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Dynamics of reactive distillation for the production of ethyl acetate: experiments at a pilot plant and modelling

M. F. Fernandez[a,b,c,d,e], B. Barroso[e], X. M. Meyer[a*], M. Meyer[a], M.-V. Le Lann[b,c], G. Le Roux[d], M. Brehelin[e]

[a] *Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 4 Allée Emile Monso, F-31030 Toulouse, France*
[b] *CNRS; LAAS; 7 avenue du Colonel Roche, F-31077 Toulouse, France*
[c] *Université de Toulouse ; UPS, INSA , INP, ISAE ; LAAS; F-31077 Toulouse, France*
[d] *Department of Chemical Engineering, Polytechnic School of the University of São Paulo, Avenida Professor Lineu Prestes, 05088-900 São Paulo, Brazil*
[e] *Rhodia – Centre de Recherche et de Technologie de Lyon, , 85 avenue des Frères Perret - BP 62 – F-69192 St Fons, France*

Abstract

In order to understand the complex behaviour of the reactive distillation process and to be able to provide an accurate design of a reactive column, detailed analyses on both continuous and transient regime become necessary. The objective is the definition of a reliable simulation model, based on experimental data obtained from a real pilot-scale plant device for the heterogeneously catalysed esterification of acetic acid and ethanol to form ethyl acetate and water. The choice of the parameters for the continuous equilibrium model was discussed and the simulation results provided good agreement with experimental data, revealing an interesting sensitivity of the catalyst activity to the feed composition. Once column configuration and operational parameters were validated, dynamic experiments were realized so as to interpret the sensitivity of different disturbances. Feed flow rates, reflux ratio and heat duty were perturbed and the consequent open loop transient responses were identified. The assessment of hydrodynamic parameters and the validation of the transient data allow the definition of a reliable dynamic model that represents tendencies and behaviours of the process well. The resulting model is to be applied into a more complex controllability methodology.

Keywords: reactive distillation, modelling, heterogeneous catalyst, ethyl acetate, experimental validation

1. Introduction

In the context of process intensification, the reactive distillation (RD) is known to be a good way to improve process performances by integrating reaction and distillation in a single multifunctional process unit. Both research studies and industrial applications have shown the advantages of this integration, such as equilibrium limitations overcome, higher selectivity achievements, process cost reduction, plant size reduction. In turn, the combination of separation by distillation and reaction zones leads to complex interactions among vapour-liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for the design of these systems. These interactions result in important nonlinearities and multiplicities in the process dynamics, which also hinder its control and supervision. So as to better understand the process behaviour and the present nonlinearities, the dynamic analysis of RD systems

has attracted great attention in recent academic and industrial studies.
The LGC (Laboratoire de Génie Chimique, Toulouse, France) develops a methodology for the conception of RD systems (Thery et al., 2005) that has been successively extended and applied to academic and industrial case studies. However, when the conceptual design of a RD process is optimally obtained based on static analysis, regarding only economics and environmental criteria, the result may be a plant very difficult to control. Thus, there is an important concern about complementing this work by integrating controllability and diagnosticability aspects. Because the LAAS (Laboratoire d'Analyse et d'Architecture des Systèmes, Toulouse, France) develops a methodology for systems diagnosis (Kempowsky et al., 2002) and sensor selection based on classification methods (Hedjazi et al., 2010), the application of this approach at the conceptual design of the RD is attractive and it has not yet been proposed.
In the context of the proposal of a methodology that considers controllability aspects from the conceptual design step, the objective of this work is the definition of a reliable RD model on both steady state and transient regimes, based on several experimental data obtained in a real pilot plant device for the production of ethyl acetate.

