Transposition of an exothermic reaction to a continuous intensifies reactor

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ABSTRACT

The aim of this study is the transposition of an exothermic reaction carried out in a batch reactor to a continuous intensified one. The esterification of propionic anhydride with 2-butanol was selected as a case study. The decomposition reactions of the reactants and the products were studied by DSC whereas the heat of solution of the two reactants were determined by isothermal calorimetry. An extensive experimental programme was then carried out using the Mettler RC-1 reaction calorimeter in order to characterize the thermal and kinetic behaviour of the reaction under isothermal conditions. The thermal conversion was compared with the molar conversion obtained by simulation based on a kinetics from the literature. Optimal and safe operating conditions were eventually defined for a continuous heat exchanger type reactor. Dedicated software was used to assess the feasibility of the esterification in this reactor by calculating the conversion and temperature profiles along the process and utility lines.

Keywords: process intensification, chemical reactor, safety, esterification, simulation.

NOTATIONS

Ea_i : activation energy (J.mol^{-1})

C_{anhp} : propionic anhydride concentration (mol.L^{-1})

C_{2b} : 2-butanol concentration (mol.L^{-1})

C_{acP} : acid propionic concentration (mol.L^{-1})

k_i : reaction rate constant (L.mol^{-1}.s^{-1})

ko_i : frequency factor

R : gas constant (J.K^{-1}.mol^{-1})

1 INTRODUCTION

In the event of loss of control of the cooling system of a reactor during the process, exothermic reactions can lead to thermal runaway, which can in turn lead to loss of confinement of toxic and/or flammable substances. Safety thus is an important operational objective when processes are developed or optimised. Most processes in the specialty

chemical industry are batch or semi-batch operations. These types of reactors can offer large production volumes and are quite flexible. However controlling the temperature and heat transfer becomes more difficult as the size of the reactor increases (1). New perspectives are appearing by process intensification: that is, miniaturised and continuous technologies developed to attain better heat transfer and safer conditions. The aim of this work is to study how an exothermic reaction can be carried out in a new compact, intensified, continuous, multifunctional reactor. This pilot reactor is composed of three sections made up of a 6-plate sandwich heat exchanger. The main advantage of this type of reactor is in coupling high heat exchange capacities with plug flow behaviour of the process fluid in a modular apparatus. This arrangement offers a better heat transfer area, heat transfer coefficient and temperature control. The esterification of propionic anhydride by 2-butanol was chosen as a model reaction. A large set of experimental data is available and has been used to characterise the thermodynamic and kinetic behaviour of the reaction. The non-catalysed reaction exhibits second-order kinetics. An autocatalytic type behaviour is observed when sulphuric acid is added to the reaction mixture as catalyst. Moreover a specific software tool has been used to estimate the process behaviour during the synthesis as well as to determine the optimal operating conditions for safety control. The simulation algorithm is based on a complex dynamic model of the intensified reactor. It gives as results the concentration and temperature profiles along the reaction line.

2   CASE STUDY: ANHYDRIDE PROPIONIC ESTERIFICATION

2.1   Introduction

The esterification of propionic anhydride by 2-butanol leads to butyl propionate and propionic acid (see fig.1). This synthesis is exothermic: Ubrich et al (2) found a value of $\Delta Hr = -62.5 \pm 1$ $kJ.mol^{-1}$. The reaction is relatively simple to carry out in a homogeneous liquid phase. This reaction thus constitutes a relevant case in the studies relating to the assessment of the chemical risk (3).
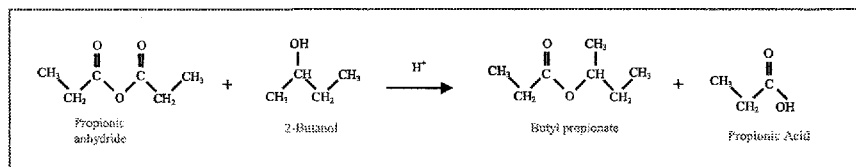

Figure 1.   Reaction scheme for the esterification of propionic anhydride by 2-butanol

According to Galvan et al. (4), the reaction rate is a function of catalyst: without catalyst the reaction is second-order but has a kind of autocatalytic behaviour when sulphuric acid is present in the reaction mixture.

