



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of some Toulouse researchers and makes it freely available over the web where possible.

This is an author's version published in : <http://oatao.univ-toulouse.fr/9924>

Official URL : <https://doi.org/10.1016/j.cherd.2013.05.013>

To cite this version :

Fernandez, Mayra Figueiredo[✉] and Barroso, Benoît and Meyer, Xuân-Mi[✉] and Meyer, Michel[✉] and Le Lann, Marie-Véronique[✉] and Le Roux, Galo Carrillo and Brehelin, Mathias *Experiments and dynamic modeling of a reactive distillation column for the production of ethyl acetate by considering the heterogeneous catalyst pilot complexities.* (2013) *Chemical Engineering Research and Design*, vol. 91 (n° 12). pp. 2309-2322. ISSN 0263-8762

Any correspondence concerning this service should be sent to the repository administrator : tech-oatao@listes-diff.inp-toulouse.fr

Experiments and dynamic modeling of a reactive distillation column for the production of ethyl acetate by considering the heterogeneous catalyst pilot complexities

Mayra F. Fernandez^{a,b,c,d,e,f}, Benoît Barroso^f, Xuân-Mi Meyer^{a,b,*}, Michel Meyer^{a,b}, Marie-Véronique Le Lann^{c,d}, Galo C. Le Roux^e, Mathias Brehelin^f

^a Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 4 Allée Emile Monso, F-31030 Toulouse, France

^b CNRS, Laboratoire de Génie Chimique, F-31030 Toulouse, France

^c CNRS, LAAS, 7 avenue du Colonel Roche, F-31077 Toulouse, France

^d Université de Toulouse, INSA, LAAS, F-31077 Toulouse, France

^e Department of Chemical Engineering, Polytechnic School of the University of São Paulo, Avenida Professor Lineu Prestes, 05088-900 São Paulo, Brazil

^f Solvay – Research and Innovation Center, 85 avenue des Frères Perret, BP 62, F-69192 St Fons, France

A B S T R A C T

Great effort has been applied to model and simulate the dynamic behavior of the reactive distillation as a successful process intensification example. However, very little experimental work has been carried out in transient conditions. The work presents a series of experiments for the production of ethyl acetate from esterification of acetic acid and ethanol in a reactive distillation pilot column. The steady-state approach performed experiments with both excess of alcohol and stoichiometric feed configuration. Predicted and measured results show good agreement and reveal a strong dependency of the structured packing catalyst activity on the pilot geometry and its operating conditions. The transient process behavior of the heterogeneously catalyzed system was deeply investigated and continuous and dynamic data were collected for an equilibrium model validation, after different perturbations on parameters. The experimental validation is shown to be essential to provide realistic hydrodynamic parameters, to understand the sensitive parameters such as heat losses and to adapt values for the catalyst holdup as a function of the system.

Keywords: Reactive distillation; Modeling; Heterogeneous catalyst; Ethyl acetate; Experimental validation

1. Introduction

In recent years, increasing attention has been directed toward reactive distillation processes as a successful process intensification example. Reactive distillation means the simultaneous implementation of reaction and distillation in a counter currently operated column, where chemical reactions (mainly equilibrium limited reactions) are superimposed on vapor liquid equilibrium. Conversion can be increased far beyond what is expected by the chemical equilibrium due to the continuous removal of reaction products from the

reactive zone, reducing costs and contributing to a sustainable production. However, the reactive distillation process is a complex system in which the combination of separation and reaction operations leads to non-linear interactions between phase equilibrium, mass transfer rates, diffusion and chemical kinetics. As a consequence, the analysis of transient regime operation is made necessary to better understand the process behavior and the present nonlinearities.

The dynamic behavior of reactive separation systems has attracted attention in recent academic and industrial studies. Although great effort has been applied to model and

* Corresponding author at: Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 4 Allée Emile Monso, F-31030 Toulouse, France. Tel.: +33 05 34 32 36 52.

E-mail address: xuan.meyer@ensiacet.fr (X.-M. Meyer).

to simulate the dynamic behavior of the process, very little experimental work has been carried out in transient conditions. Some authors developed rigorous dynamic models, but only experimental data from steady state operations were considered for model validation. Kenig et al. (1999) developed a rigorous rate-based dynamic model for reactive absorption processes that was validated by the comparison of the sour gases reactive absorption in air purification packed columns simulation against pilot-plant steady-state experiments. Mihal et al. (2009) studied a hybrid reactive separation system consisting of a heterogeneously catalyzed reactive distillation column and a pervaporation membrane located in the distillate stream. The steady state behavior model was validated by comparison with the experiment data from the work done by Kotora et al. (2008) and the system dynamic behavior was investigated by simulation. Other authors reported dynamic experimental data on batch-operated columns for the production of methyl acetate: Schneider et al. (1999) included the explicit calculation of heat and mass transfer rates in a rigorous dynamic rate-based approach and the experiments on a batch distillation column showed good agreement with simulation results. Noeres et al. (2004) considered a rigorous rate-based dynamic model for designing a batch heterogeneously catalyzed reactive distillation and good agreement was verified for compositions and temperatures through the column after forced perturbations on reflux ratio. Singh et al. (2005) studied esterification reaction of acetic acid with n-butanol in a packed distillation column with the commercial catalytic packing KATAPAK-S and non-catalytic wire gauze. A dynamic equilibrium stage model was developed to analyze the influence of various operating parameters and several trials were carried out; reasonably good agreement between the experimental and simulation results was said to be verified, but results were only shown for one representative attempt. Xu et al. (2005) developed a detailed three-phase non-equilibrium dynamic model for simulating batch and continuous catalytic distillation processes. The simulation results were in good agreement with the experimental data obtained from the production of diacetone alcohol. Experiments were performed with the column under total reflux and the transient behavior was studied after a decrease of the reboiler duty. Finally, Völker et al. (2007) conducted closed-loop experiments to validate a control structure. The authors designed a multivariable controller for a medium-scale reactive distillation column and semi-batch experiments on closed-loop configuration were conducted so as to demonstrate control performance for the production of methyl acetate by esterification. Sequential perturbations on reflux ratio and on acid feed were introduced to a batch operation reactive column.

To our knowledge, there is a lack of experimental studies concerning the ethyl acetate reactive distillation system in continuous dynamic conditions in the literature. A detailed experimental analysis would be of great importance in order to provide a good representative simulation model for the heterogeneously catalyzed system. The parameters concerning column geometry (reboiler design, column diameter), technology (catalyst, packing characteristics) and hydrodynamics (liquid retentions, flooding considerations) require realistic values that can only be well identified based on experimental validation. The objective of our study is thus the definition of both steady-state and dynamic models and the generation of the required experimental data on a continuous heterogeneously catalyzed reactive pilot column. Several experimental

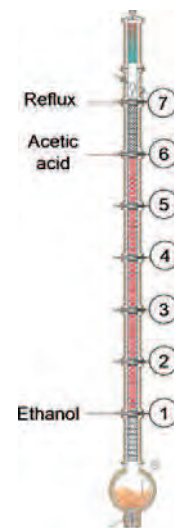


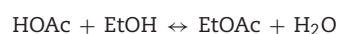
Fig. 1 – Column simplified scheme.

trials were conducted to investigate the transient process behavior and to collect continuous and dynamic data for model validation. Discussions were developed concerning the complexities of the reactive distillation process, the possible steady state multiplicities and the sensitivities due to heat losses, specific operating conditions and the heterogeneous catalysis. The importance of considering all these peculiarities in the interpretation of a dynamic model is highlighted and hence the developed model combining information from the steady state and from the dynamic regime is accepted for the representation of the ethyl acetate system.

2. Materials and methods

2.1. Pilot characteristics

The reactive distillation for the heterogeneous catalyzed esterification of ethanol (EtOH) and acetic acid (HOAc) to ethyl acetate (EtOAc) and water (H₂O) is studied. Experiments were carried out in a lab-scale pilot column. The considered reaction is written as:



The pilot plant consists of a glass column with an inner diameter of 75 mm and a height of 7 m. It is divided into 7 modular sections of 1 m, with a liquid distributor at the top of each section, numbered bottom-up (D1–D7). The distributors allow a uniform distribution of the liquid feed in the packing, avoiding any liquid flow throughout the wall. The distillation pilot column is schematized in Fig. 1. The packing structure has the following characteristics:

- The modular section at the top of the column is filled with the structured packing Sulzer DX (number of theoretical stages ~8).
- The 5 central modular sections are filled with the reactive structured packing KATAPAK SP-Labo, with an acidic ion-exchange resin as the heterogeneous catalyst. The structured packing enlarges the internal surface and promotes turbulences so that the mass transfer between the liquid and the vapor phase, and the interaction of the liquid phase and the reactive catalyst pores are increased (number of theoretical stages ~11).

- The modular section at the bottom of the column is filled with the structured packing Sulzer CY (number of theoretical stages ~ 8).

The column works at atmospheric pressure and is thermally insulated. The column operates with three different feed flows: the acetic acid feed is injected at distributor D6, the ethanol feed is injected at distributor D1 and a third feed flow, which is called Reflux, is assimilated to an external reflux and is introduced into the column at distributor D7. This external reflux is representative of the organic phase coming from a decanter in which different streams of the process are mixed.

A classical glass condenser is vertically positioned above the column; the vapor stream would be fully condensed and withdrawn as the distillate flow. After passing through the condenser, the distillate goes to a heat exchanger to be cooled to ambient temperature by glycolic water at 5°C so as to avoid the evaporation of the ethyl acetate during sample withdrawal. The distillate goes further to a 5-l decanter where it splits into two different phases. The interface level is regulated manually because the production of the aqueous phase is relatively small.

The column reboiler is equipped with a sensor of coaxial waves to measure the liquid level and a facility enables the liquid level regulation in the reboiler by acting on the outlet residue flow rate. The heat of the column is regulated by controlling the temperature of the circulating oil inside the reboiler heat element. In order to maintain a constant heat during pilot experiments (so as to ensure constant distillate flow rate), the difference between the oil temperature and the liquid temperature was maintained constant. The external perturbations were neglected.