2. Pilot Presentation

The RD of the heterogeneous catalysed esterification of ethanol (EtOH) and acetic acid (HOAc) to ethyl acetate (EtOAc) and water (H2O) is studied in the pilot-scale column on the research centre of Rhodia at Lyon, France. The pilot consists of a glass column with an inner diameter of 75mm and a height of 7m, divided into 7 modular sections of 1m with a liquid distributor on the top. The column is thermally insulated and it works at atmospheric pressure. Three feed flows are present: the acetic acid, the ethanol and the reflux, which represents an external reflux. The column has a hybrid configuration, divided into three parts: the rectifying zone (top section), the reactive zone (five middle sections) and the stripping zone (bottom section). The pilot is schematized in Figure 1, where the liquid distributors are numbered from the bottom to the top and the packing structure has the following characteristics:

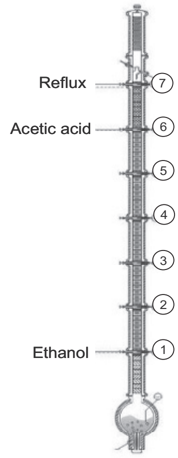

Fig.1.
Pilot schema

- one modular section is filled with the structured packing SulzerDX (NET~8)
- five modular sections are filled with the reactive structured packing Katapak SP-Labo with an acidic ion-exchange resin as heterogeneous catalyst (NET~11)
- one modular section is filled with the structured packing SulzerCY (NET~8)

The essays were chosen to work under ethanol excess feed configuration in order to consume all the acid and to meet the stringent acid specification for acetates. For the purpose of comparison, an additional essay at steady state with stoichiometric feed configuration was conducted. It is worth mentioning that the system conditions were not optimised to provide the best productivity; pilot constraints were accepted and the experiments were conducted following the process dynamic tendencies and responses to disturbances. All essays were performed as follows: after total-reflux conditions, the three feed streams and the product lines were switched on. The system was observed until steady state conditions were reached. A disturbance of one parameter was caused in the column, by trying to keep all other parameters constant. Liquid samples were withdrawn from the distributors, the distillate and the bottom line, and different methods were applied to analyse their composition: gas chromatography, Karl Fischer and acid-base titration.

3. Experimental results at steady state

Table 1 shows the essays configuration, the perturbation carried out and the results on conversion rate:

Essay	Steady state configuration	Dynamic perturbation	Feed ratio EtOH/HOAc	Acid conversion	Alcohol conversion
A	ethanol excess	-	1.13	97.2%	86.2%
B	stoichiometric	-	1.04	93.7%	90.0%
C	ethanol excess	+10% reflux	1.12	96.1%	86.1%
D	ethanol excess	-10% reflux	1.12	97.7%	86.1%
E	ethanol excess	+10% acid	1.13	97.8%	86.5%
F	ethanol excess	+10% alcohol	1.12	96.7%	86.7%
G	ethanol excess	-5% heat duty	1.13	98.4%	86.3%

Table 1. Operation conditions and resulting conversion rates

For the analysis of the steady-state regimes, Figure 2 shows the composition and the temperature profiles for essay E at steady state, before perturbation; the vertical axis accounts for column height:

