

## Influence of the Optimisation Approach on the Determination of Operating Conditions of Batch Global Syntheses

S. Elgue, J.M. Le Lann, M. Cabassud, L. Prat, J. Cézerac\*

Laboratoire de Génie Chimique, UMR 5503, CNRS/INPT(ENSIACET)/UPS,  
5 rue Paulin Talabot, B.P. 1301, 31106 Toulouse Cedex 1, France,  
sebastien.elgue@ensiacet.fr

\*Sanofi-Synthelabo, 45 Chemin de Météline, B.P. 15, 04201 Sisteron Cedex, France

Optimisation of fine chemistry syntheses is often restricted to a dissociated approach of the process, lying in the separated determination of optimal conditions of each operating step. In this paper, an optimisation framework integrating a global optimisation approach is presented. Based on an accurate modelling of reaction-separation processes linked with an efficient SQP method, this framework allows optimising various fine chemistry syntheses. The purpose of the present paper focuses on the validation and the application of this framework. Thus, compared with a classical approach, the application to a propylene glycol synthesis highlights the benefits and the limits of the proposed methodology.

*Keywords:*

Optimisation, dynamic simulation, hybrid system, batch operations

### Introduction

The synthesis of fine chemicals or pharmaceuticals, widely carried out in batch processes, implies many successive reaction and separation steps. Thus, synthesis optimisation is often restricted to the determination of the optimal operating conditions of each step separately. This approach is based on the use of reliable optimisation tools and has involved the development of various optimal control studies in reaction and distillation.<sup>1,2</sup>

Nevertheless, such an approach does not definitely lead to the optimal conditions for a global synthesis. For example, optimising the conversion of a reaction for which separation between the desired product and the by-products is more difficult than between the reactants, will involve an important operating cost, due to further difficulties in the separation scheme. Thus, necessity to simultaneously integrate all the process steps in a single global optimisation approach clearly appears. Recent issues in the dynamic simulation and optimisation have been exploited to accomplish this goal. Thus, in literature optimisation works based on a global approach recently appears.<sup>3–5</sup> These works because of the global process configuration (e.g. reactive distillation process), because of the modelling simplifications and because of the optimisation procedure do not allow grasping the benefits linked to a global approach.

The purpose of the present study is to propose, by mean of a global synthesis optimisation framework, a comparison between a classical and a global optimisation approach. Applied to a standard reaction-separation synthesis, this comparison emphasises the characteristics of each approach. This paper is also divided into two parts. The first part details the optimisation framework, based on a dynamic simulator associated with an efficient optimisation method and presents the associated validation carried out through a process of methyl acetate production. The second part focuses on the optimisation of propylene glycol synthesis and highlights the global approach benefits and limits.

### Simulation environment

Because of the step by step structure of global syntheses, the simulation tool developed is based on a hybrid modular model. The continuous part represents the behaviour of batch equipments, the discontinuous part, the train of the different steps occurring during the synthesis of a product. The modular description integrates three detailed modules: a feed-batch reactor module, a column module, an overhead condenser module. By association of these modules, various fine chemistry processes can be represented: fine chemical reactor, evaporator reactor, reactor with overhead condenser, reactor with overhead column, batch distillation column, reactive batch distillation column, etc.

## Model equations

The rigorous and detailed description of each module involves modelling aspects resulting on a differential algebraic equations (DAE) system. Differential equations consist of total and component material balances, total energy balance and continuity equation in the case of steam vapour heating. Algebraic equations are composed of vapour-liquid equilibrium relationships, summation equations and physical property estimations. In order to simplify the model establishment, the following assumptions are applied:

- perfect mixing,
- vapour-liquid equilibrium with possible introduction of Murphree,
- negligible vapour holdup. Chemical reactions in the vapour phase are not considered,
- constant volume of liquid holdup (except for the reactor),
- total condenser with a possible sub-cooling.

In order to be able to represent a wide variety of fine chemistry processes, a general model integrating simultaneously the three modules has been considered. Then, according to the synthesis process, the column and/or the condenser are neglected by an efficiency and a holdup set to zero. Hence, the general process model scheme is as shown in figure 1, with plates numbered from top to bottom.