The acetic acid feed line is electrically heated up to 30°C, so as to avoid its solidification (its melting point is about 16.6°C). The flow meter measurements are numerically smoothed before its consideration in the regulators, which act on the frequency of the pump variations. Thus, regular and constant flows are obtained over time.

It is worth mentioning that the pilot plant configuration and operating conditions were not designed to provide the best productivity or product purity, but to acquire data on column characteristics and system behavior, following its dynamic tendencies and responses to perturbations.

2.2. Data acquisition

The plant instrumentation provides seven temperature measurements in the vapor phase of each liquid distributor, and two temperature measurements in the liquid phase of the reboiler and distillate line. In addition, temperature measurements of the cooling liquid entering and exiting the condenser and the oil that heats the reboiler are provided. The five flow rates – three feed flows, the produced distillate and residue – and the pressure drop on the column are also registered. Measurements of both the flow rate and the temperature of the cooling fluid are placed in the condenser input and output. All the process variables, such as flow rates, temperatures, reboiler liquid level and system pressure are collected and monitored by a standard digital process control system.

During experimental tests, liquid phase samples were withdrawn from four liquid distributors D2, D3, D4 and D5 (because D1, D6 and D7 received the feed flows and their valves were not available) as well as from the distillate. At the bottom of the column, the geometry of the reboiler results in an

important residence time. In order to withdraw a representative sample of the composition at the bottom line, a derivation of the down-coming liquid was introduced just above the reboiler.

The esterification reaction studied incorporates four components: ethanol, acetic acid, ethyl acetate and water. With the purpose of quantifying the composition of all quaternary system components, three different analytical methods were applied: gas chromatography, Karl Fischer method and acid–base titration.

Then, the data reconciliation procedure was conducted by a computational tool. The set of data consists of 5 flow-rate and 20 mass compositions measurements. Random errors are assumed to follow a normal distribution and the reconciliation procedure minimizes the weighted least squares of the errors between the reconciled and the measured variables. The weight is the inverse of the measures covariance matrix, which is a classic approach called Gauss–Markov estimator (Walter and Pronzato, 2010). By balances, reaction equations and physical constraints considerations, the calculations were made and they resulted in values of flow rates and compositions that respect the column mass balance with high accuracy (error $< 10^{-6}$).

2.3. Experimental procedure

Before starting the experimental tests with the esterification components, some experiments were carried out with water in order to calibrate the pumps, to estimate heat losses, to verify heat equipments, to determine start-up and shut-down procedures.

All the tests were performed as follows: the day before the experiment, the column was heated up under total reflux conditions without any feeds and remained in these conditions for at least 12 h. At the beginning of the test, the next morning, the three feed streams: acid, alcohol and external reflux were switched on and the system was observed until steady state conditions were reached. Stable operational conditions were normally reached after approximately 7 h of experiment. Due to the fact that only temperatures were measured online, the identification of steady state conditions was assumed to happen when temperatures were stable at the column distributors. The knowledge of the compositions was only possible after the experimental runs, because offline laboratory analyses were adopted, which required more time for preparation and calculations.

Through 12 experiments, different perturbations were performed and a substantial number of data were collected, such as flow rate measures, temperature and composition profiles. The tests were chosen to work under alcohol excess feed configuration in order to consume all the acid and to meet the stringent acid specification for acetates. For the purposes of comparison, an additional test at steady state with

Table 1 – Operating parameters of tests.

Test	Steady-state configuration	Dynamic perturbation
1	Ethanol excess	–
2	Stoichiometric feed	–
3	Ethanol excess	+10% reflux mass flow
4	Ethanol excess	–10% reflux mass flow
5	Ethanol excess	+10% acid mass flow
6	Ethanol excess	+10% ethanol mass flow
7	Ethanol excess	Heat perturbation

Table 2 – Product streams compositions.

Test	Feed ratio (molar) EtOH/HOAc	Distillate (%mass)			Bottom (%mass)			
		EtOAc	EtOH	H ₂ O	HOAc	H ₂ O	EtOH	EtOAc
1	1.13	89.2	3.7	7.1	11.9	88.1	0.0	0.0
2	1.04	91.5	2.6	5.9	21.2	78.9	0.0	0.0
3	1.12	88.7	3.7	7.6	17.4	82.6	0.0	0.0
4	1.12	88.8	3.5	7.7	11.2	88.8	0.0	0.0
5	1.13	89.9	3.6	6.5	8.6	91.4	0.0	0.0
6	1.12	89.1	3.5	7.4	14.4	85.6	0.0	0.0
7	1.13	88.8	3.5	7.7	7.8	92.2	0.0	0.0

Table 3 – Reactant conversion rates.

Test	X _{HOAc}	X _{EtOH}
1	97.2%	86.2%
2	93.6%	90.0%
3	96.1%	86.1%
4	97.7%	86.1%
5	97.8%	86.5%
6	96.7%	86.7%
7	98.4%	86.9%

stoichiometric feed configuration was conducted. Table 1 shows the operating feed conditions and the perturbation conducted at each test.

In tests n°3, 4, 5, 6 and 7, after steady-state conditions were obtained, a perturbation of one parameter was caused in the column, with the attempt to keep all the other parameters constant. These perturbations strongly disturbed the system – temperatures changed rapidly – and its behavior was monitored for the next approximately 4 or 5 h. As a consequence of the laboratory opening times constraints, there was not always sufficient time to wait for the system to reach the new operating point.

3. Experimental results

3.1. Steady state analysis

Except for test n°2 (different feed ratio), the target steady state, with ethanol excess feed configuration, was the same for all the tests. The feed ratio and the results of the product stream compositions are shown in Table 2.

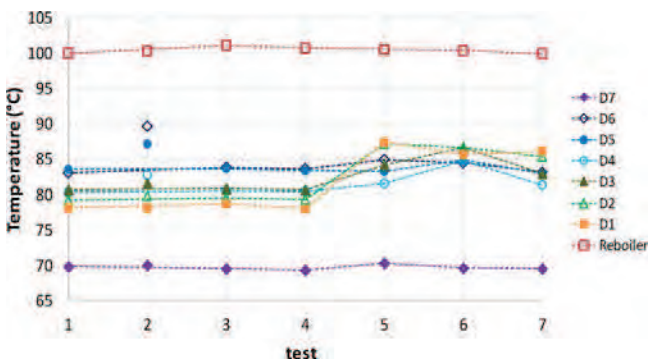


Fig. 2 – Temperature measurements at each distributor, for all tests.

While distillate compositions were nearly the same for all tests, the compositions at the bottom were less reproducible. Conversion rates were calculated (Table 3):

$$X_{EtOH} = \frac{N_{EtOH}^{feed} - N_{EtOH}^{bottom}}{N_{EtOH}^{feed}} \quad X_{HOAc} = \frac{N_{HOAc}^{feed} - N_{HOAc}^{bottom}}{N_{HOAc}^{feed}}$$

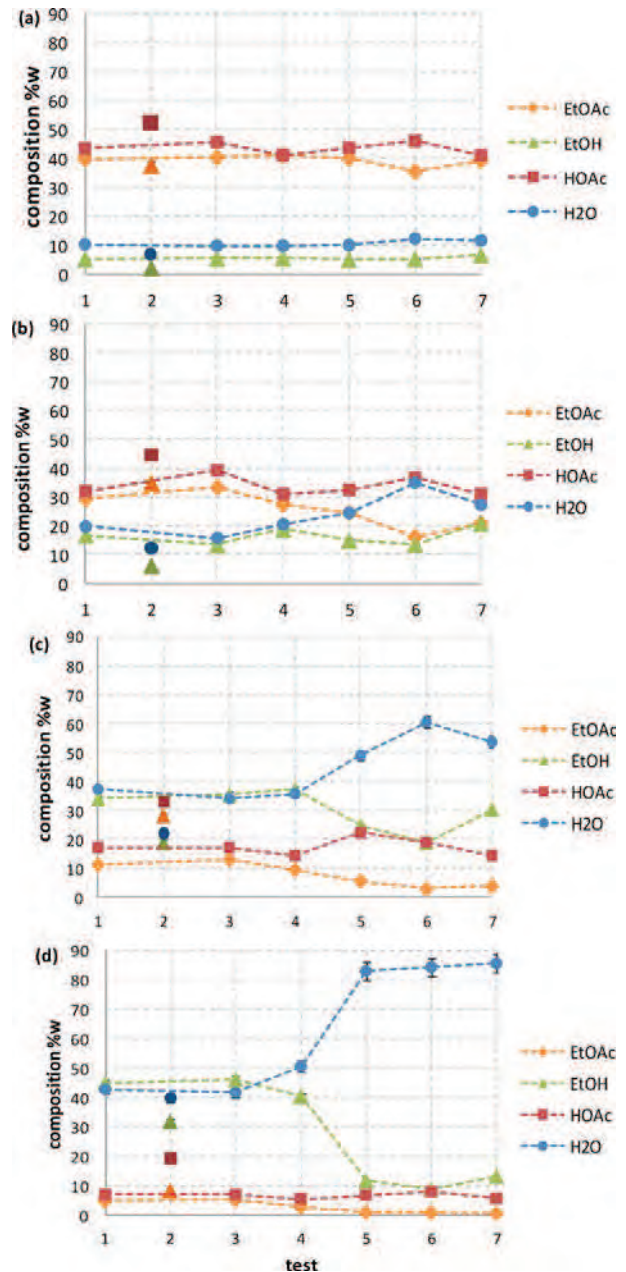


Fig. 3 – Compositions at D5 (a), D4 (b), D3 (c) and D2 (d).

For an approximately 12% ethanol molar excess feed (tests n°1, 3, 4, 5, 6 and 7), the conversion rates were almost the same with a mean value of 96.9% for acetic acid and 86.9% for ethanol.

As shown in Fig. 2, temperatures from the column lower sections had a marked increase after test n°4. The steady states obtained at the beginning of the experimental campaign (test n°1, 3, 4) were different from the later ones (tests n°5, 6, 7), although they remain similar among them.