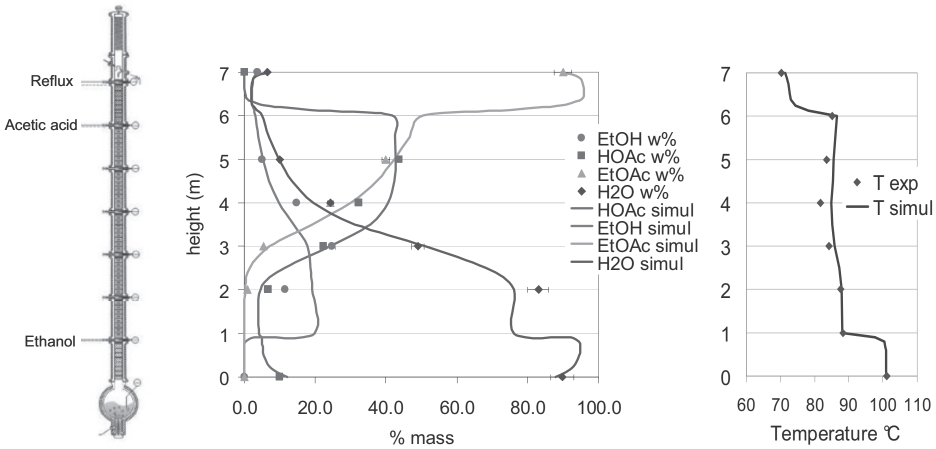

Fig. 2. Composition and temperature profiles throughout the pilot column

4. Experimental results at dynamic regime

Five dynamic experiments were carried out, providing representative results for the process responses after disturbances in alcohol and acid feed flow rates, reflux ratio and heat duty. Sufficient data was obtained from the compositions and temperatures through the column. In essays C and D a disturbance in the reflux was imposed by increasing and decreasing 10% of its flow rate, respectively. Figures 3 and 4 illustrate the values for the distillate compositions and for the temperatures on the central liquid distributors:

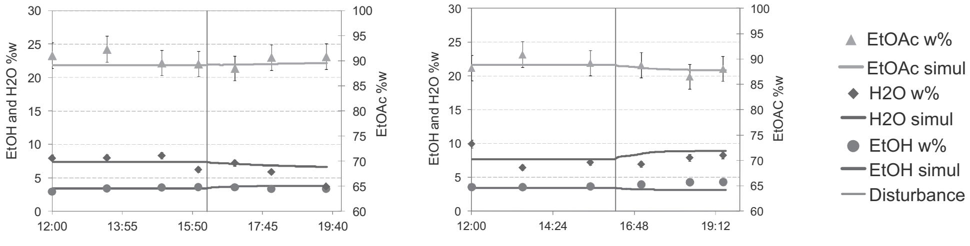

Fig. 3. Dynamic behaviour of distillate compositions on essay C and essay D, respectively

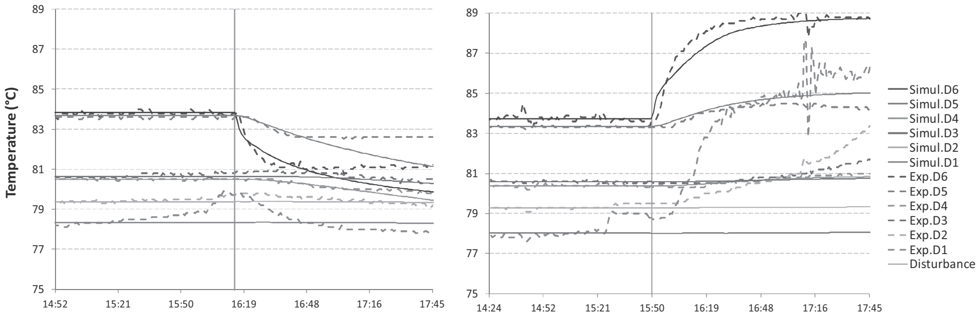

Fig. 4. Dynamic behaviour of temperatures on essay C and essay D, respectively

5. Modelling and Discussion

The Aspen Plus® software was used to develop a continuous model for the process simulation. The intrinsic parameters such as thermodynamics and kinetics were chosen from Rhodia previous studies; the NRTL activity coefficient model was considered for the phase equilibrium and the Hayden–O'Conell model with association parameters was used to account for the acid dimerisation in the vapour phase. The operational variables as flow rates, pressure and heat duty were adapted from the conditions of each essay, and the heat loss was calculated from the temperatures and the materials present in the pilot. The column was represented by 27 theoretical equilibrium stages and the reboiler. Predicted and measured values of the product streams flow rates and compositions show good agreement for all essays. Figure 2 presents the simulation results as continuous lines and the experimental samplings with points and it can be concluded that the RD continuous equilibrium model is validated for the ethyl acetate system.