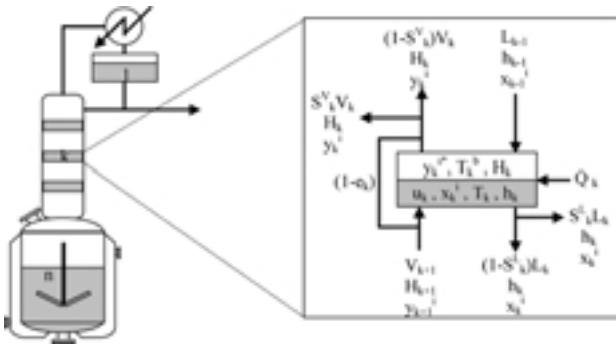


Fig. 1 – Model general scheme

Several literature works have influenced establishment of the reactor model<sup>6,7</sup> and of the column and condenser models<sup>8,9</sup>. According to these works, for a generic plate  $k$ , representing either the reactor, either the condenser or either a column tray, the following equations can be written:

Total mass balance

$$\frac{du_k}{dt} = F_k + (1 - S_{k+1}^V)V_{k+1} + (1 - S_{k-1}^L)L_{k-1} - (1) \\ - V_k - L_k + \left( \sum_i \sum_j C_S^{i,j} \times r^j \right) v_k + R_k L_1$$

Component  $i$  mass balance

$$\frac{d(u_k x_k^i)}{dt} = F_k x_k^{f,i} + (1 - S_{k+1}^V)V_{k+1} y_{k+1}^i (2) \\ + (1 - S_{k-1}^L)L_{k-1} x_{k-1}^i - V_k y_k^i - L_k x_k^i \\ + \left( \sum_j C_S^{i,j} \times r^j \right) v_k + R_k L_1 x_1^i$$

Energy balance

$$\frac{d(u_k h_k)}{dt} = F_k h_k^f + (1 - S_{k+1}^V)V_{k+1} H_{k+1} (3) \\ + (1 - S_{k-1}^L)L_{k-1} h_{k-1} - V_k H_k - L_k h_k \\ + \left( \sum_j \Delta H r^j \times r^j \right) v_k + R_k L_1 h_1 + Q_k$$

Equilibrium relationship

$$y_{k+1}^i (1 - e_k) + e_k K_k^i x_k^i - y_k^i = 0 (4)$$

Vapour enthalpy balance (for column only)

$$H_{k+1} (1 - e_k) + e_k H_k^* - H_k = 0 (5)$$

For the condenser, plate 1:

$$Q_1 = U_{c,cf} A_{c,cf} (T_{cf} - T_1) - (1 - S_2^V)V_2 \Delta H c_1, (6)$$

$$e_1 = 1, \quad R_1 = 0$$

For the reactor, plate  $n$ :

$$Q_n = U_{r,rw} A_{r,rw} (T_{rw} - T_n), \quad e_n = 1, \quad R_n = 0 (7)$$

In order to keep a general formulation of the equations system, a general reflux term has been defined into mass and energy balances ( $R_k L_1$ ). Physically, the liquid reflux from the condenser is introduced in the top of column (second stage). Consequently, vector  $R_k$  represents the plate  $k$  reflux ratio (with  $R_k = 0$  if  $k = 2$  and  $R_k = R$  if  $k = 2$ ) and  $L_1$  the reflux flow rate descended from the condenser.

Previous equations constitute the basic mathematical model. Summation equations, equations of the thermodynamic models (molar enthalpy, molar holdup and VLE constant), side streams equations and thermal equations complete this mathematical model. Thermal modelling is particularly detailed in order to allow temperature control, notably during constant temperature policy. A heat transfer fluid circulating in the jacket ensures heating and cool-

ing. Thus, equations 8 to 10 describe the reactor thermal behaviour. Correlations based on the geometrical characteristics of the reactor are used to determine heat transfer coefficients.<sup>10</sup> A complete physical property estimation system with associated data bank is also used<sup>11</sup>.

