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Intensification of Ester Production in a Continuous Reactor

Sebastien Elgue
Audrey Devatine
Laurent E. Prat
Patrick Cognet[□]
Michel Cabassud
Chrisitophe Gourdon
Fabrice Chopard¹

Institut National Polytechnique de Toulouse
Université de Toulouse
Laboratoire de Génie Chimique UMR CNRS 5503

¹ Alfa-Laval Vicarb
B.P. 200, 38522 Saint Egrève Cedex, France

1. Introduction

In the field of fine chemicals or pharmaceuticals, from flexibility and multifunctional considerations, batch reactor constitutes the standard production unit. Because of heat transfer restriction and in order to dissipate reaction heat, productions are often carried out in diluted medium and operated in semi-batch mode. Such issues explain the recent increasing interest in the batch to continuous

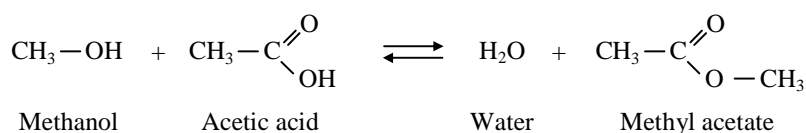
switching (Stitt, 2002) and in process intensification (Green et al., 1999, Hendershot, 1999, Stankiewicz et al., 2002). In this purpose, new continuous devices based on the plug-flow reactor principle have been developed. In fact, plug-flow reactor represents the exact continuous substitution of a pure batch reactor. To operate as pure batch, these devices require both enhanced heat transfer and mixing performances. In this way, a new kind of continuous reactor has been studied: the heat exchanger reactor (Riley et al., 1998, Phillips et al., 1997).

A continuous heat exchanger reactor, the “Open Plate Reactor (OPR)” has been developed by Alfa Laval Vicarb. It allows complex chemical reactions to be performed with a very accurate thermal control, by combining high thermal capacity with improved mixing conditions (Prat et al., 2005). This reactor therefore appears particularly suited to process intensification as it allows, at the same time, enhanced energy efficiency, improved productivity (increase of reactants concentration) and reduced impact on the environment (reduction of solvent consumption and therefore of separation steps).

According to its thermal and mixing performances, the open plate reactor is a promising apparatus for fast and highly exothermic systems as it allows non-classical temperature and concentration domains to be considered. Different experimental studies dealing with acid/base or sodium thiosulfate oxidation reactions highlight this statement (Prat et al., 2005). The aim of the present paper is to show that such reactors could also offer interesting perspectives for slow reactions by intensifying operating conditions. Production of methyl acetate, an esterification class reaction, has been considered to this purpose. Because operating conditions are different than those classically used, a kinetic experimental study has been realised and kinetic model proposed.

2. Methyl acetate production

Methyl acetate is produced via the esterification of methanol with acetic acid. The reaction is a homogeneous liquid phase process, where the limiting conversion of the reactants is determined by an equilibrium, according to the following reaction scheme:



The reaction rate is very slow and is generally enhanced with an added homogeneous catalyst such as sulphuric acid (H₂SO₄). In fact, the initiating step

in the reaction mechanism is the protonation of the carboxylic acid. Kinetics of the reaction is well-known for a long time (Rolfe et al., 1934, Hilton, 1939) and have recently received growing interest since the development of reactive distillation (Agreda et al., 1990, Pöpken et al., 2000, Bonaillie et al., 2001, Balland et al., 2002). Considering the heat generated, the reaction is assumed athermic.

Relating to reaction intensification, as we aim to work in a specific domain in terms of operating conditions such as temperature, pressure and catalyst concentration, some uncertainties appear with regards to kinetic models of literature. To solve this issue, a new model has been determined from experimental studies carried out at atmospheric pressure with different temperature and catalyst concentrations (see table 1).

Table 1: operating conditions of kinetic experiments

Temperature	Catalyst concentration		
	3 mL.L ⁻¹	6 mL.L ⁻¹	10 mL.L ⁻¹
20°C			x
33°C			x
43°C		x	x
48°C	x	x	x
53°C	x	x	x
57°C	x	x	x

The experimental device consists of a stirred jacketed lab scale glass batch reactor (2 L) with an overhead condenser. The jacket is provided by water circulating in a close loop from a thermostated bath that allows the reactive medium temperature to be kept constant. After reactants addition, samples are withdrawn at close time intervals and analysed by gas chromatography (Varian GC 3800) in order to determine the reactive medium composition. A specific column (Cpsil 5 CB 50 m x 0.53 mm i.d. - 5 µm film thickness) and Flame Ionization Detector (FID) have been used to detect and separate each organic component. Unfortunately, water can not be detected and propanol has to be used as internal standard.