In Fig. 3, it can be observed that the compositions in D4 and D5 kept almost constant, while compositions in D2 and D3 strongly changed in the last tests of the campaign; this fact confirms the observation of the increment in the column lower sections temperatures. Actually, with the increase in water content and the decrease in ethanol content, higher values of temperature are expected. The obtaining of two different steady states through the experiments is thus accepted and this is further understood with the simulation results. It is worth noting that, despite the presence of different profiles inside the column, the compositions of product streams remain similar. This can be the consequence of the separation-orientation sections above and below the reactive section.

3.2. Study of the transient regimes

The experimental campaign resulted in five tests with representative transient data. The perturbations occurred under open-loop conditions, by changing only one variable. The moment of the perturbation is represented in the graphs by a vertical straight line.

The perturbation of reflux rate and feed flow rates were imposed as step changes and they correspond to the experimental perturbation because the action was conducted at the values given to the pumps, which respond almost instantaneously. The perturbation on the heat duty was conducted by dropping the set point of the heat duty controller, i.e. a negative step change of 3°C of the temperature difference between oil and reboiler liquid.

3.2.1. Test n°3: +10% of external reflux flow rate

Before the perturbation, the temperature in the reboiler was approximately 100°C and all the other temperatures throughout the column were between 70 and 85°C. The temperatures evolution along test n°3 is represented in Fig. 4. The temperature changes occur first at the stages in which the reactants feed streams are injected: liquid distributors D1 and D6. Their responses are faster and have a higher gain than the other ones. Then, the temperatures at D4 and D5 also decreased, and new steady state conditions seem to be obtained 2 h after the perturbation.

Regarding compositions before the perturbation (Fig. 5), the composition at the distillate was observed to be more stable than the composition at the bottom of the column. The contents of water and ethanol at the bottom were not constant even when the constant temperatures allow the assumption that the steady state conditions were reached. This fact highlights the disadvantage of not having online composition measures during the operation of these intensified systems. The increment of the reflux ratio, at constant heat conditions, resulted in an increase in distillate flow rate and in distillate ester content and a decrease in the water content. At the bottom, both water and acid contents decreased resulting in a higher ethanol fraction (Fig. 6).

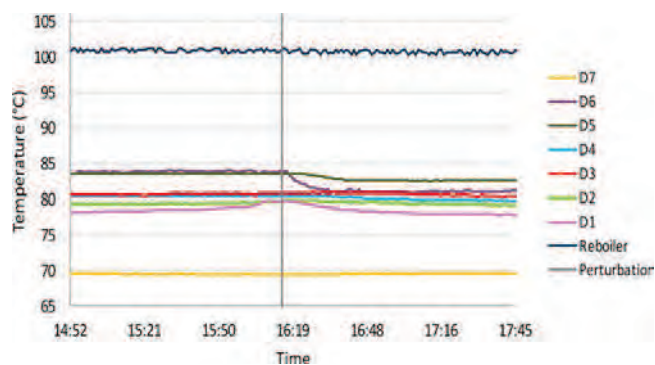


Fig. 4 – Temperatures before and after a 10% external reflux feed flow rate increase.

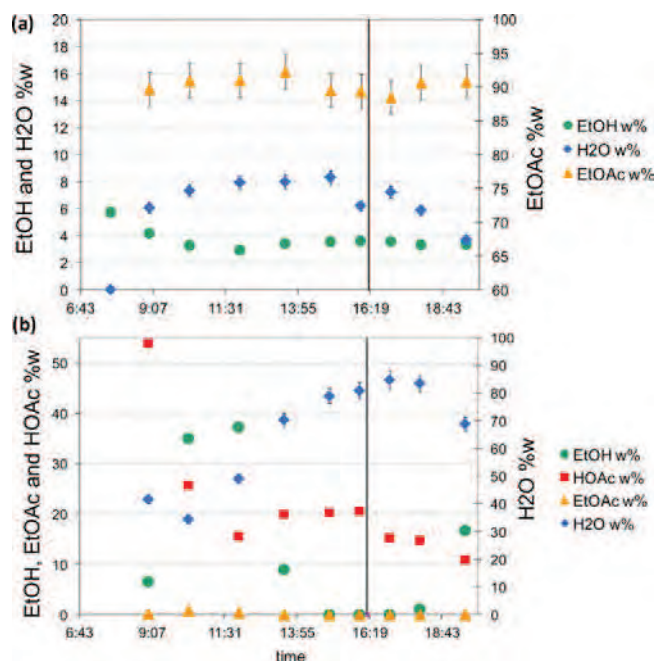


Fig. 5 – Mass compositions at the distillate (a) and at the bottom (b) before and after a 10% increase of the external reflux feed flow rate.

3.2.2. Test n°4: –10% of external reflux flow rate

After approximately 2 h of assumed steady state conditions, the external reflux mass flow rate was reduced by 10%. An unexpected behavior was verified in the temperature at D1 before the reflux perturbation: a positive step of approximately 2°C suddenly occurred. This temperature seems to be highly sensitive to the operation conditions and this fact can be verified also after perturbation, because the temperatures from D1 and D6 were the first ones to react. Both of them are measured where the reactant feeds are located, and this behavior was also verified for test n°3. The other temperatures also rose over time, and marked gradients were observed at D2 and D3.

Regarding composition (Fig. 7), as expected, the behavior was in the opposite direction of the one observed for test n°3: there was a decrease in distillate flow rate and in distillate ester content, being replaced by water and ethanol. At the column bottom, the water content increased, replacing the

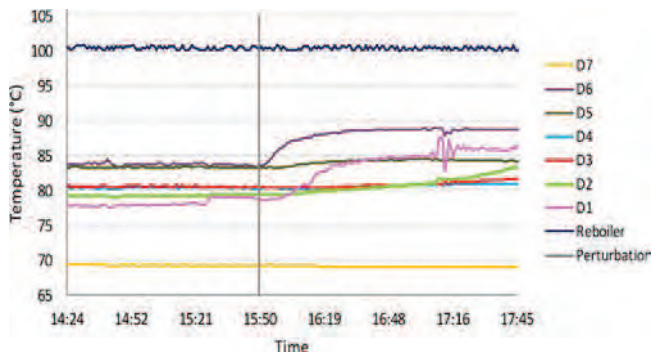


Fig. 6 – Temperature in liquid distributors before and after a 10% decrease of the external reflux feed flow rate.

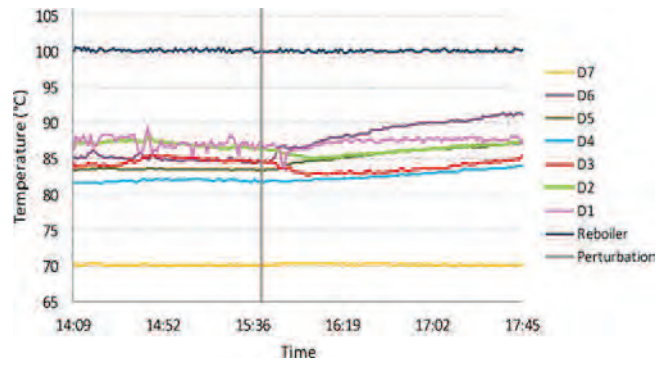


Fig. 8 – Temperature in liquid distributors before and after a 10% increase of the acetic acid feed flow rate.

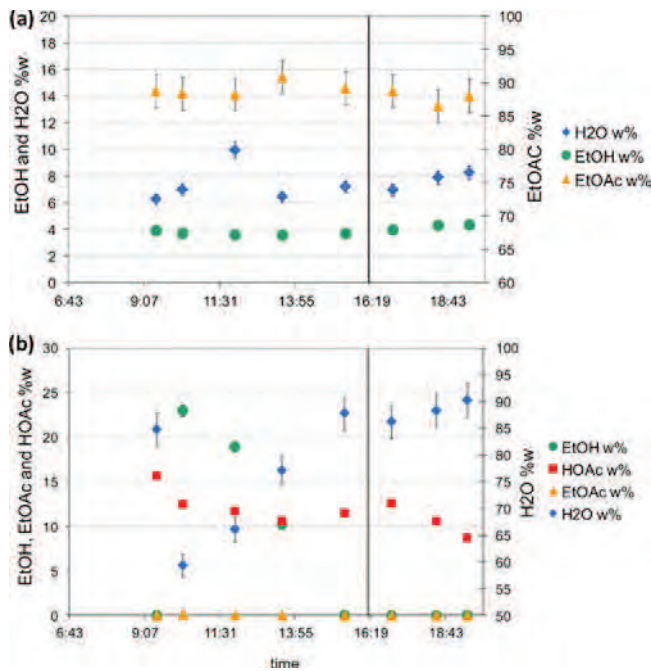


Fig. 7 – Mass compositions at the distillate (a) and at the bottom (b) before and after a 10% decrease of the external reflux feed flow rate.

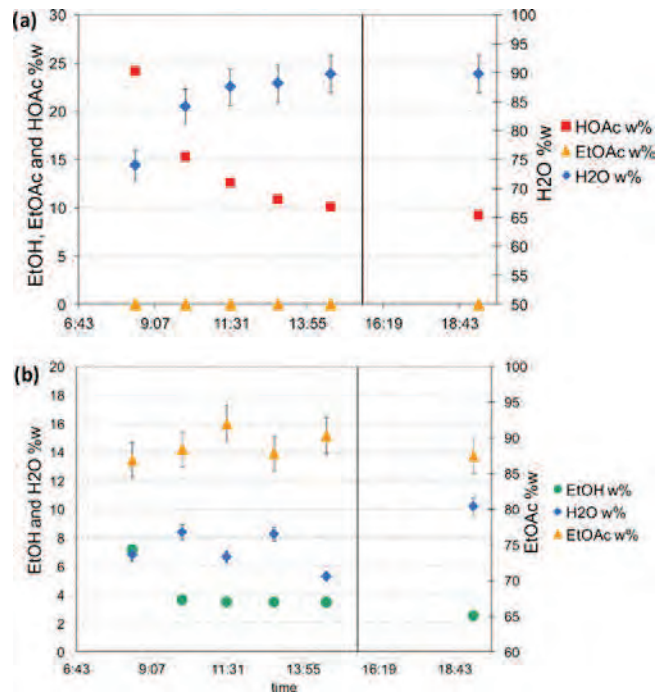


Fig. 9 – Mass compositions at the distillate (a) and at the bottom (b) before and after a 10% increase of the acetic acid feed flow rate.

