so the overall reaction rate in the whole reaction vessel can be estimated directly from the following relationship:

$$R_{\mathrm{A}} = k_{\mathrm{eff}} c_{\mathrm{A,L2}} c_{\mathrm{W,L2}} V_{\mathrm{L2}} \tag{4}$$

The contribution of the catalyst in the effective kinetic constant, k_{eff}, has been expressed with the acidity Hammett function H_0 [6], in terms of the H^+ ions concentration in the aqueous phase, c_{H^+} (mol/m^3). It reads as follows:

$$H_0 = 10.11 - 7.15 c_{\mathrm{H}^+}^{0.0494} \tag{5}$$

Several expressions for the effective kinetic constant have been proposed and tested in these studies. The best results have been obtained with the following relationship:

$$k_{\mathrm{eff}} = (A_1 + A_2 c_{\mathrm{H}^+}) \exp\left(\frac{E}{RT - m_{H_0}} H_0\right) \tag{6}$$

Using the presented above expressions (Eqs. (4)–(6)), the constants in Eq. (6) have been determined with a non-linear regression. The results of isothermal and batch experiments performed in the RC1 reaction calorimeter [1] have been employed. The estimated values of these constants as well as the correlation coefficient are as follows: $A_1 = 104.57\,\mathrm{m^3/(mol\,s)}$, $A_2 = 0.58\ \mathrm{m^6/(mol^2\,s)}$, $E = 73{,}244$ J/mol), $m_{H_0} = -0.051$, $r^2 = 0.997$. The derived kinetic rate Eqs. (3)–(6), with the listed above kinetic parameters, are valid within the following range of the operating conditions: $288\,\mathrm{K} \leq T \leq 313\,\mathrm{K}$, $0.0 \leq c_{\mathrm{H}^+} = 1.2 \times 10^3$, $32 \times 10^3 \leq c_{\mathrm{W,L2}} \leq 55 \times 10^3$, $0 \leq c_{\mathrm{C,L2}} \leq 5.5 \times 10^3$, $0 \leq c_{\mathrm{A,L2}} \leq 0.76 \times 10^3$, where the concentrations of the catalyst and all reactants are expressed in mol per m^3 of the aqueous phase.

For the investigated hydrolysis reaction the following equations have been proposed to model the behaviour of the stirred tank reactor:

- Molar balance for the *i*th reactant

$$\frac{dn_i}{dt} = q_{i,\mathrm{mol}} \pm R_i \qquad (7)$$

where $q_{i,\mathrm{mol}}$ (mol/s) is the molar addition rate of the *i*th reactant for the experiments performed at semibatch conditions. The above balance equation supplies the amount of each reactant in the whole reactor. The conversion rate of the anhydrite is calculated according to the kinetic relationship of Eq. (4), while the conversion/production rates for water and the propionic acid are estimated recalculating the rate R_A according to the stoichiometric equation, respectively. Notice that the conversion rate R_A is related to the actual volume of the aqueous phase, assuming simultaneously that this phase is saturated with the propionic anhydrite. Changes in the volume of organic and aqueous phases as well as changes in the concentration of the ions H^+, all causes by the reaction progress, have always been taken into account.

- Heat balance of the reactor

$$\sum_{i=\mathrm{A,C,W}} n_i c_{\mathrm{p},i} \frac{dT_R}{dt} = Q_R - Q_F - Q_L - Q_D \qquad (8)$$

where the powers Q_i are estimated as it is stated in nomenclature.

In the considered case the mass transfer resistances in both, organic and aqueous, phases could be neglected. The overall rates of the anhydrite conversion, the predicted with the elaborated kinetic model $R_{A,\mathrm{mod}}$ and the experimentaly measured in the RC1 reaction calorimeter, $R_{A,\mathrm{exp}}$ [1] have been compared to verify the proposed kinetic expressions, e.g. see Fig. 4. It is evident from the diagram that the proposed model is able to predict the behaviour of the reactor at different reaction temperature. Quite good accuracy of the elaborated kinetic model can be observed at other operating conditions.

It has been explained that, because the reaction takes place mainly in the bulk of the aqueous phase (see Fig. 3); therefore the volume increase of this phase, taking place during the reaction progress, significantly affects the observed overall conversion rate of the anhydrite.