In stoichiometric conditions, the equilibrium limits conversion to 66 %, as methanol is a primary alcohol. In order to reach high conversion level, experiments have been carried out with acetic acid excess (1.2 L of acetic acid and 0.3 L of methanol). As methanol (reactant) and methyl acetate (product) compositions are followed according to time, conversion may be estimated by

two ways (equations 1 and 2). A comparison of each allows the molecular balance to be verified, as shown on figures 1 and 2.

$$Conv = \frac{n_{MeOH}^0 - n_{MeOH}}{n_{MeOH}^0} \times 100 \quad \text{estimation from methanol} \quad (1)$$

$$Conv = \frac{n_{Acetate}}{n_{MeOH}^0} \times 100 \quad \text{estimation from methyl acetate} \quad (2)$$

with: Conv : reaction conversion (%)
 n_{MeOH}^0 : initial molar holdup of methanol (mol)
 n_{MeOH} : molar holdup of methanol detected at a given time (mol)
 $n_{Acetate}$: molar holdup of methyl acetate detected at a given time (mol)

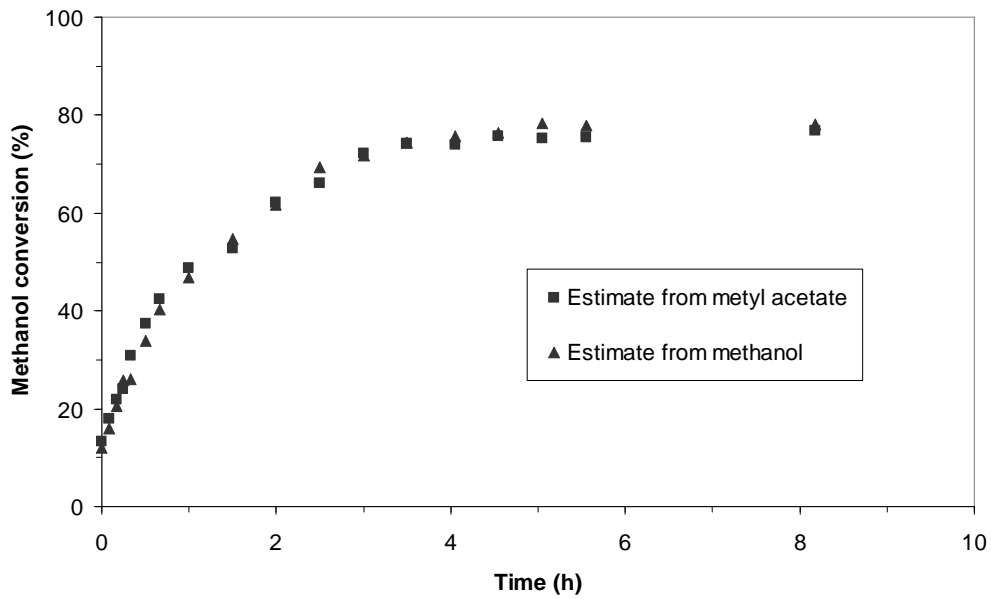


Figure 1: kinetic experiment at 48°C with 6 mL.L⁻¹ of catalyst

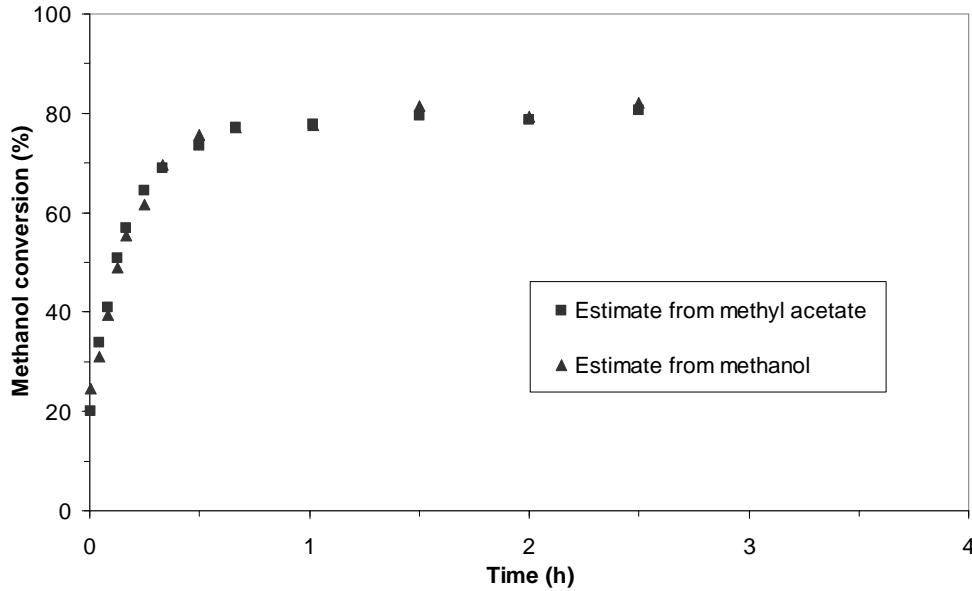


Figure 2: kinetic experiment at 57°C with 10 mL.L⁻¹ of catalyst

A model of methyl acetate esterification has been investigated in order to take into account the influence on the reaction rate of temperature and catalyst amount. Stoichiometry of the reactions (esterification of acetic acid with methanol and hydrolysis of methyl acetate) is assumed to be as described in literature (Agreda et al., 1990, Pöpken et al., 2000, Bonaille et al., 2001). An Arrhenius law is applied to model kinetics, assuming that catalyst concentration presents a linear influence on reaction-rates according to literature (Bonaille et al., 2001):