2.2   Reaction rate without catalyst

When the reaction is performed with no strong acid as catalyst, the reaction is slow and follows second-order kinetics, first order in each reactant (4):

$$r = k_1 \cdot C_{anhp} \cdot C_{2b} \quad [\text{eq. 1}] \qquad \text{with} \qquad k_1 = 5.36178.10^7 \cdot \exp(-80478.64/(R \cdot Tr)) \quad [\text{eq. 2}]$$

2.3 Reaction with sulphuric acid as catalyst

In the presence of sulphuric acid, Zaldivar et al (5) made the following observations:

- The reaction rate seems to be proportional to the acid concentration,
- The reaction rate increases with propionic acid concentration, causing a kind of autocatalytic behaviour (see equations [eq. 4] and [eq. 5]),
- After having reached a certain concentration, propionic acid no longer influences the reaction rate.

Since the various theoretical reaction pathways are complex, an empirical model was devised assuming the existence of two catalysts ($cat1, cat2$) (6). The transformation of the initial catalyst was developed by taking into account acidity function (7).

Thus, the reaction rate of the main reaction can be written as (4) :

$$r_1 = (k_1 + k_2 \cdot C_{cat1}) \cdot C_{anhp} \cdot C_{2b} + k_3 \cdot C_{cat2} \cdot C_{anhp} \quad \text{[eq. 3]}$$

The reaction rate due to the formation of the second catalyst is also taken into account:

$$r_{cat} = k_4 \cdot 10^{-Hr} \cdot C_{cat1} \cdot C_{2b} \quad \text{[eq. 4]}$$

Lastly, the expression of the acidity function is:

$$Hr = -(p_1 \cdot C_{cat1} + p_2 \cdot C_{acP}) \cdot \left(p_3 + \frac{p_4}{Tr} \right) \quad \text{[eq. 5]}$$

Reaction rate constants follow Arrhenius law:

$$k_i = ko_i \cdot \exp(-Ea_i / (R \cdot Tr)) \quad \text{[eq. 6]}$$

The kinetic parameters are given in table 1.

Table 1. Kinetic parameters equations from [eq. 1] to [eq. 5]. (5)

i	ko_i	Ea_i (J.mol^{-1})	p$_i$
1	5.36178 10^{7} [a]	80478,64	2,002.10^{-1}
2	2.8074 10^{10} [b]	79159,5	3,205.10^{-2}
3	3.9480 10^{10} [a]	69974,6	-21,3754
4	1.4031 10^{8} [a]	76617,2	12706

[a] L.mol^{-1}.s^{-1} [b] L^2.mol^{-2}.s^{-1}

3 PRELIMINARY CALORIMETRIC STUDIES

3.1 Microcalorimetry DSC

DSC (Differential Scanning Calorimeter) was used to study the thermal stability of various samples. Only a few milligrams of each were needed.

A first series of experiments was carried out on the pure reagents and the reaction products. The samples were heated from room temperature to 400 °C at a rate of 5 °C/min. Table 2 gives the onset temperature and the temperature at the peak as well as the energy released during the decomposition. These values are compared with the reference data bases available in the literature. Following the same operating conditions, a complementary test was carried

out using a mixture of 1.10 mg for each of the two reagents. The DSC curve obtained is shown in Figure 2: heat flow released during experiment (expressed in $W.g^{-1}$) is plotted against temperature (expressed in °C).

Table 2. Results of the DSC experiments on pure products.

Pure Products	Mass (mg)	Tonset[a] (°C)	Tmax[b] (°C)	ΔH_{dec}[c] (J/g)	Tonset$_{bib}$[d] (°C)
2-Butanol	2.54	183.5	187.0	- 42	184.6
Propionic anhydride	2.22	~ 155	167.5	- 47	154
Propionic acid	1.82	188.4	209.8	- 35	186.6
Butyl Propionate	2.05	~ 170	174.2 – 209.2	- 70	----

[a] Tonset : temperature of decomposition (°C)

[b] Tmax : temperature corresponding to the maximum energy released by the decomposition(°C)

[c] ΔH_{dec} : energy of decomposition ($J.g^{-1}$)

[d] Tonset$_{bib}$: temperature of decomposition, data from bibliography (8).