3.2.3. Test n°5: +10% of acetic acid feed flow rate

During test n°5, the acetic acid feed flow rate was increased by 10% and consequently almost all the temperatures rose, but they showed different responses. Temperatures at D4 and D5 remain with constant positive gradient until the end of the experiment. At distributor D6, a step of approximately 2°C was verified and the temperature continued to increase after it. The temperature at D3 decreased right after the perturbation but its behavior changed later and it started to rise. The temperatures from both distributors D1 and D2 showed oscillations but remain with mean values closer to the ones observed at nominal regime. Actually, the top sections of the column were more affected by the perturbation on acid feed than the bottom sections, due to the proximity to acid feed location. The experiment was stopped before a new steady state was reached (Figs. 8–12).

The compositions analysis exhibits that the water content in the distillate rose and it became less pure in ester. The bottom composition behavior testifies that the system was not exactly in steady state conditions before the perturbation of acid feed.

3.2.4. Test n°6: +10% of ethanol feed flow rate

After the perturbation by decreasing the ethanol feed flow rate, the temperatures decreased through the column due to the stronger presence of a light component. Their responses were less strong than in the case of the increase in acid flow rate. The temperatures at D1, D2, D3 and D4 changed faster than

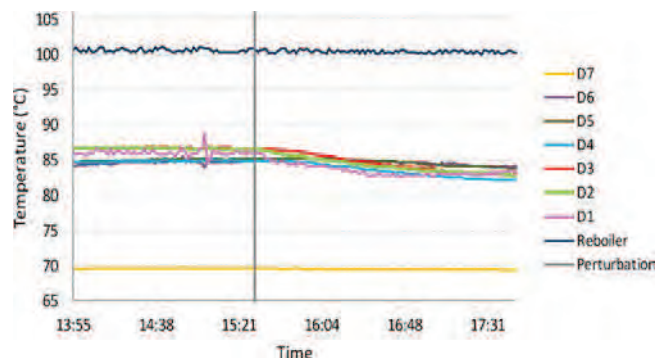


Fig. 10 – Temperature in liquid distributors before and after a 10% increase of ethanol feed flow rate.

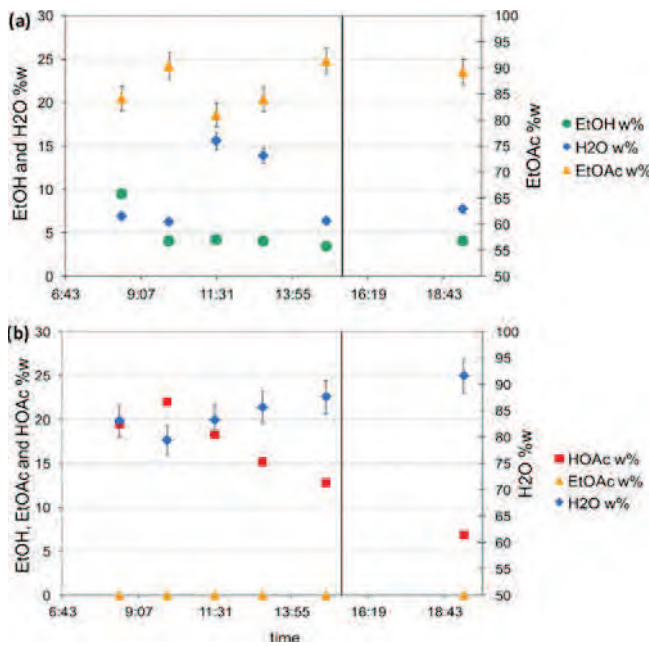


Fig. 11 – Compositions at the distillate (a) and at the bottom (b) before and after a 10% increase of ethanol feed flow rate.

the temperatures at D5 and D6. Temperature at D1 drifted at approximately 1 h 30 after the perturbation.

As a result of the perturbation, a stronger influence was verified in the bottom composition; the increment of ethanol resulted in a higher conversion, dropping the amount of acetic acid.

3.2.5. Test n°7: reduction of heat duty

After the decrease of 3°C in the temperature difference between heat oil and reboiler liquid, the temperatures at the bottom sections, D1 to D3, were observed to drop with similar velocity among them, but the measures in the top sections remained constant. Actually, with less heat to the column, less vapor is produced and the amount of the inner liquid increases.

The first consequence in production was a sharp decrease in distillate flow rate, followed by a decline in heavy component content through the column. Both contents of ester on distillate and ethanol at the bottom thus increased (Fig. 13).

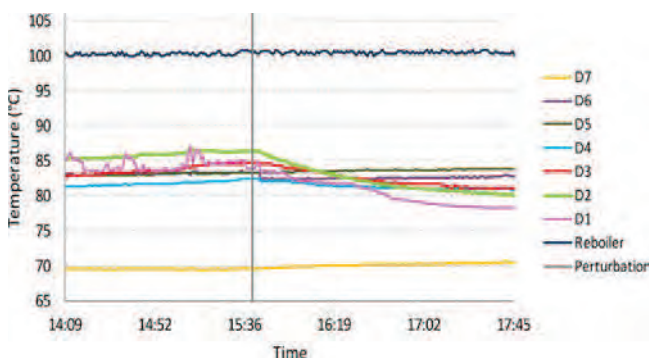


Fig. 12 – Temperature in liquid distributors before and after a reduction of heat duty.

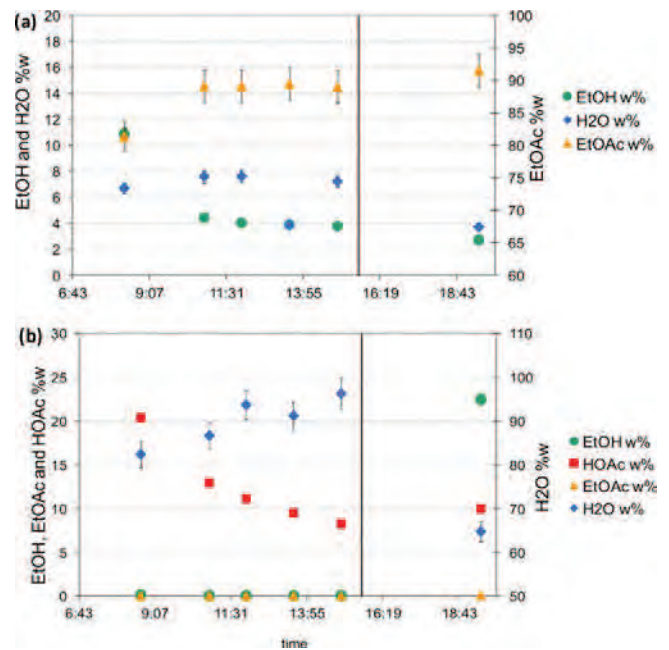


Fig. 13 – Mass compositions at the distillate (a) and at the bottom (b) before and after a reduction of heat duty.

4. Steady state model

To represent the continuous reactive distillation system, a model was developed with the Aspen Plus® software. An equilibrium stage model was considered and it should be adapted for the process simulation and behavior prediction. It is worth mentioning that non-equilibrium models normally provide more details and more precise information to the simulation than the equilibrium models in the case of conventional packed distillation columns. However, the availability of reliable mass transfer correlations for the catalytic packing would be a prerequisite for the use of a non-equilibrium stage model. Even though Behrens et al. (2006) proposes such correlation for KATAPAK®-SP, it cannot be considered reliable, since HETP-values resulting from this correlation are always independent of the type of packing, the test system, as well as the gas load and the liquid misdistribution effects. Consequently, the use of such correlations would not improve the accuracy of the simulation results, but could even lower their quality since the variation in separation performance is not considered for their definition.

Table 4 presents the different parameters to be determined for the equilibrium model. The intrinsic parameters were chosen from previous studies on thermodynamics and kinetics and from pilot analysis. The NRTL activity coefficient model was considered for the phase equilibrium and the Hayden–O’Connell equation of state was used to account for the equilibrium chemical reaction, two different kinetically

Table 4 – Parameters defined into the Aspen Plus® steady state model.

Intrinsic parameters	Operating parameters	Adjustable parameters
- thermodynamics	- flow rates	- reaction efficiency
- kinetics	- heat duty	- heat loss
- pilot geometry	- pressure	
- technology		

Table 5 – Adjustable coefficient for reaction efficiency.

Ethanol excess	Stoichiometric feed (test n°3)
C=0.5	C=1

controlled reactions were defined: one to represent the direct reaction and another to represent the inverse one. The operating parameters such as flow rates, pressure and heat duty were adapted from the conditions of each test. Concerning the adjustable parameters, it was necessary to adapt values of the global reaction efficiency to better fit the simulated conversion to experimental results. Different feed ratios were verified to influence the compositions through the column and, as a consequence, the catalyst resin activity. To deal with this fact, an adjustable coefficient C was considered; this fact is further clarified in Table 5.

The heat loss was initially calculated from temperatures and materials present into the column and the resulting value is 200 W, in which approximately 25% is the loss at the reboiler and the rest is linearly distributed throughout the column. However, it was also observed that the environmental conditions of each day strongly affect the pilot operation conditions and the adjustment of this parameter should be considered in the model.

Fig. 14 compares the simulated mass composition of the distillate and of the bottom with the experimental results. They show good agreement between them.

Fig. 15 is a superposition of simulations and experimental results of tests n°1, 3 and 4. The simulated profiles are drawn by continue lines (–) and their experimental values are represented with diamond-shapes (◆). The straight horizontal continuous lines represent the range of measured compositions and it can be verified that simulation curves show agreement with the straight continue lines, concluding the reliability of the model.