$$r = k_0^1 \exp\left(-\frac{E_a^1}{RT}\right) [\text{CH}_3\text{COOH}][\text{CH}_3\text{OH}] - k_0^2 \exp\left(-\frac{E_a^2}{RT}\right) [\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}] \quad (3)$$

with:

- r: reaction rate (mol.m⁻³.s⁻¹. $[\text{H}_2\text{SO}_4]$)
- E_a: activation energy (J.mol⁻¹)
- k₀: pre-exponential factor (m³.mol⁻¹.s⁻¹. $[\text{H}_2\text{SO}_4]$)
- R: universal gas constant (J.K⁻¹.mol⁻¹)
- T: temperature (K⁻¹)
- superscript 1: related to esterification
- superscript 2: related to hydrolysis

The kinetic parameters obtained from our set of experiments (see table 2) show a more important sensitivity to temperature related to a higher activation energy for both esterification and hydrolysis. Moreover and unlike literature modelling (Bonaille et al., 2001), such activation energies reveal a slight dependence on temperature of the equilibrium constant.

Table 2: estimated kinetic parameters compared to literature ones

Kinetic parameters	Pre-exponential factor ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{ml}^{-1} \cdot \text{L}$ of H_2SO_4)		Activation energy ($\text{J} \cdot \text{mol}^{-1}$)	
	Esterification	Hydrolysis	Esterification	Hydrolysis
New model	4.21	0.322	53800	52580
Cited Literature	0.055	0.011	41800	41800