A notable observation when comparing the results of essay A and B was that different feed ratios influence compositions trough the column and, consequently, the catalyst resin activity. Accordingly, it was necessary to adapt values of the reaction efficiency in order to better fit the simulated conversion ratio to experimental results. To deal with this fact in Aspen Plus®, an adjustable coefficient C was considered in the reaction kinetics equations, allowing the definition of higher efficiency for the stoichiometric feed configuration (C=1) when comparing to the ethanol excess feed configuration (C=0.5). Some explanations can be considered for this behaviour:

- Water inhibits the activity of the ions exchanger resin (catalyst); with stoichiometric feed, the water composition inside the column is lower than with ethanol excess feed.
- The software supposes that the liquid reaction occurs at continuous stirred tank conditions. However, the supposed liquid flow conditions were not encountered in the essays, where Péclet number is approximately 30.
- Liquid flow through the catalyst bags is affected by its composition: preferential paths are caused by the resin non-homogeneous inflation or by the variable wettability.

In contrast with the reactive zone that has a flat temperature profile, the separative zones show strong temperature gradient. A temperature measure inside a separative zone will be highly sensitive to a dysfunction or a change on the steady state conditions. It is thus possible to infer the regulation of hybrid reactive columns by measures placed in the separative zones; this fact is acknowledged in the literature (Kumar and Kaishta 2009).

Once column configuration and operational parameters were validated, the system behaviour in transient regime can be analysed by the definition of a dynamic model. The need of the experimental campaign is highlighted to the acquisition of parameters such as column geometry, technology and hydrodynamics. The values for reboiler design, diameter of the column and height of theoretical stages were chosen from pilot observation. A different initial liquid volume fraction was adopted for stages with structured reactive packing and flooding calculations were permitted. This information was introduced into the Aspen Plus® model and the steady state obtained was the initialisation for the simulations using Aspen Plus Dynamics®.

Figure 4 reveals that model predictions and experimental results are in good agreement for essay C. Although some predicted values do not exactly match the final experimental data, the trends and the velocities are similar for both temperature and composition analysis. This result is also valid for essays F and G. Concerning essay D, it is observed that the temperatures from distributors 1 and 2 derived and the cause of this phenomenon is not considered in the model. This behaviour was also found in distributors 3 and 6 during the essay E. It is assumed that these temperatures are strongly sensitive to an operation condition that is not repeatable for all essays and it was not identified during pilot manipulations. The fact that the feeds are positioned on distributors 1 and 6 may induce additional perturbations that cause the greater uncertainties at these stages. It is also possible that, during some essays (about 14h from morning to evening), the evolution of the ambient temperature caused different heat loss values, while the model considers it constant. This hypothesis may be accepted because the pilot dimensions provide large superficial contact with the environment. It is expected that this geometric issue will not be encountered in industrial scale devices.

Finally, the developed model combines information from the steady state and from the dynamic regime of the ethyl acetate system and it can be accepted for the representation of the process behaviour. All the phenomena experimentally observed will be included in the controllability and the diagnosticability analysis.

6. Conclusions and future work

An experimental campaign was conducted for the production of ethyl acetate from esterification of acetic acid and ethanol in a pilot reactive column. Several essays were conducted with the first aim of reaching steady state conditions for a feed configuration with excess of ethanol. A thorough analysis at steady state was performed and the process was simulated using the Aspen Plus® software. Good agreement was verified between experimental and simulation results. One additional essay was conducted under stoichiometric feed configuration and it was verified that the feed composition strongly influences the catalyst activity. Five experimental essays have been performed so as to study the system dynamics and they provided representative results. Sufficient data was available for definition of the geometry, the technology and the hydrodynamics of the pilot. Disturbances were carried out in alcohol and acid feed streams, reflux and heat duty and both the composition and the temperature profiles through the column were followed. A reliable dynamic model was validated to be the basis of a future study on controllability and diagnosticability of RD processes.

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