The first peak gives the energy released by the main reaction and the second area corresponds to the energy of decomposition. According to table 2 and figure 2, the temperature of the reaction mixture must not exceed 150 °C to avoid any decomposition.
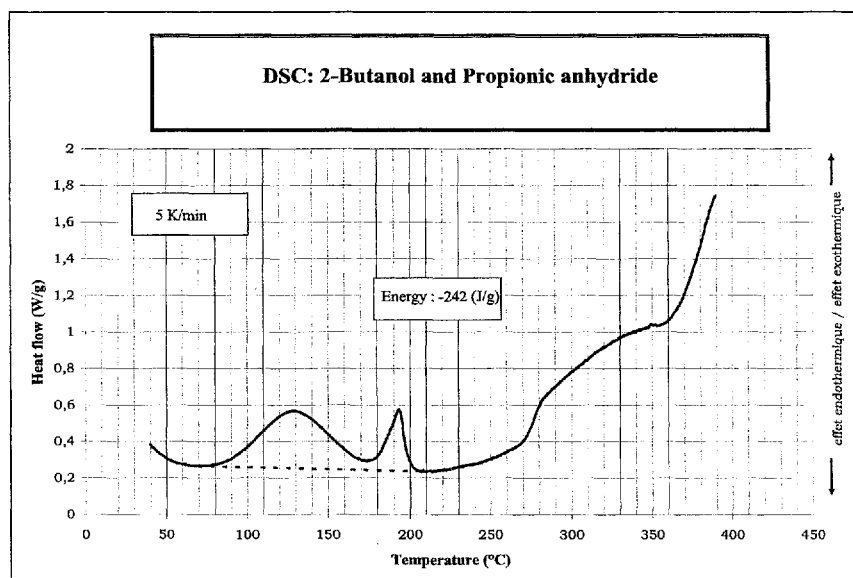

Figure 2. Microcalorimetry DSC for a mixture of propionic anhydride and 2-butanol

3.2 Isothermal Calorimetry C80

Alos et al. (9) noticed an endothermic effect when propionic anhydride is mixed with 2-butanol. The C80 isothermal calorimeter was used to determine the heat of solution. 2.10^{-3} mol of each reactant was placed in the calorimeter in separate compartments. After the calorimeter was stabilised at 40 °C, the reactants were mixed together inside the calorimeter. The non-catalysed esterification reaction rate is very slow, thus the heating effect observed is due to the solution. The results show that the enthalpy of solution is 22.1 $J.g^{-1}$.

4   KINETIC MODELLING AND SIMULATION

The kinetic model is essential in predicting the behaviour of the continuous intensified reactor. A computer simulation program was used to validate the kinetic model suggested in the literature and detailed in paragraph 2.

The standard 2 litre Mettler RC-1 reactor in the semi batch mode was modelled. The reactor was filled with the specified quantity of 2-butanol with or without sulphuric depending on the experiment. The simulation takes into account the step of adding the second reagent (propionic anhydride) and the second step where the reaction was allowed to go to completion after the addition. The following assumptions were made:
- The mixture temperature is maintained constant by the jacket regulation,
- The system is agitated perfectly: temperature as well as chemical and physical properties of reaction mixture are uniform,
- Reaction mixture is a homogenous liquid phase,
- The variation of volume due to the mixture and dilution are neglected.

The dynamic formulation of the model leads to a system of differential and algebraic equations. The simulation produces the concentration profiles and the volume vs time.

5   EXPERIMENTAL STUDY IN THE RC-1 CALORIMETER

5.1   Experimental procedure
Ten experiments were carried out in the reaction calorimeter RC1 for jacket temperatures ranging from 30 to 70 °C and sulphuric acid concentrations ranging from 0.3 % to 0.8 % (expressed as a percentage of the weight of butyl alcohol). The 2-butanol was introduced into the reactor as well as the proper quantity of sulphuric acid. The stirring speed was fixed at 200 RPM. When the mixture temperature was equilibrated, 6.86 mol of propionic anhydride was pumped into the reactor at a constant flow rate over a 15 minutes period. During the reaction, the reaction temperature was maintained constant by controlling the temperature jacket. However, the second reagent was added in several times when the instantaneous heat release was likely to exceed the cooling capacity of the calorimeter.

5.2   Experimental results
The results were recorded by the WinRC® (10) software. During acquisition, it records on line all the pertinent thermal parameters. After the experiment, it calculates the heat flux due to the reaction as a function of time (Qr in W) and calculates the enthalpy of reaction for a specific area chosen by the user (ΔH_r en kJ.mol^{-1}). The software also calculates the thermal conversion (X en %) within the integration limits.