Notice that the elaborated kinetic expressions are entirely based on the experimental data, not on a true or assumed reaction mechanism. Determination of the kinetic model based on the real mechanism of the hydrolysis reaction was impossible, mainly due to

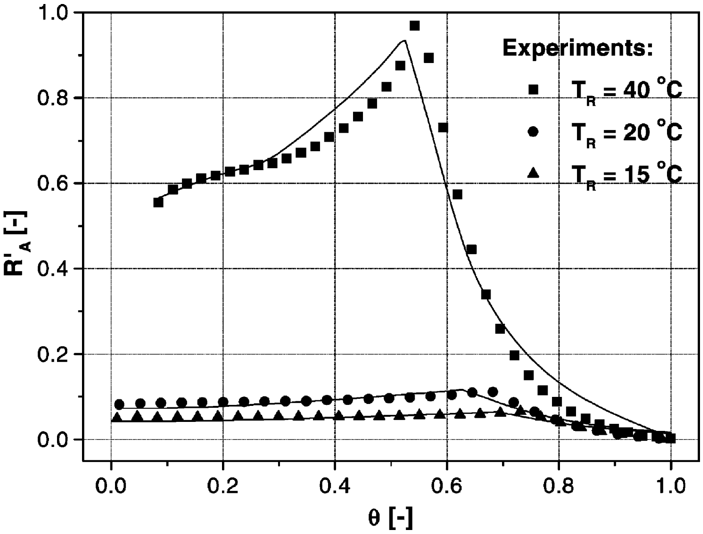

Fig. 4. Comparison of the dimensionless anhydrite conversion rates, R'_A: experimental (points) and predicted with the conventional model of the reactor (lines). Experimental conditions: experiments performed in the RC1 reaction calorimeter, $V = 2\,\mathrm{dm}^3$, stirrer speed $N = 600$ rpm, initial molar fraction of the catalyst $X_S = 0.0118$, initial volume fraction of the organic phase $\Phi = 0.322$. The true conversion rates can be calculated as: $R_A = R'_A R_{A,\mathrm{max}}$, where $R_{A,\mathrm{max}} = 0.004706$ mol/s.

difficulties in qualitative and quantitative analysis of all appearing intermediates. For this reason the effective kinetic constant, k_{eff}, which includes the influence of the catalyst on the reaction rate, has been introduced.

4. Neural model of the reactor (NMR)

Models based on artificial neural networks exhibit a rule following behaviour without containing any explicit representation of this rule [2]. Such kind of models is based on experimental data only. In the proposed approach the global variables, such as the concentrations of reactants and catalyst in the whole reactor $X_i = n_i / \sum n_i$ (not in each phase separately) as well as the temperature of the reacting mixture T_{R}, have been used to define uniquely the state of the reacting system. The overall conversion rate of the anhydrite R_{A} describes here the rate of changes in the system. Such an approach, where the reacting heterogenous liquid–liquid systems are described with the neural net based on the global variables, has been successfully applied before [2,3]. So, the following configuration of the input–output variables has been here used

$$R'_{\mathrm{A}} = f(T'_{\mathrm{R}}, X_{\mathrm{A}}, X_{\mathrm{C}}, X_{\mathrm{W}}, X_{\mathrm{S}}) \quad (9)$$

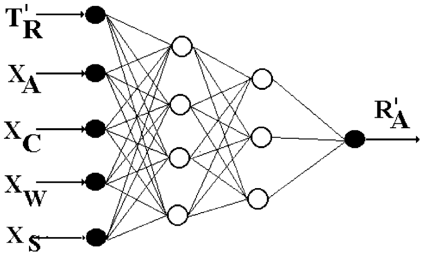

Fig. 5. Schematic diagram of the neural network applied to model the reaction kinetics.

where the conversion rate and the temperature are normalized as it is stated in nomenclature.

The neural network, shown in Fig. 5, has been employed to approximate the unknown function *f*, which converts the vector of state variables into the overall conversion rate of the anhydrite. Notice, that with such an approach no a priori knowledge on the reaction mechanism and system properties (e.g. distribution of reactants among the phases) is needed to model the reactor. The function *f* can be here considered as mathematical superposition of all functions, which describe the reaction kinetics as well as characterize the thermodynamic and physico-chemical properties of the system.