Reactor wall energy balance

$$m_{rw} C_{p,rw} \frac{dT_{rw}}{dt} = U_{r,rw} A_{r,rw} (T_n - T_{rw}) \quad (8)$$

$$+ U_{rw,amb} A_{rw,amb} (T_{amb} - T_{rw})$$

$$+ D_{rw,hf} C_{p,rw,hf} \rho_{hf} (T_{hf} - T_{rw})$$

Jacket energy balance

$$m_{hf} C_{p,hf} \frac{dT_{hf}}{dt} = U_{rw,hf} A_{rw,hf} (T_{rw} - T_{hf}) \quad (9)$$

$$+ U_{hf,jw} A_{hf,jw} (T_{jw} - T_{hf})$$

$$+ D_{hf} C_{p,hf} \rho_{hf} (T_{hf}^{in} - T_{hf})$$

Jacket wall energy balance

$$m_{jw} C_{p,jw} \frac{dT_{jw}}{dt} = U_{jw,amb} A_{jw,amb} (T_{amb} - T_{jw}) \quad (10)$$

$$+ U_{hf,jw} A_{hf,jw} (T_{hf} - T_{jw})$$

### Numerical solution

The complete model representing the dynamic behaviour of global syntheses leads to a set of differential and algebraic equations, with the following characteristics:

- huge dimension,
- strong non-linearity,
- stiffness.

DISCO,<sup>12</sup> a general solver of DAE system, based on the Gear method obtains the numerical solution of the developed model. Besides its accuracy and numerical robustness, DISCO allows from its events detection facilities and automatic initialisation procedure, to develop a complex procedure of the dynamic process management.

### Process dynamic management

The global synthesis treatment requires to simulate the train of different steps and particularly to account for the startup and the shutdown of these steps. Thus, one process step is divided into many modelling sub-steps. Rigorous modelling requires a specific model for each of these sub-steps and so transitions from one to another may lead to discontinuities in the mathematical model structure. The

management procedure of this dynamic consists of the following scheme:

- detection of the associated event (i.e. for evaporation: temperature reaching the bubble point),
- resulting modifications in the mathematical model, corresponding to the occurring step,
- accurate initialisation of the new mathematical model,
- integration of the new mathematical model.

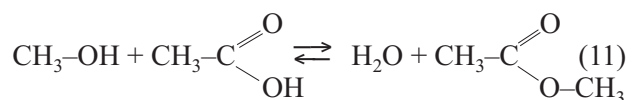
The relative heaviness of this procedure is however compensated, in CPU time terms, by the DISCO integration velocity and accuracy, due to the use of operator sparse and to its automatic initialisation procedure for the new DAE system. This procedure has been satisfactorily validated in the context of batch distillation columns startup.

### Experimental validation

The global synthesis model involves different modelling aspects: reaction and separation aspects. In order to validate simultaneously all these aspects, a complex process of reactive batch distillation has been studied. It has to be noted that separation aspects have also been separately validated on an industrial solvent changing process<sup>13</sup>.

### Experimental

Bonnaillie et al.<sup>14</sup> considered a methyl acetate production process by reactive distillation. The batch pilot plant and the experimental results of their study have been exploited in the validation of the general model of the present work. The batch pilot plant involves a glass reactor with an overhead distillation column. The bottom plant is composed of a stirred jacketed glass reactor of 5 litres volume. The jacket is provided with a heat transfer fluid circulating in a boiler at around 160 °C. The overhead distillation column consists of a multiknit packed column (50 cm in length and 10 cm in diameter) with a condenser and a distillate tank. The condenser involves a spiral coil heat exchanger provided with cooling water. An adjustable timer regulates periodic switching between distillate tank and reflux to the column, with a constant reflux policy.



Methanol    Acetic acid    Water    Methyl acetate  
(65 °C)    (118 °C)    (100 °C)    (57 °C)

Production of methyl acetate is ensured by the addition of acetic acid to methanol with sulfuric

acid as homogeneous catalyst, as can be shown on the reaction scheme (11). Comparison of boiling point temperatures shows the higher volatility of methyl acetate relative to the other components. Thus, methyl acetate removals, by distillation, enable the reaction to reach higher conversion than theoretical equilibrium value. Three experiments have been exploited: experiment with reaction only, experiment with distillation only (following a reaction phase), experiment of reactive distillation, i.e. coupling of reaction and distillation. The experimental conditions are listed in table 1.