For the same steady state outputs, the composition profiles varied inside the reactive zone (height between 1 m and 6 m), but their values were almost similar inside the separation-only zones. In contrast with the reactive section that has a

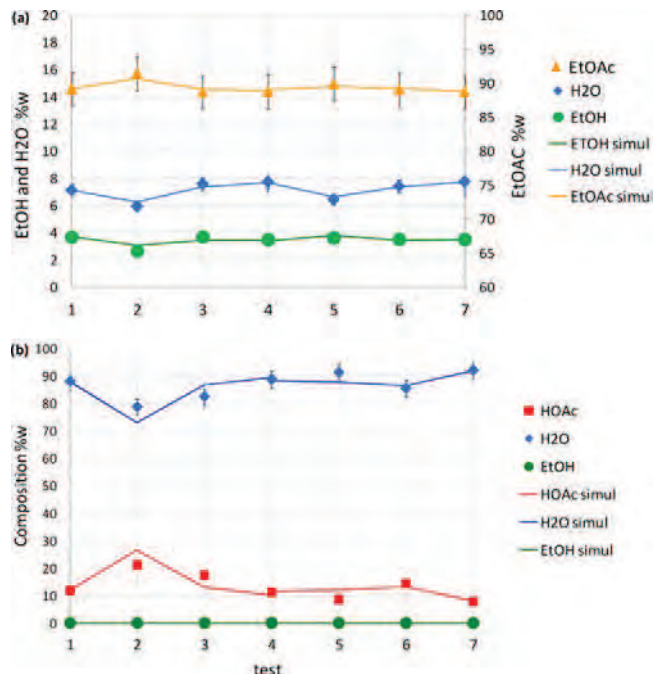


Fig. 14 – Mass fractions at the distillate (a) and at the bottom (b).

flat temperature profile, the separative sections show marked temperature gradients. A temperature measurement inside the separative section would be highly sensitive to a system dysfunction or a change in the steady state conditions. It is thus possible to infer the regulation of hybrid reactive columns by measures placed in the separative sections. This fact is verified in the literature by different authors (Lai et al., 2007; Kumar and Kaistha, 2009).

4.1. Understanding the adjustable coefficient for reaction efficiency

As mentioned before, to adapt the global reaction efficiency in Aspen Plus®, an adjustable coefficient was considered in the

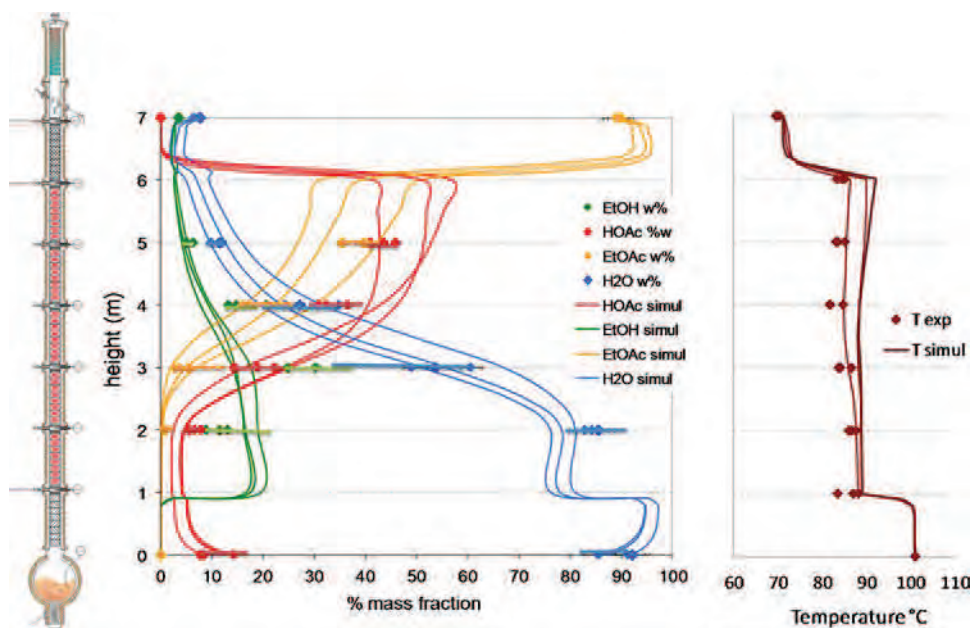


Fig. 15 – Steady state composition and temperature profiles.

reaction kinetics equations to account for the heterogeneous catalyst activity sensitivities. The kinetic law became:

direct reaction : $\text{HOAc} + \text{EtOH} \rightarrow \text{EtOAc} + \text{H}_2\text{O}$

inverse reaction : $\text{EtOAc} + \text{H}_2\text{O} \rightarrow \text{HOAc} + \text{EtOH}$

$$r_{\text{dir}} = C \cdot k_{o,\text{dir}} \cdot [\text{HOAc}] \cdot [\text{EtOH}] \cdot \exp\left(-\frac{E_{a,\text{dir}}}{RT}\right)$$

$$r_{\text{inve}} = C \cdot k_{o,\text{inv}} \cdot [\text{EtOAc}] \cdot [\text{H}_2\text{O}] \cdot \exp\left(-\frac{E_{a,\text{inv}}}{RT}\right)$$

Some assumptions can be drawn to justify this coefficient:

- Water inhibits the activity of the ions exchanger resin, when simultaneously present with the organic compounds that should react (Brehelin, 2006; Darge and Thyron, 1993; Grob and Hasse, 2006). When aqueous components are present, disadvantageous transfer characteristics occur for the organic components on the catalytic packing due to different transfer rates between water and organic molecules to the pores of the catalyst; when the feed is at stoichiometric proportion, the composition of water through the column is observed to be significantly lower than when the feed is at ethanol excess (Fig. 16).
- The model supposes that the liquid reaction occurs at continuous stirred tank conditions. However, the supposed liquid flow conditions are not verified in our tests, where the Peclet number is approximately 30.
- Liquid flow through the catalyst bags can be influenced by some phenomena that depend on the solution composition: the existence of preferential paths caused by the non-homogeneous swelling of the resin or the variable wettability of the catalyst structure in function of water solution content.

The need for this adjustable coefficient in the catalyst activity has already been discussed in the literature (Harbou et al., 2011; Beckmann et al., 2002). The authors believe that the specific characteristics of the catalytic packing and the

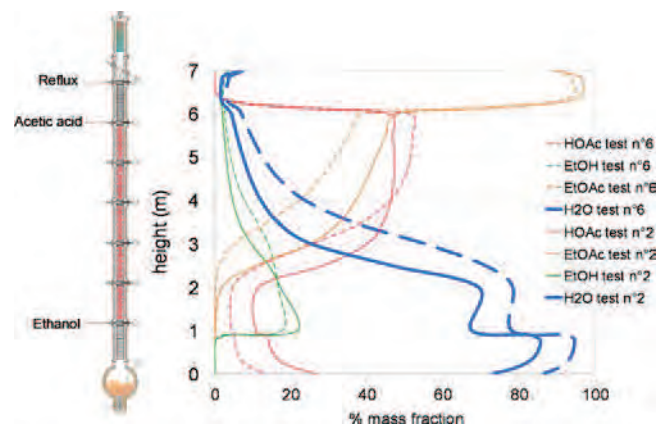


Fig. 16 – Comparison of composition profiles for test n°2 (stoichiometric feed) and n°6 (ethanol excess).

disadvantageous flow characteristics, in addition to the different physical properties of the solutions, such as the relative volatilities, explain the different behavior of the process. Their considerations are coherent with the assumptions taken in this work.

The variation in compositions profiles, regarding results from one test with stoichiometric feed (test n°2) and another one with ethanol excess feed (test n°6) – representative of tests n°1, 3, 4, 5 and 7 – is compared in Fig. 16. It can be observed that the composition in distillate is nearly the same, but the increased amount of acetic acid under stoichiometric feed conditions exits the column by changing the bottom composition (Fig. 17).

4.2. Understanding the adjustable coefficient for heat losses

Despite the fact that the target steady-state was the same for the twelve tests, two different steady-state conditions were obtained. Different weather conditions and thus different heat losses happened during the tests and it can be concluded that the heat loss has an important influence on the pilot operating conditions. In order to improve the system representation, the initial heat loss calculated for the column was changed so as to decrease the distillate flow rate and to better fit the

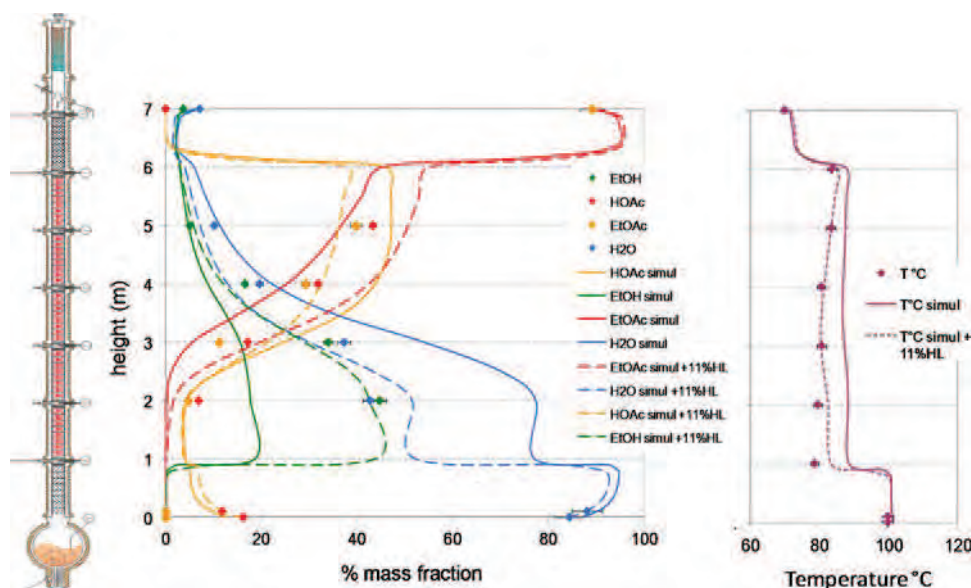


Fig. 17 – Influence of heat loss on composition and temperature profiles, test n°1.

composition profiles. More representative values were found when the heat loss was increased by 11% in tests n°1, 3 and 4. When simulating the process with this new value, the distillate flow rate is reduced by 1.2%, which is almost invisible in historical data, but sufficient to improve the predicted profiles at the column bottom sections. Thus, the difference among the steady states obtained throughout the campaign could be the closer attention granted to the pilot manipulation as from test n°4.