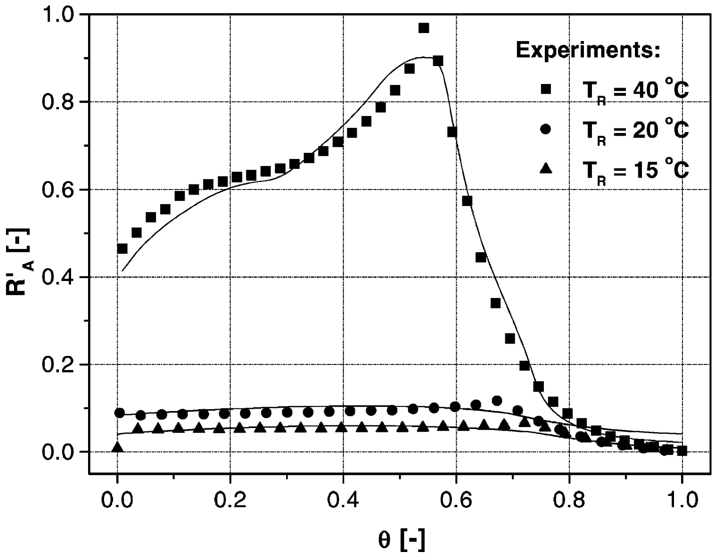

Fig. 6. Comparison of the dimensionless anhydrite conversion rates, R'_{A}: experimental (points) and predicted with the neural model of the reactor, NMR (lines). Experimental conditions as in Fig. 4.

The net has been trained with a learning data set, which was extracted from the experimental results. To this end several experimental runs, carried out at the isothermal and batch operating conditions in the RC1 reactor [1], have been taken. The set containing as many as 2040 learning patterns has been presented to the network to determine the network parameters (weights). Further the trained net has been implemented into the conventional model equations (see Eqs. (7) and (8)), supplying the conversion rate at any conditions. For the net consisting of one hidden layer the following relationship is employed to calculate the output signal

$$y_{\mathrm{k}} = \sigma\left(\sum_{i=0}^{K} W_{\mathrm{k}i}^{(\mathrm{o})}\sigma\left(\sum_{j=0}^{N} W_{ij}^{(\mathrm{h})} x_j\right)\right) \qquad (10)$$

where the vector of the input signals $\boldsymbol{X} = [T'_{\mathrm{R}}, X_{\mathrm{A}}, X_{\mathrm{C}}, X_{\mathrm{W}}, X_{\mathrm{S}}]$, while the single output signal $\boldsymbol{Y} = [R'_{\mathrm{A}}]$.

Such a model, where the structure of the conventional model is kept and the neural net approximates only the unknown part of model, is called the hybrid model [2].

The neural net represents here not only the kinetics of the catalytic hydrolysis reaction, but in a general case also mass transfer phenomena are taken into account. For this reason the stirrer speed, N, should be taken as the additional input variable in Eq. (9) [2]. It has been found that for the considered case this variable can be skipped at a sufficiently high stirring rate.

Accuracy of the elaborated hybrid neural model of the reactor (NMR) can be assessed in Fig. 6, where a comparison of the experimental and predicted conversion rates are shown. Also with the neural model quite good accuracy of predictions, comparable with that obtained with the conventional model of the reactor (CMR), is observed.

5. Summary

Two modelling methods have been proposed and tested. The first one based on the theory of mass transfer with simultaneous catalytic reaction and the second one based on application of neural networks. From the experiments carried out in the stirred cell reactor it has been found that the investigated hydrolysis reaction is a slow reaction and it takes place mainly in the bulk of the aqueous phase. Then the kinetic expressions, taking account the influence of the catalyst on the reaction rate, as well as the reactor model have been elaborated and tested.

In parallel the second model employing the neural net has been developed. In this approach any a priori knowledge on the reaction kinetics has not been used and the net has been trained basing on the experimental data only. So, all unknown kinetic relationships have been represented with one neural net, which approximates the function being a mathematical superposition of these relationships.

The accuracy of predictions are for both methods comparable. In the case of neural modelling much less experimental effort is required, because special and time consuming experiments carried out to detect the reaction regime, significance of mass transfer phenomena, distribution of reactants between the reacting phases or to determine the specific interfacial area are usually not necessary.

Acknowledgements

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