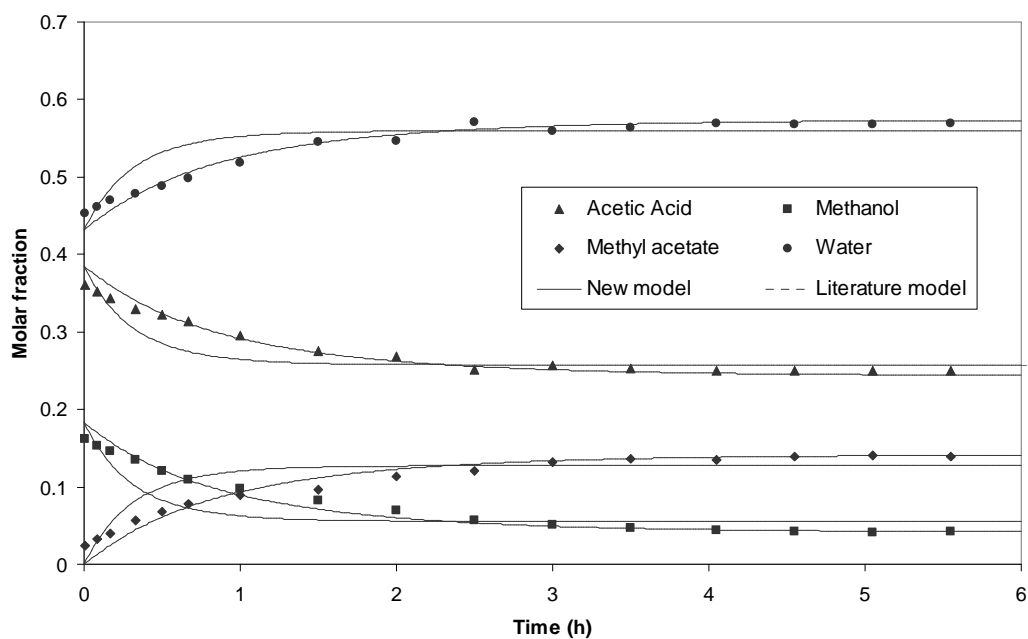


Figure 3: model validation on experiment at 48°C with 6 mL.L⁻¹ of catalyst

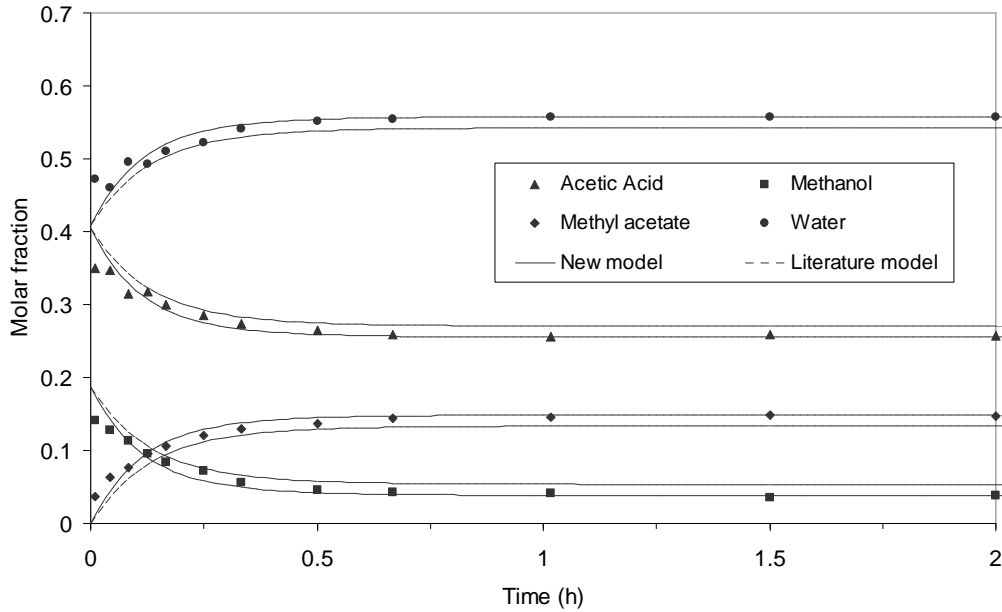


Figure 4: model validation on experiment at 57°C with 10 mL.L⁻¹ of catalyst

In order to demonstrate the accuracy of the model, evolutions of the reactive medium composition have been compared to models prediction (figures 3 and 4). The good agreement observed at different levels of temperature and catalyst concentration confirms the validity of the new modelling in term of reaction rate formulation and in term of parameters estimation.

In order to grasp the differences between literature models and the new one, a comparison of the related reaction constants according to temperature (equation 4) has been performed on figure 5. Relating to the new model, such comparison shows different values of the reaction rate and a higher influence of temperature. However, all models appear to converge on the same value for temperature in a 60-70°C range, that corresponds to standard operating conditions of reactive distillation at atmospheric pressure (boiling point at atmospheric pressure is equal to 57°C for methyl acetate and to 65°C for methanol) which have been recently studied in detail. Such considerations back up the confidence that can be placed in the present model at standard and also new investigated operating conditions.

$$k = k_0^i \exp\left(-\frac{E_a^i}{RT}\right) \quad (4)$$

with: k : reaction constant ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \cdot [\text{H}_2\text{SO}_4]$)
 E_a : activation energy ($\text{J} \cdot \text{mol}^{-1}$)
 k_0 : pre-exponential factor ($\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \cdot [\text{H}_2\text{SO}_4]$)

R: universal gas constant ($J.K^{-1}.mol^{-1}$)
T: temperature (K^{-1})
superscript i: related to the considered reaction

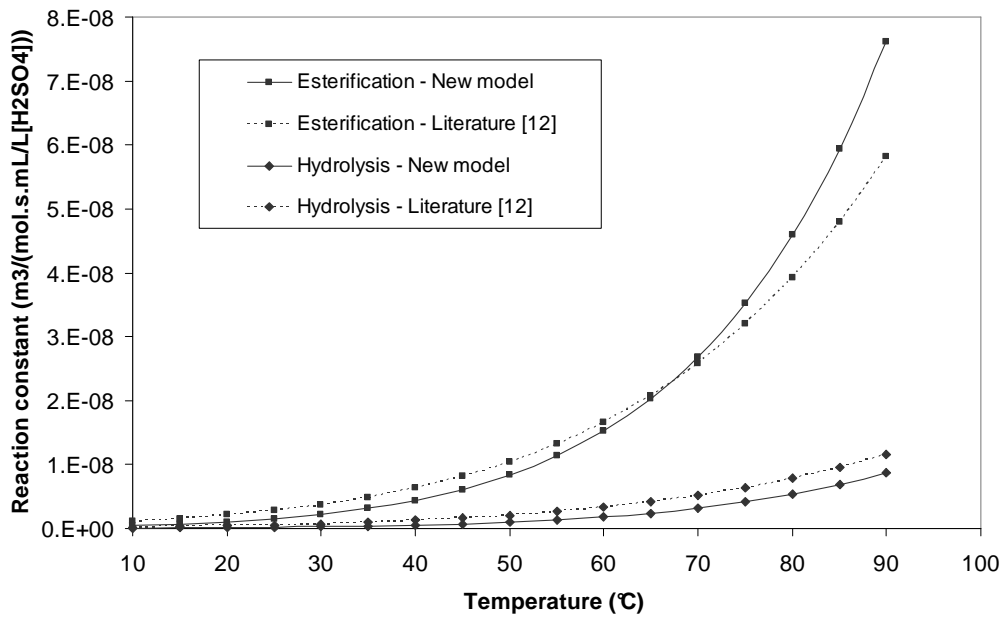


Figure 5: comparison of reaction constants according to modelling

3. Continuous reactor description

The “Open Plate Reactor” developed by Alfa Laval Vicarb is based on a modified heat exchanger design and consists of a modular structure built by the stacking of different plates related to the circulation of reaction medium and utility fluid. Some specific flow inserts inside plates enhance the mixing and residence time and guarantee good heat transfer capacity (Chopard, 2001, Chopard, 2002, Bouafi et al., 2004).