5.3　Kinetic validation

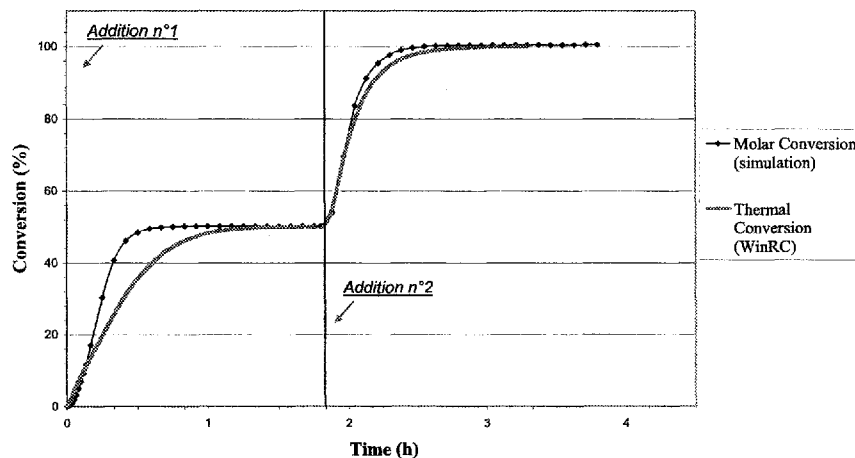**Figure 3.　Conversion profiles results from simulation and WinRC® (Tr=50°C, w_suf=0,3%)**

If we assume that heat released is due only to the main reaction, thermal conversion can be compared with molar conversion. Thus, the experimental thermal conversion is compared with the molar conversion obtained by simulation. An example is given in figure 3. The curves are in good agreement. We thus deem the kinetic model valid.

6　ESTERIFICATION IN THE CONTINUOUS INTENSIFIED REACTOR

6.1　Heat-Exchanger/Reactor OPR (Open Plate Reactor)

The thermal and kinetic behaviour of the esterification of propionic anhydride by 2-butanol has now been characterized. The objective is then to study the operating conditions of this reaction in the heat/exchanger OPR (Open Plate Reactor) developed by Alfa Laval Vicarb. The OPR is a small, multifunctional, continuous reactor which is built like a multi-plate heat exchanger divided into sections (11). As shown in figure 4, each section is made up of a reactive plate where the reaction mixture flows, surrounded by two cooling plates containing the utility fluid. This new concept of "reactor/ heat exchanger" makes it possible to perform complex chemical reactions with a very accurate thermal control. The OPR appears particularly well-suited to process intensification, as it makes possible an increase of reactant concentration and a reduction of solvent consumption at the same time. The pilot is composed of three sections and has a total capacity of 1.5 L. Previous studies have shown that the OPR can be consider as plug flow for a flow-rate of reagents equal to 50 L.h^{-1}. The operating system allows a maximum cooling fluid flow-rate of 5 m^3.h^{-1}.
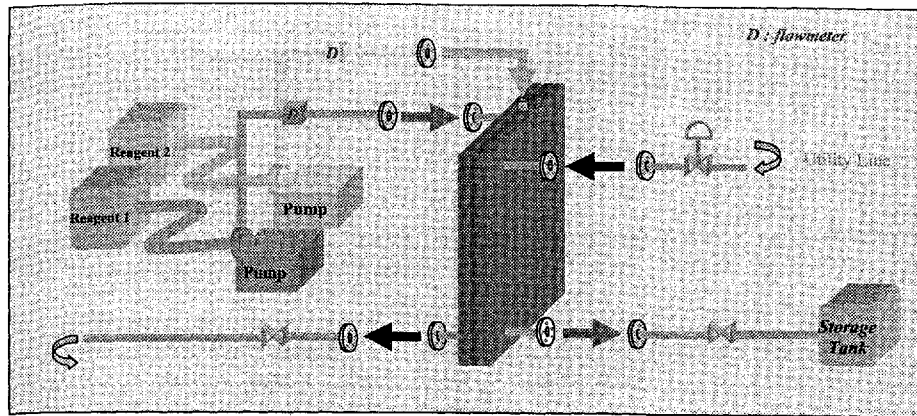
Figure 4. Simplified representation of the "heat-exchanger/reactor" OPR