Table 1 – *Experimental conditions*

Experiment	Initial molar ratio	Reflux ratio	Catalyst amount
a Reaction	1.4	$\infty$	5 ml
b Distillation	1.4	2.5	5 ml
c Coupling	1.4	$\infty$ , 2.5	5 ml

### Simulation validation

In order to verify the mathematical model accuracy, the experiments carried out by Bonnaille et al.<sup>14</sup> have been simulated. The same thermodynamic (NRTL) and kinetic models have been used. It has to be noted that reaction rate model is a simple kinetic model (12), in agreement with data reported in literature<sup>15</sup>.

$$r = k_{\text{ester}} \exp\left(\frac{-E_A}{RT}\right) \left( C_{\text{AAc}} \cdot C_{\text{MeOH}} - \frac{C_{\text{H}_2\text{O}} \cdot C_{\text{MeAc}}}{K_{\text{eq}}} \right) \quad (12)$$

with:

$$k_{\text{ester}} - \text{pre-exponential factor} = 3300 \text{ l} \cdot \text{mol}^{-1} \cdot \text{mn}^{-1} \cdot \text{ml}^{-1} \text{ H}_2\text{SO}_4$$

$$E_A - \text{activation energy} = 41800 \text{ J} \cdot \text{mol}^{-1}$$

$$K_{\text{eq}} - \text{equilibrium constant} = 5$$

Simulations are based on the description of the packed column by means of discrete stages with constant volume holdup and integrating Murphree efficiency (see model equations). Previous work<sup>14</sup> shows that the considered packed column comprises 6 theoretical stage and studies the influence of the kinetic and thermodynamic modelling on the representation accuracy.

For each experiment (reaction, distillation and coupling) the

simulations are compared to samples withdrawn into the reactor (fig. 2 to 4). Figure 3 and 4 show, during distillation and coupling experiments, light differences between experimental and simulated compositions. These differences are explainable, on the one hand by the strong thermodynamic non-ideality of the mixture and on the other hand by the kinetic model simplicity. In fact complex kinetic models<sup>16</sup> and models taking into account the non-ideality of the mixture and so integrating thermodynamic models<sup>17,18</sup> would probably provide more accuracy. Nevertheless, the good agreement between experiments and their mathematical representations allows validating the simulation environment. Simulations also show, through coupling results, the advantages linked to reactive distillation and emphasise the necessity of taking into account all the synthesis operating steps (in this case, reaction and distillation) in optimal conditions determination.

### Dynamic optimisation

Various successive operating steps generally constitute a global synthesis: reaction steps, concentration and purification steps. Thus, taking into account each step influence in the determination of the synthesis optimal operating conditions appears necessary. Consequently, optimisation variables of the global problem consist of the specific control variables of each step: reactor temperature or reactants addition rate for reaction step, reflux ratio for distillation step, etc. Specificities of the different process steps, for example production rate or product purity for reaction step, are then considered as global final constraints. Thus, the dynamic optimisation problem of global syntheses consists of a general optimal control problem.