The phenomenon of steady-state multiplicities, commonly studied in reactive distillation columns, could also influence the attainment of different steady states through the experimental campaign. A deeper analysis of these possibilities is developed in the section dealing with the dynamic simulation of the process.

5. Dynamic model

Once the column configuration and the operating parameters were validated, the system behavior in transient regime was analyzed developing a dynamic model. Here, the need of the experimental campaign is highlighted for the acquisition of realistic values for column geometry, technology and hydrodynamics. These parameters are very important to initialize the dynamic simulation and a small deviation can induce errors in the sensitivities, the instabilities and the responses of the process.

The values for reboiler design, diameter of the column and height of theoretical stages were directly considered from pilot observation. The liquid holdup in the reboiler was assumed constant during the experimental tests and the dynamic simulation, due to the presence of a level regulation. Specific liquid volume fractions were initialized for stages with structured reactive packing and flooding calculations were permitted. All the required informations were fed into the Aspen Plus® model and the steady state obtained was automatically exported as the initialization for the dynamic simulation in Aspen Plus Dynamics®. The values concerning column technology, geometry, heat loss, pressure, system thermodynamics and reaction kinetics remain constant during dynamic calculations.

The dynamic model operates under open-loop control conditions, i.e. the regulations are set in mode manual and directly deliver the fixed manipulated variables and no information from the outputs is considered. For the purpose of better representing the experiments, the heat duty and the reflux ratio are the specifications for the simulation degrees of freedom and the products flow rates and throughputs are the system responses.

First, the dynamic model represents the steady state evolution over time. The result is a stable steady state that remains in the values obtained with the Aspen Plus® simulation. Due to the difference that some simulated steady state showed as compared to the experimental results, a temperature bias was considered in each measure so as to compare the dynamic responses gains and delays in the next discussions. In order to represent all the transient responses, each perturbation was introduced into the model. Aspen Plus Dynamics® provides the values of a wide range of process variables through the transient regimes; the evolution of the temperature values and the compositions in the distillate and in the bottom product can be thus analyzed. For clarity purposes and due to the fact that the most important temperature responses

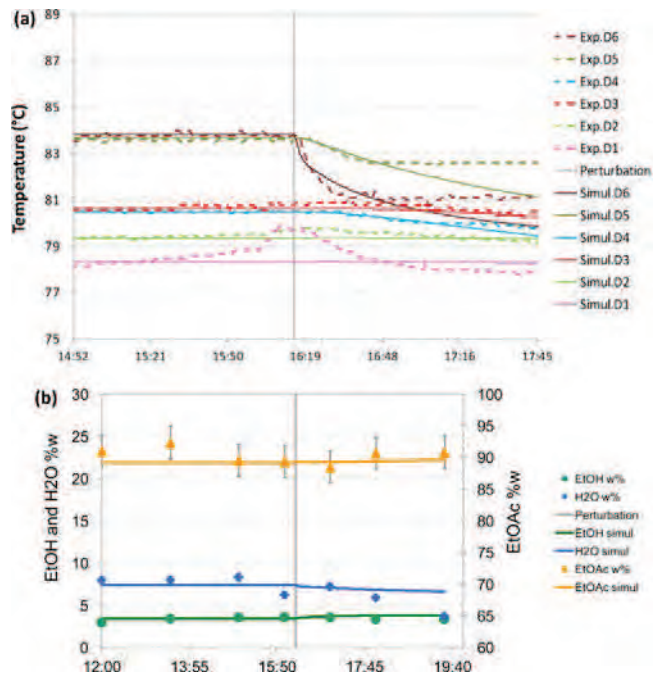


Fig. 18 – Experimental versus simulated temperature (a) and distillate mass composition (b) evolution in test n°3.

are verified inside the column, the graphs are presented with the temperatures from distributors D2 to D7, for the period of approximately 2 h before until 2 h after the perturbation; product output temperatures do not exert such strong influences.

5.1. Test n°3: +10% of external reflux flow rate

As can be seen in Fig. 18a, model predictions and experimental results are in good agreement for temperature. Nonetheless, the final values for the new steady state do not exactly match the experimental data for D5 and D6, the distributors closer to the top of the column. The unexpected behavior verified in D1, which increased before the perturbation and decreased later, was not predicted by the model. In Fig. 18b, the simulated behavior is in good agreement with the measured ethyl acetate and ethanol contents, but the experimental values for water content decrease faster than the model.

5.2. Test n°4: –10% of external reflux flow rate

The responses from the model and from the experimental data agree in directions, gain magnitudes and time constants for D3 to D6. Fig. 19a allows observing that the temperatures at D1 and D2 drifted and the cause of this phenomenon is not considered in the model. It can be concluded that this behavior is not a direct consequence of the perturbation. The distillate composition evolution is well represented by the model in Fig. 19b.

5.3. Test n°5: +10% of acid feed flow rate

In the case of test n°5, the model predictions showed similar responses directions to the experiments, but their behavior were not the same: the experimental data had more instability after the perturbation and although the temperatures at D1, D2 and D3 returned to their previous values, the attainment of a new steady state cannot be assured in the next 2 h.

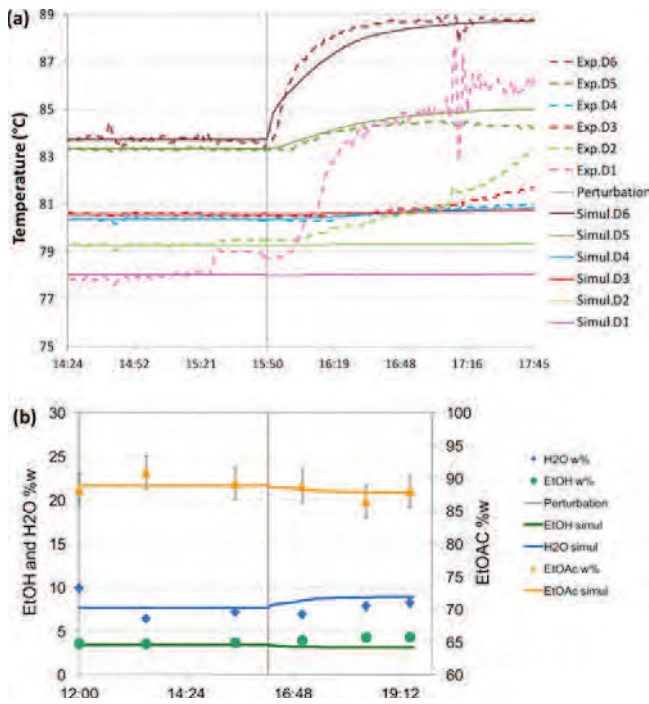


Fig. 19 – Experimental versus simulated temperature (a) and distillate mass composition (b) evolution in test n°4.

Similarly to the unexpected behavior observed during test n° 4, some temperatures (D5 and D6) drifted and the cause of this phenomenon is not considered in the model. When comparing the predicted and the measured values for distillate composition (Fig. 20b), their magnitudes after the perturbation are not the same. In coherence with the temperatures evolution, the pilot was observed to exert stronger influences than the ones predicted by the model.

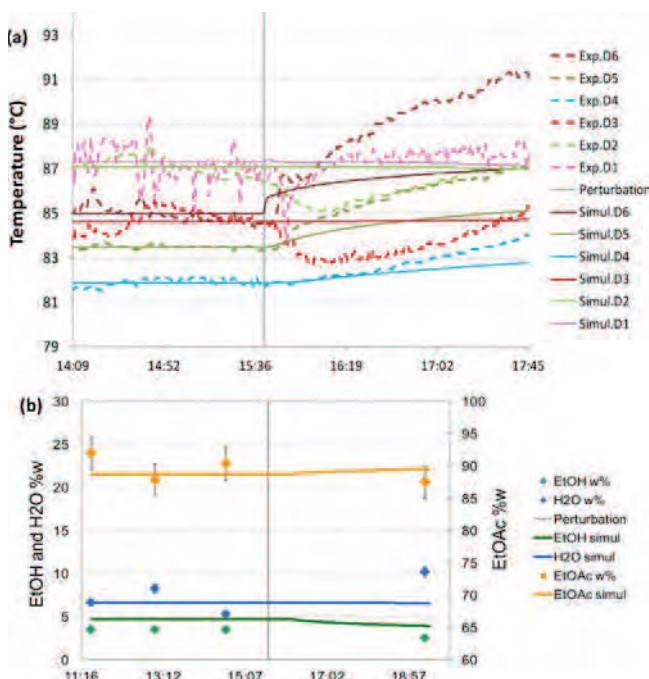


Fig. 20 – Experimental versus simulated temperature (a) and distillate mass composition (b) evolution in test n°5.

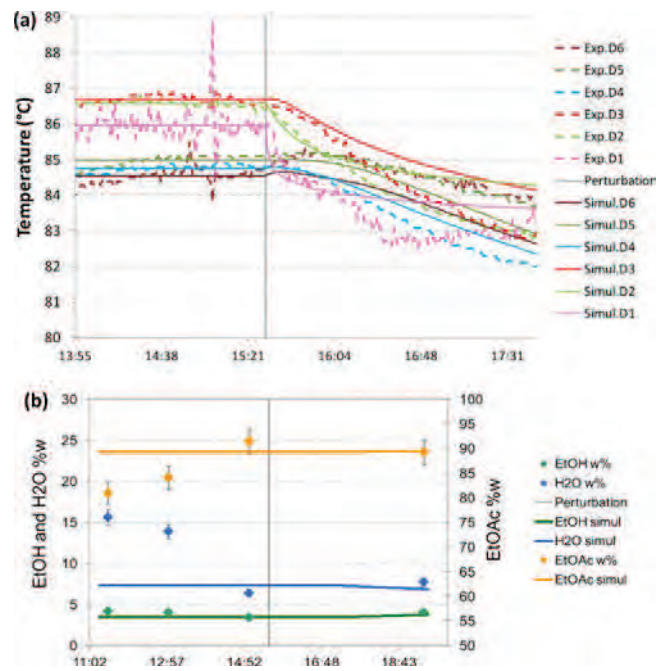


Fig. 21 – Experimental versus simulated temperature (a) and distillate mass composition (b) evolution in test n°6.