6.2 Data processing tool

A specific computer simulation program has been developed in paralleled to the development of the reactor. The software takes into account the specific geometry of the intensified reactor and provides the temperature profiles of the cooling fluid as well as the temperature profile and conversion profile along the reaction line. Preliminary reaction tests carried out on the OPR have been used to validate the simulation framework. In this way, the more interesting results have been obtained from the study of the oxidation of sodium thiosulfate by hydrogen peroxide since this reaction presents fast kinetics. By means of temperature records all along the reactor and of the final reaction yield, like showed in figure 5, the thiosulfate oxidation reaction allows to successfully validate the simulation framework.
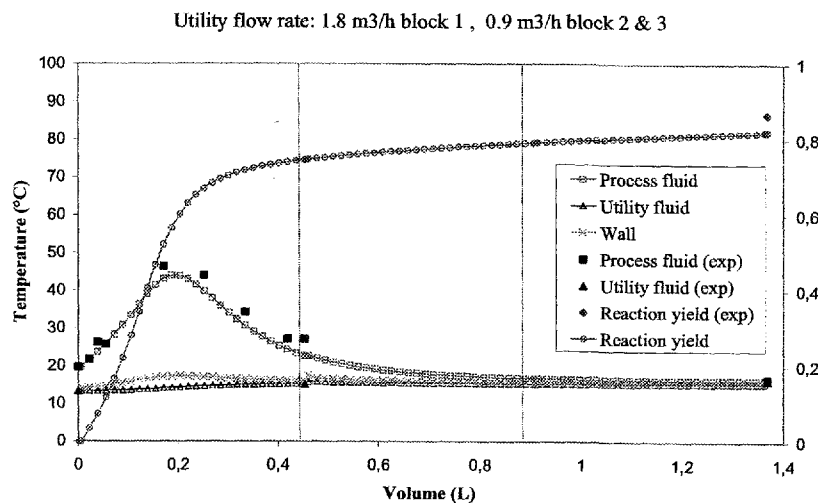

Figure 5. Temperature profiles comparison: simulation and experimental results

6.3 Specific simulations

The use of the data processing tool makes it possible to asses the feasibility and potential of carrying out the esterification in this reactor. The main parameters to be modified are the initial sulphuric acid concentration, inlet temperature and cooling fluid flow-rate. It is then possible to determine operating conditions in terms of molar conversion while maintaining proper heat transfer and an overall temperature lower than 100 °C. One result is presented in figure 6 and shows that for a reactor composed of three sections, corresponding to a 3 minute residence time, conversion can reach 45 % for this reaction.
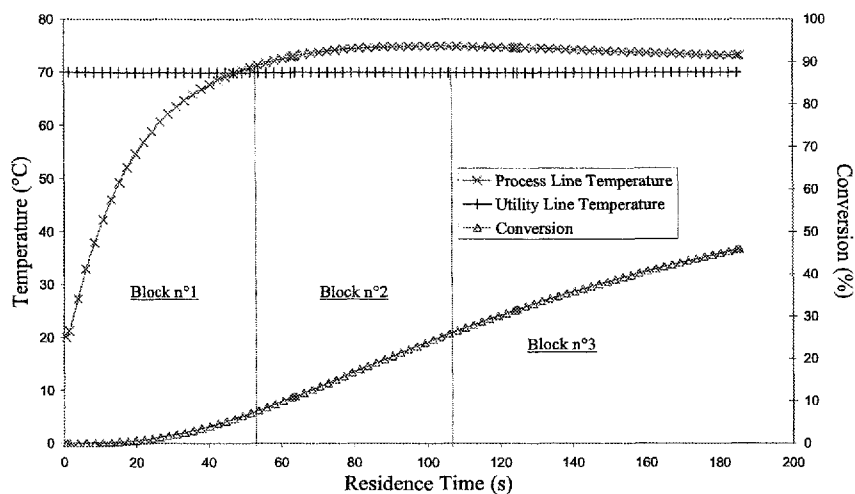

Figure 6. Temperature profiles and molar conversion along the reactor OPR for the propionic anhydride esterification

7   CONCLUSION

A kinetic model taken from the literature for the production of butyl propionate by reacting propionic anhydride with 2-butanol has been validated by experiments done in a 2 litres, Mettler RC-1 semi-batch reaction calorimeter. The kinetic model was then used as input to a computer simulation of an Open Plate Reactor to determine the feasibility of using this new compact continuous reactor to produce butyl propionate. The operating conditions were optimised using the results of the computer simulations and show that the transposition is indeed feasible. Experimental verification in the OPR pilot Reactor are under way.

ACKNOWLEDGEMENT

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