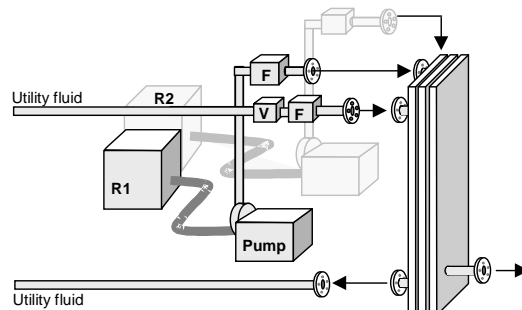


Figure 6: pilot plant

The pilot reactor used in the present study consists of three blocks (each block is composed of one reactive plate surrounded by two utility plates) with the following flow configuration: co-current for the first and third, counter-current for the second. Two loops ensure the introduction of reactants inside the reactor: main loop (R1) and secondary loop (R2) that offers the ability of multiple injection points. In the frame of the present study, as reaction is slow and athermic, one single secondary injection located at the reactor beginning has been considered. The range of the standard operating conditions extends from 20 to 200 L.h⁻¹ for the process fluid (R1 + R2) and from 0.2 to 10 m³.h⁻¹ for the utility fluid. The nominal operating conditions of the pilot plant are about 50 L.h⁻¹ for the process fluid that ensures at the same time good mixing of the reactants and enhanced thermal performances (Prat et al., 2005).

Temperature measurement facilities are implemented all along reactive and utility lines in order to provide temperature profiles: 10 sensors located on the reactive side and 3 sensors on the utility one. As reaction is assumed to be athermic, the temperature profile of the reactive medium consists of reactants heating. Therefore only the beginning part of the reactor requires numerous temperature records. Consequently, thermocouples of the reactive side are mainly set-up at the reactor beginning, in the first block (see table 3).

Table 3: location of temperature sensors

Sensors	Location related to process fluid channel	
	Traversed volume (L)	Time to reach thermocouple at 50 L.h ⁻¹ (s)
<i>Process fluid</i>		
Inlet	0.0	0.0
Block 1 – Th. A	0.0237	1.7
Block 1 – Th. B	0.0405	2.9
Block 1 – Th. C	0.0573	4.1
Block 1 – Th. D	0.1747	12.6
Block 1 – Th. E	0.2586	18.6
Block 1 – Th. F	0.3425	24.7
Block 1 – Th. G	0.4264	30.7
Outlet block 1	0.4600	33.1
Outlet block 3	1.3800	99.4
<i>Utility fluid</i>		
Inlet	0.0	0.0
Outlet block 1	0.4600	33.1
Outlet block 3	1.3800	99.4

4. Intensification methodology

The aim of the present study is to show the feasibility of high conversion esterification in a new concept of continuous reactor. As methyl acetate production is very low in batch operation (from about 1 to more than 24 hours according to temperature and catalyst concentration), the reaction needs operating conditions to be intensified in a continuous operation perspective. To achieve this goal and according to batch experiment results (see section 2) the influence of different operating conditions may be considered:

- Increase of reactive medium temperature.
- Increase of residence time.
- Increase of catalyst concentration.

Two parameters allow reactive medium temperature to be increased: the utility fluid temperature and to a slight extent the utility fluid flow-rate. Nevertheless, for productivity and safety reasons, the reactive medium boiling point has to be strictly avoided. In this way, the operating pressure needs to be increased. As the maximal pressure available on the pilot device is equal to 5 bars that corresponds to 111°C boiling point for methanol and 112°C for methyl acetate (the most volatile components), it has been decided to restrict utility fluid temperature to 90°C. The residence time of the reactive medium may be increased on one hand by reducing the flow-rate that may lead to limited heating performance and on the other hand by geometrically increasing the reactor volume. In the pilot version of the OPR implemented at the LGC, such factors are limited 20 L.h⁻¹ and 9 blocks (about 4 L) for respectively flow-rate and residence time. With regards to catalyst concentration, as kinetics has been validated for concentration below 10 mL.L⁻¹, the maximal value is set to 10 mL.L⁻¹.