5.4. Test n°6: +10% of ethanol feed flow rate

After the increase of the ethanol amount in the column, both measured and simulated temperature values followed the same tendencies, at approximately the same velocity (Fig. 21). Yet, a new steady state was not reached in either the cases and the values at the end of the test were not the same between the model and the experiment. The final distillate composition has similar measured and predicted values. There were no important consequences due to this perturbation.

5.5. Test n°7: reduction of heat duty

The perturbation on heat duty during test n°7 was carried out by dropping by 3 °C the difference between heat oil temperature and reboiler liquid. The real response of the heat device could be analyzed by the dynamic evolution of the oil temperature and for the purposes of representation on the model, a 20-min ramp that decreased the heat duty by 5% was assumed. The beginning and the end of this ramp are represented by two different vertical lines in the graphs (Fig. 22). The composition analysis exhibits that steady state conditions were not really verified in the experimental results and thus, stabilities of these temperatures after the perturbation could be expected. Again, the model responds slower than the measured data after the perturbation. An interesting observation is that the temperature at D1 shows an oscillation, which is followed by the model. Later, both results stabilize, but at different values.

The responses of the distillate composition have the same direction in the model and in the experiment. In coherence with the temperature responses, the model responds slower than the measured data to the perturbation.

Finally, after the analysis of each test and the model representation, it can be assumed that the column temperatures are strongly sensitive to external conditions and that the observed drifts in temperatures are the consequence of an operation condition that is not repeatable for all the tests and it was not identified during pilot manipulations. External conditions

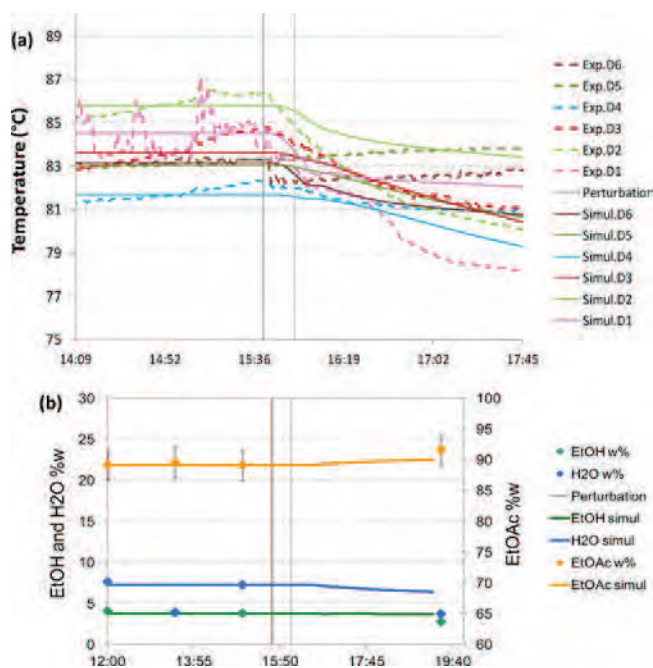


Fig. 22 – Experimental versus simulated temperature (a) and distillate mass composition (b) evolution in test n°7.

were observed to have strong influence on the system due to the pilot geometry and this hypothesis may be accepted because the pilot dimensions provide large superficial contact with the environment. For example, it is possible that, during some tests (approximately 14 h from morning to evening), the evolution of the ambient temperature inside the laboratory resulted in different heat loss values, but the model considers it constant. This geometric issue is expected not to occur in industrial-scale devices.

The analysis of the column transient regime shows greater discrepancy of the predicted and measured temperatures at D1 and D6; the fact that the feeds are positioned at these stages may induce additional perturbations. Moreover, several studies have shown that, as a consequence of the nonlinear interactions, complex open-loop behaviors such as steady state multiplicities, trajectories with complex attracting sets and dynamic bifurcations can occur quite frequently in reactive distillation, depending on the characteristics of the reaction system and on the operation conditions (Rosales-Quintero and Vargas-Villamil, 2009; Ramzan et al., 2010; Chen et al., 2002). The authors detect the difficult operating regions in parameter space focusing the use of commercially available process simulators. Gehrke and Marquardt (1997) and Reder et al. (1999) deeply analyzed the multiplicity phenomenon: they employed continuation algorithms in a simulation software and found an infinite number of steady state solutions in the column with an infinite number of trays at infinite reflux ratio. It is, however, understood that an extended number of steady states will most likely not occur in a real column. The authors performed some experimental tests, in which sustained oscillations could be found and three multiple steady states were attained in the real column for roughly the same bottoms flow rate. These complexes evidences are in coherence with the results found in this work.

More precisely, Kumar and Kaistha (2008) and Lee et al. (2006) found through simulation that at fixed reflux rate, output multiplicity, with multiple output values for the same reboiler duty, causes the column to drift to an undesirable

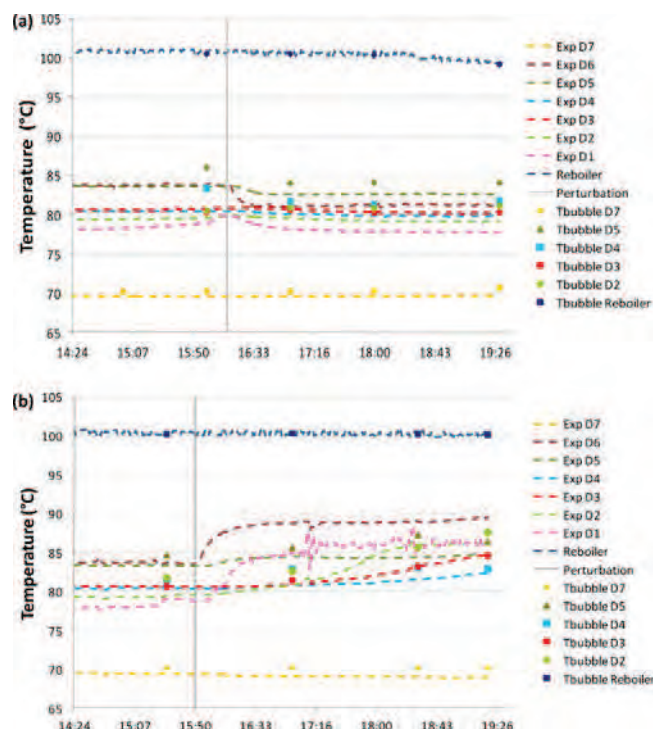


Fig. 23 – Comparison of measured and samplings bubble temperatures for test n°3 (a) and test n°4 (b).

steady-state under open loop operation. Both works agree that it can be avoided for a fixed reflux ratio policy. Due to the fact that our pilot is under fixed reflux rate configuration, the results may be of importance for further studies aiming at an experimental confirmation of the steady state multiplicities.

5.6. Verification of the temperature sensors reliability

During the experimental campaign, some drifts in temperatures were observed – mainly during tests n°4 and 5 – and this phenomenon could not be precisely explained. Any specific action or any change in operational conditions was identified as the reason for this behavior.

Samplings of the solution inside the column were withdrawn during the experiment and compositions were measured by analytical methods. Their theoretical bubble temperature were calculated and compared to the experimentally measured temperatures to verify the reliability of the temperature measures.

It is worth noting that each liquid distributor has two accesses; one is the entry for the thermocouple – present in all distributors – and the other one allows either the placement of a valve to withdraw liquid samples or the introduction of a feed stream. Thus, it was not possible to obtain samplings from D1 and D6, because they receive feed streams. This fact is an inconvenient because some unexpected behaviors were observed exactly at these locations and they cannot be verified. We accept the results from the comparison at other distributors.

It can be concluded from Fig. 23 that the experimental measures are coherent with the samplings in the majority of cases. This fact validates the reliability of the temperature sensors and thus the existence of unexplainable perturbations in the column, which were not predicted by the model.

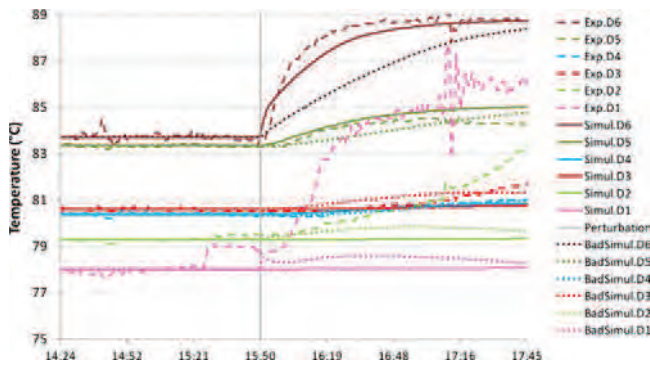


Fig. 24 – Experimental and simulated temperature evolution in test n°5, where “Simul” represents the adapted values for the hydrodynamics and “BadSimul” considers the default values.

5.7. Understanding the adjustable initial values for liquid holdup

In order to obtain a reliable dynamic model of the process it is known that its geometric, technological and hydraulic parameters need to be detailed. When these parameters concern external measures, such as column height and diameter or reboiler and condenser dimensions, for example, the values can be obtained from pilot observation. However, when the parameters concern internal measures such as the flow hydraulics due to packing characteristics, the evaluation becomes more difficult. It may be possible to accept the manufacturer specifications for some packing types, but in the case of structured reactive packing, the simple acceptance of the manufacturer specifications would not be very reliable.

Concerning the structured packing provided by Sulzer Chemtech® and used in our separative sections, extensive data obtained from experimental studies can be found in the literature. Dima et al. (2006) and Olujić et al. (2007) investigate the hydrodynamics of a counter-current gas-liquid flow laboratory-scale column structured with SulzerBX and MellapakPlus, respectively. The dynamic holdup was calculated in function of the liquid load and values from 0.02 to 0.10 were found for the initial liquid holdup at each stage. The process simulator AspenPlus® proposes a default fraction value of 0.05. The values are in agreement.