From an intensification viewpoint, since some features of the pilot version of the “Open Plate Reactor” limit our latitude (maximal pressure of 5 bars and so maximal temperature of 90°C, number of blocks equal to 3) a specific methodology has been adopted. In fact, intensification is performed by simulation, by mean of a modelling tool (Elgue et al., 2005, Elgue et al., 2006). This tool is based on a complex dynamic modelling of the reactor that allows to take into account at the same time hydrodynamic, thermal and reaction aspects. First, a preliminary step based on experimental studies is carried out to allow tool predictions to be validated. In this way, impact on the reactor behaviour of key parameters (reactive medium temperature, residence time, catalyst amount) is studied in detail. Then, the operating conditions of the intensified operation are determined by simulation.

An operation carried out at nominal “Open Plate Reactor” conditions is used as reference (see table 4). Acetic acid (66 % mass) with catalyst (6 mL.L⁻¹ of

sulphuric acid) at a flow-rate equal to 40 L.h⁻¹ composes main fluid (R1). Methanol (85 % mass) is then injected at reactor beginning with a flow-rate equal to 10 L.h⁻¹. Initially, reactants are at room temperature. Ethylene glycol is provided as a utility fluid with the following conditions: flow-rate equal to 1680 L.h⁻¹ and 57.1°C temperature. In order to estimate the conversion at reactor outlet, different samples are withdrawn and analysed by chromatography (method is described in Bonaillie et al., 2001). The conversion values deduced from each sample are given in table 4, in the different columns related to conversion. Such procedure has been adopted for each experiment and allows the reproducibility of the conversion estimation obtained by chromatography to be validated.

Table 4: operating conditions of “Open Plate Reactor” experiments

Experiment	Reactive medium		Utility fluid		Conversion (%)		
	Flow-rate (L.h ⁻¹)	Catalyst (mL.L ⁻¹)	Flow-rate (L.h ⁻¹)	Temperature (°C)	1	2	3
Reference	50	6	1680	57.1°C	5.7	6.2	
1	25	6	1660	57.3°C	12.4	11.9	13.0
2	50	8	2300	74.2°C	17.3	17.3	

Two additional experiments have been carried out to assess the impact on the reactor behaviour of residence time (experiment 1) and of both reactive medium temperature and catalyst concentration (experiment 2). Related operating conditions are detailed in table 4. During experiment 2, the influence of both temperature and catalyst concentration is considered. This does not allow all influence to be seen separately. Nevertheless, the objective of this experiment does not lie in the estimation of the temperature or the catalyst impact which has already been determined during the kinetics study. The point is to validate the predictions under specific conditions which have not been considered: chosen temperature above the boiling point at atmospheric pressure.

In order to validate the tool predictions, for each experiment, simulation results have been compared to the reactor experimental behaviour in terms of temperatures and conversion (figures 7 to 9). With regards to conversion, analysis of the reactive medium is performed by gas chromatography as described in section 2.

Process: 50 L/h, 6 mL Catalyst - Utility: 1680 L/h, 57.1°C

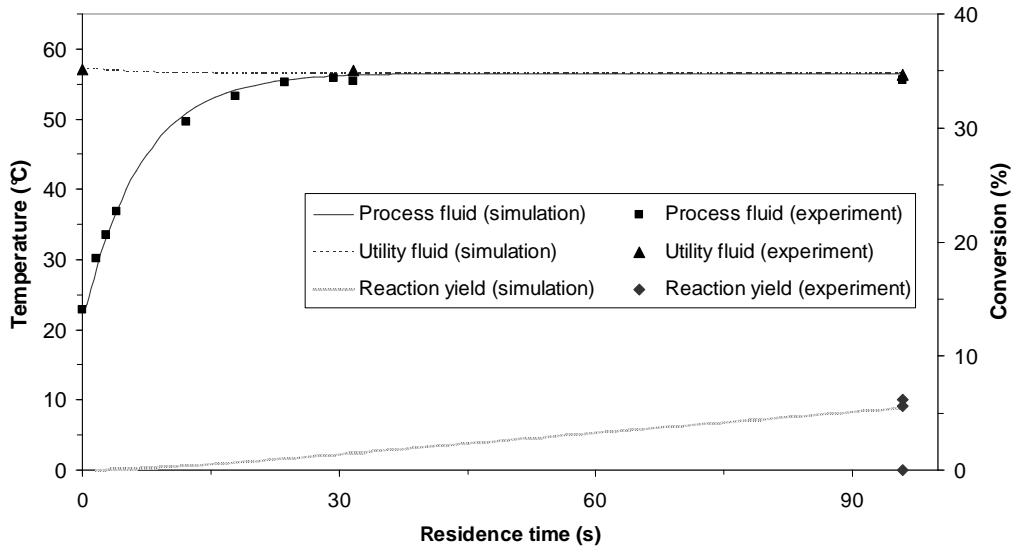


Figure 7: reference OPR experiment

Process: 25 L/h, 6 mL Catalyst - Utility: 1660 L/h, 57.3°C

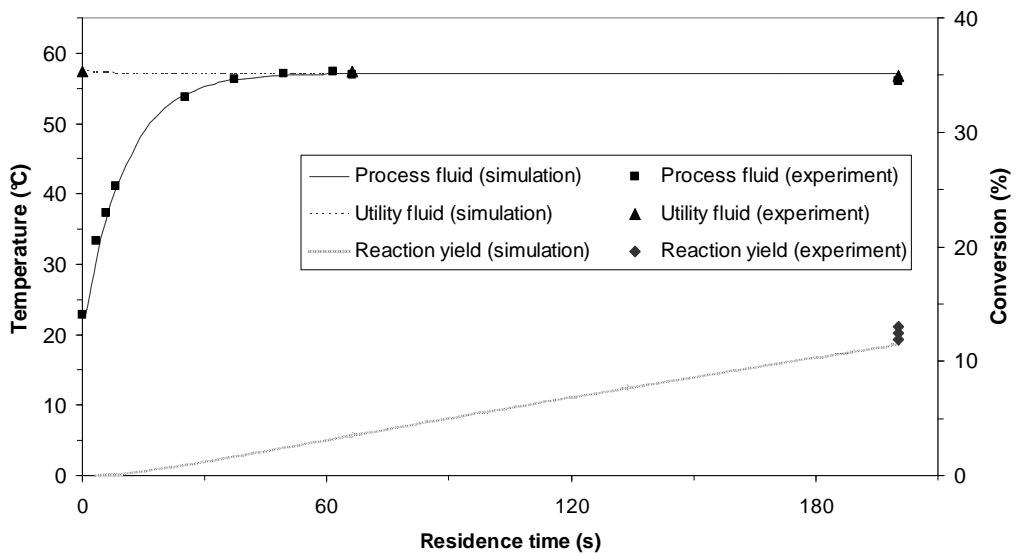


Figure 8: influence of residence time on OPR behaviour

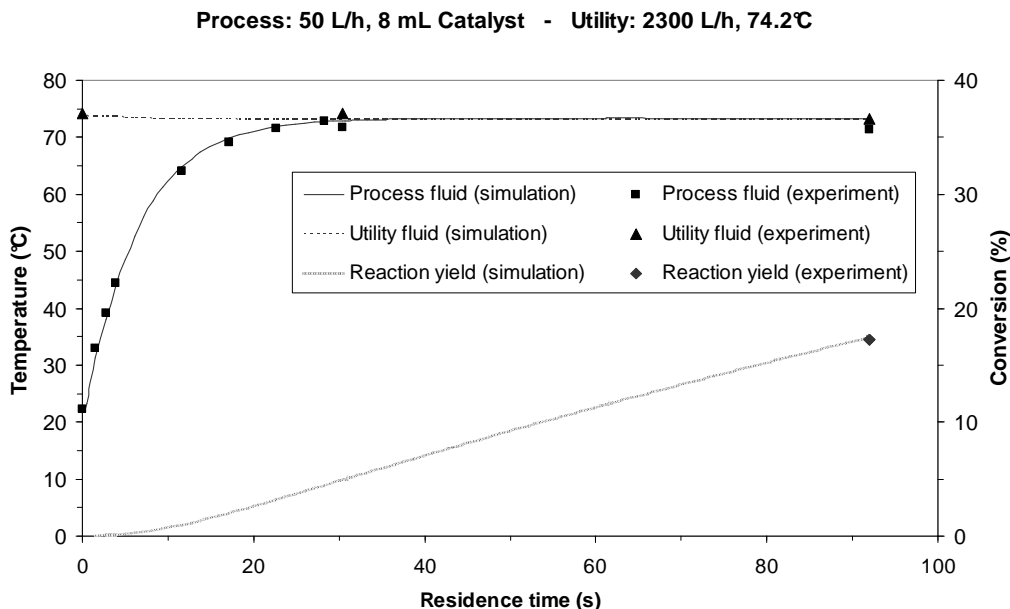


Figure 9: influence of catalyst concentration and utility conditions on OPR behaviour

For each experiment, the good agreement observed between simulated and experimental results allows the model to be validated. Accuracy of the predictions is then highlighted with respect to both temperature and conversion (figures 7 to 9). Such accuracy is all the more interesting in that in this application, heat transfer and reaction aspects are strongly connected, due to sensitivity of the conversion to heating. Moreover, such accuracy validates once again the developed esterification model in the specific domain, in terms of temperature and catalyst amount.

From the knowledge obtained during “Open Plate Reactor” experiments and thanks to the modelling tool, a complete intensified esterification has been studied. All key parameters have been set to their maximal values, that leads to an equilibrium (71 % conversion) obtained in about 10 minutes. The resultant operating conditions are described in table 5.