KATAPAK-SP Labo was used in the reactive section, which is a structured catalyst support for use in gas-liquid reaction systems in which catalyst pellets such as ion-exchange resins can be embedded. By combining catalyst containing wire gauze layers (catalytic layers) with layers of wire gauze packing (separation layers), it can achieve separation efficiencies equivalent to up to 4 theoretical stages per meter and catalyst volume fractions up to 50% (Gotze and Bailer, 2001). The performance of the KATAPAK-SP depends however on many parameters; the most important are dynamic liquid hold-up, pressure drop, residence time behavior, liquid physical properties and catalytic load point. Behrens et al. (2008) experimentally determined the static and dynamic liquid holdup characteristics of the catalyst-filled pockets as

encountered in KATAPAK-SP. The authors explained that the value for dynamic liquid holdup was between those for the static liquid holdup and for the catalytic load point. A methanol-water mixture was used and static liquid holdup fractions higher than 0.3 were verified. Kramer (1998) also stated that under gas-liquid trickling flow conditions, the static holdup at a packed bed of spherical particles may represent up to 25% or 33% of the total liquid holdup. It can be thus concluded that the initial liquid fraction in the reactive section is much higher than the holdups in the separative sections. It was then necessary to define different values to model the initial liquid fraction at each section of the column. The values that better represent the system behavior are given in Table 6.

All the required specifications for the structured catalytic packing highlight the need of special attention when modeling a heterogeneous catalyzed column, where the presence of solid particles strongly influences the system. The value adopted for the reactive section (the most different from the default value proposed by AspenPlus®) is deeply related to the specific operational conditions of the process and this is far from the idea of proposing a generic approach. The difficulties observed with the heterogeneous catalyzed columns explain why the great majority of industrial columns are under homogeneous catalysis configuration.

For the purpose of comparison, Fig. 24 shows the experimental and different predicted values for the temperature evolution in the column during test n°5, for example. The continuous lines represent the model with the adapted and coherent values for the hydrodynamic parameters and the dotted lines account for the simulation with the default values. It can be verified that the right definition of the hydraulic parameters is of great importance of the model reliability.

6. Conclusions and perspectives

An experimental campaign was conducted for the production of ethyl acetate from esterification of acetic acid and ethanol in a heterogeneously catalyzed reactive pilot column. Several tests were performed to determine the steady state conditions for a feed configuration with excess ethanol. A thorough analysis on steady state characteristics was performed and each test was simulated using the Aspen Plus® software. Good agreement was obtained between experimental and simulation results. One additional test was conducted under stoichiometric feed configuration and it was verified that the feed composition strongly influences the catalyst activity so that the reliability of the model requires an adaptation of the reaction kinetics for each operating condition. Important sensitivities of the pilot to heat duty and heat losses were also observed. In order to study the reactive system dynamics, five experimental tests were performed and they provided representative results. Perturbations were carried out in alcohol and acid feed streams, reflux rate and heat duty and sufficient data was available for defining realistic geometry, technology and hydrodynamics of the pilot. The model was developed in Aspen Plus Dynamics® considering all the parameters and conditions present at the pilot and a specific discussion on the best representation of the heterogeneously catalyst and the related holdup was developed. The system hydraulics is also shown to be strongly dependent on the present solution and its operating conditions. The values for liquid holdup must be adapted from those

Table 6 – Initial stage liquid fraction for each packing.

SulzerDX	KatapakSP-Labo	SulzerCY
0.02	0.45	0.05

provided by the manufacturers or the simulation software in order to be representative. An important effort was necessary to develop a unique model that qualitatively and quantitatively represents the system tendencies and responses. The dynamic model obtained is a reliable representation of the proposed reactive distillation process and it can be used to predict other possible perturbations that an industrial site may face such as an impurity of water on the feed streams, for example. It is concluded that the reliability of a complex system model lies on the deep knowledge of its operating conditions and sensitive parameters, specially in the case of heterogeneous catalyst. The requirement of experimental manipulations to obtain coherent model considerations is highlighted.

The important interests, in comparison to previous works, is that the operating conditions were analyzed for a continuous process under different perturbations on feed flow rates, reflux flow rate and heat duty and the same derived model is in agreement with all the conditions. The application of this dynamic approach to the heterogeneously catalyzed ethyl acetate esterification is a significant new contribution to the actual research concerning reactive distillation.

References

- Beckmann, A., Nierlich, F., Popken, T., Reusch, D., Scala, C., Tuchlenski, A., 2002. Industrial experience in the scale-up of reactive distillation with examples from C4-chemistry. *Chem. Eng. Sci.* 57, 1525.
- Behrens, M., Olujic, Z., Jansens, P.J., 2006. Hydrodynamics and mass transfer performance of modular catalytic structured packings. *Chem. Eng. Res. Des.* 84 (A5), 381.
- Behrens, M., Olujic, Z., Jansens, P.J., 2008. Liquid holdup in catalyst-containing pockets of a modular catalytic structured packing. *Chem. Eng. Technol.* 31 (11), 1630.
- Brehelin, M., 2006 December. Analyse de faisabilité, conception et simulation de la distillation réactive liquide-liquide-vapeur. Application et validation expérimentale sur la production de l'acétate de n-propyle. Ph.D. Thesis, Institut National Polytechnique de Toulouse, France.
- Chen, F., Huss, R.S., Doherty, M.F., Malone, M.F., 2002. Multiple steady states in reactive distillation: kinetic effects. *Comput. Chem. Eng.* 26, 81.
- Darge, O., Thyron, F.C., 1993. Kinetics of the liquid phase esterification of acrylic acid with butanol catalysed by cation exchange resin. *J. Chem. Technol. Biotechnol.* 58, 351.
- Dima, R., Soare, G., Bozga, G., Plesu, V., 2006. Gas-liquid hydrodynamics in counter current columns with Katapak-S and BX structured packing. *Rev. Roum. Chim.* 51 (3), 219.
- Gehrke, V., Marquardt, W., 1997. A singularity theory approach to the study of reactive distillation. *Comput. Chem. Eng. (Suppl.)*, S1001.
- Gotze, L., Bailer, O., 2001. Sulzer Chemtech reactive distillation with KATAPAK®. *Catal. Today* 69, 201.
- Grob, S., Hasse, H., 2006. Reaction kinetics of the homogeneously catalyzed esterification of 1-butanol with acetic acid in a wide range of initial composition. *Ind. Eng. Chem. Res.* 45, 1869.
- Harbou, E., Schmitt, M., Parada, S., Grossmann, C., Hasse, H., 2011. Study of heterogeneously catalysed reactive distillation using the D+R tray—a novel type of laboratory equipment. *Chem. Eng. Res. Des.* 89, 1271.
- Kenig, E., Schneider, R., Gorak, A., 1999. Rigorous dynamic modelling of complex reactive absorption processes. *Chem. Eng. Sci.* 54 (21), 5195.
- Kotora, M., Buchaly, C., Kreis, P., Gorak, A., Markos, J., 2008. Reactive distillation – experimental data for propyl propionate synthesis. *Chem. Papers* 62 (1), 65.
- Kramer, G.J., 1998. Static liquid hold-up and capillary rise in packed beds. *Chem. Eng. Sci.* 53 (16), 2985.
- Kumar, M.V.P., Kaistha, N., 2008. Role of multiplicity in reactive distillation control system design. *J. Process Control* 18, 692.
- Kumar, M.V.P., Kaistha, N., 2009. Evaluation of ratio control schemes in a two-temperature control structure for a methyl acetate reactive distillation column. *Chem. Eng. Res. Des.* 87, 216.
- Lai, I., Hung, S., Hung, W., Yu, C., Lee, M., Huang, H., 2007. Design and control of reactive distillation for ethyl and isopropyl acetates production with azeotropic feeds. *Chem. Eng. Sci.* 62, 878.
- Lee, H., Huang, H., Chien, I., 2006. Bifurcation in the reactive distillation for ethyl acetate at lower Murphree plate efficiency. *J. Chem. Eng. Jpn.* 39 (6), 642.
- Noeres, C., Dadhe, K., Gesthuisen, R., Engell, S., Gorak, A., 2004. Model-based design, control and optimisation of catalytic distillation processes. *Chem. Eng. Process.* 43 (3), 421.
- Mihal, M., Švandová, Z., Markoš, J., 2009. Steady state and dynamic simulation of a hybrid reactive separation process. *Chem. Papers* 64 (2), 193.
- Olujic, Z., Behrens, M., Spiegel, L., 2007. Experimental characterization and modeling of the performance of a large-specific-area high-capacity structured packing. *Ind. Eng. Chem. Res.* 46, 883.
- Ramzan, N., Faheem, M., Gani, R., Witt, W., 2010. Multiple steady states detection in a packed-bed reactive distillation column using bifurcation analysis. *Comput. Chem. Eng.* 34 (4), 460.
- Reder, C., Gehrke, V., Marquardt, W., 1999. Steady state multiplicity in esterification distillation columns. *Comput. Chem. Eng. (Suppl.)*, S407.
- Rosales-Quintero, A., Vargas-Villamil, F.D., 2009. On the multiplicities of a catalytic distillation column for the deep hydrodesulfurization of light gas oil. *Ind. Eng. Chem. Res.* 48, 1259.
- Schneider, R., Noeres, C., Kreul, L.U., Gorak, A., 1999. Dynamic modelling and simulation of reactive batch distillation. *Comput. Chem. Eng. (Suppl.)*, S423.
- Singh, A., Hiwale, R., Mahajani, S.M., Gudi, R.D., Gangadwala, J., Kienle, A., 2005. Production of butyl acetate by catalytic distillation. Theoretical and experimental studies. *Ind. Eng. Chem. Res.* 44 (9), 3042.
- Völker, M., Sonntag, C., Engell, S., 2007. Control of integrated processes: a case study on reactive distillation in a medium-scale pilot plant. *Control Eng. Pract.* 15 (7), 863.
- Walter, E., Pronzato, L., 2010. Identification of Parametric Models: From Experimental Data. Springer, London Ltd.
- Xu, Y., Zheng, Y., Ng, F.T.T., Rempel, G.L., 2005. A three-phase nonequilibrium dynamic model for catalytic distillation. *Chem. Eng. Sci.* 60 (20), 5637.