Table 5: intensified operating conditions in “Open Plate Reactor”

Operation	Reactive medium		Utility fluid		Conversion (%)
	Flow-rate (L.h ⁻¹)	Catalyst (mL.L ⁻¹)	Flow-rate (L.h ⁻¹)	Temperature (°C)	
Intensified	20	10	2500	90.0°C	71.1

The temperature and conversion profiles reveal the ability of “Open Plate Reactor” to rapidly achieve the esterification reaction (figure 10). In fact, 66 % conversion is obtained in 6 minutes residence time and equilibrium (71 %) is reached after 10 minutes. From an intensification viewpoint, advantages of “Open Plate Reactor” compared to standard reactors lie in possibility to operate under pressure and in its enhanced heating performances. In fact, on figure 10 simulation shows that only 1 minute is required to heat the reactive medium from room temperature (about 20°C) to 90°C. Such heating ability speeds up the reaction and then leads to an improved conversion for a given residence time.

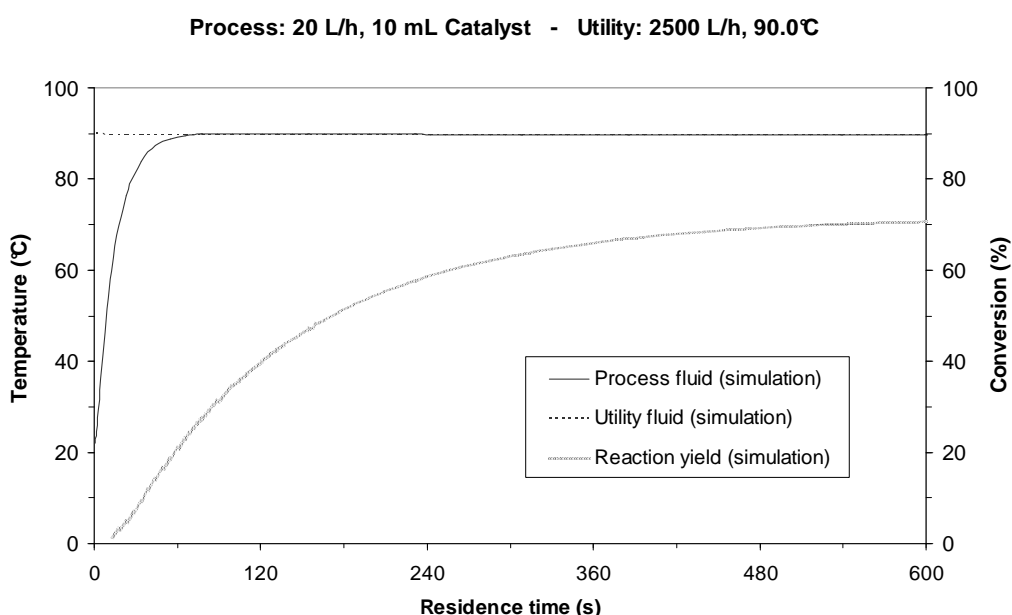


Figure 10: intensified operation in the OPR

5. Conclusion

This work describes the intensification of methyl acetate esterification reaction related to a continuous reactor designed and built by Alfa Laval Vicarb. To achieve this purpose, a kinetics model has been developed and validated for new studied conditions from experiments carried out in a lab scale batch reactor. Implemented in a simulation framework dedicated to continuous intensified reactors, this model offers intensification facilities that lead to a satisfying design of the reactor and the associated operating conditions. This intensification methodology has been supported and validated by experimental studies.

By intensification of design and operating conditions, the reactor allows methyl acetate production to be carried out in a fast and continuous operation. It allows working in non-classical temperature, pressure, residence time and concentration domains that are not often considered in standard industrial reactors. Nevertheless, the purity of methyl acetate obtained at reactor outlet is limited by the reaction equilibrium fixed by the alcohol class (first class) and the initial composition of the mixture. Therefore from a production viewpoint, the present intensified process is of low interest compared to industrial process of reactive distillation which leads to high-purity methyl acetate (Agreda et al., 1990). Nevertheless, from a safety viewpoint, the present process is of great interest as it involves very low reactive medium volumes: about 4 litres for 20 L.h⁻¹ reactive medium flow-rate. With regards to esterification reactions (which frequently occur in industrial applications), the present concept of intensified reactor could however be relevant if coupled with technology that allows products to be separated from the reactive medium. In this way, implementation of membranes (that separate water for instance), inside the reactor channel could offer many perspectives. In fact, such process could be particularly suited to esterification where reactive distillation is difficult or impossible to set-up because of the volatility configuration of components.

The main results of this study are (i) new kinetic model based on experimental work has been elaborated to reach intensified operating domain; (ii) in such conditions, a “slow” reaction has been implemented in a continuous reactor with a good conversion in a short residence time. Then this shows the possibility to couple in the same apparatus reactions with different characteristics times.

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