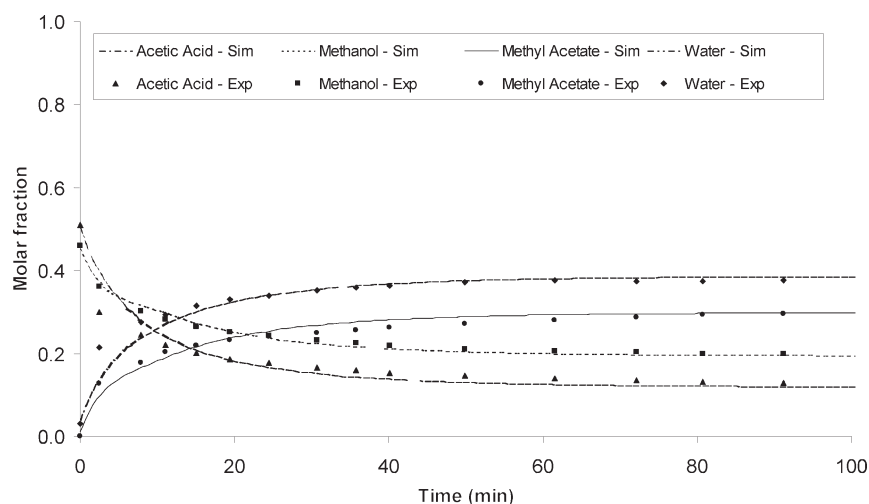


Fig. 2 – *Variation of reactor composition with time for reaction experiment*

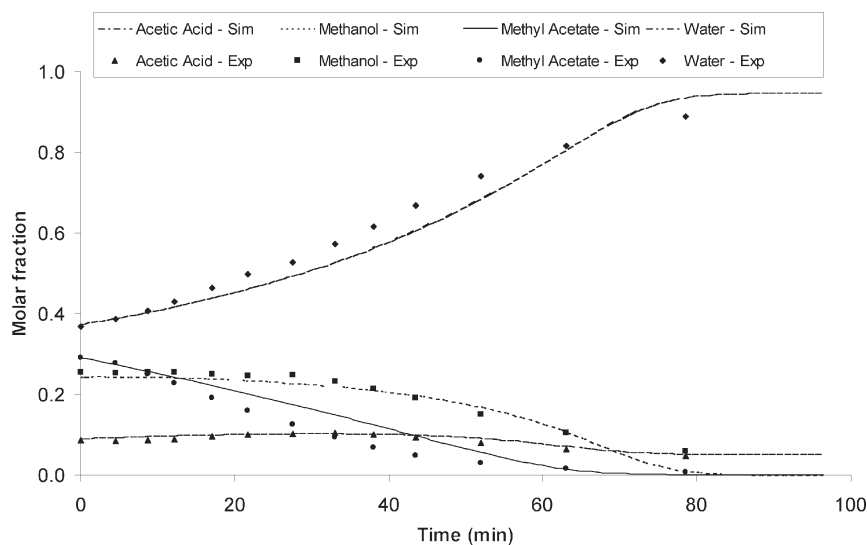


Fig. 3 – Variation of reactor composition with time for distillation experiment

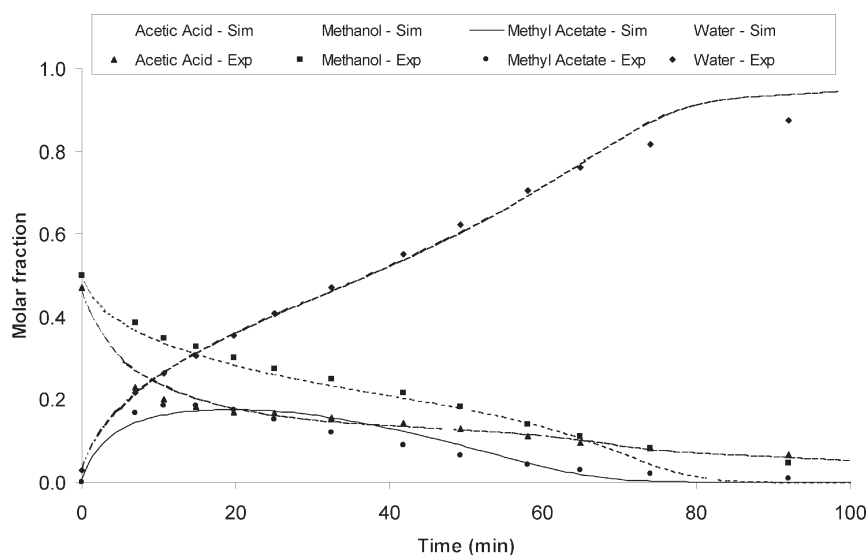


Fig. 4 – Variation of reactor composition with time for reactive distillation experiment

Non-linear programming (NLP) technique is used for solving the dynamic optimisation problem. This NLP approach involves transforming the general optimal control problem, which is of infinite dimension (the control variables are time-dependant), into a finite dimensional NLP problem by means of control vector parameterisation (CVP).<sup>19</sup> According to this parameterisation technique, the control variables are restricted to a predefined form of temporal variation which is often referred to as a basis function: Lagrange polynomials (piecewise constant, piecewise linear) or exponential based function.<sup>20</sup>

A successive quadratic programming (SQP) method<sup>21</sup> is applied to solve the resultant NLP. The chosen optimisation method requires in addition to the values of the objective function and the constraints, the knowledge of their gradients with re-

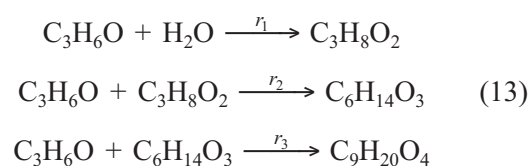
spect to control variables. For global syntheses, owing to processes complexity, analytic expression of gradients is not available. In this case, a numeric estimation can be provided by sensitivity equations or finite differentiation methods which constitute the computationally more efficient methods<sup>22</sup>. The use of specific tools (specific DAE solver<sup>12</sup> and specific optimisation method<sup>21</sup>) can not afford to easily develop sensitivity equations method. Consequently, gradients estimations are performed by finite differentiation method. The use of finite differentiation suffers from the need for careful selection of the perturbation size and for numerous additional integrations of the mathematical model. Once more, DISCO integration velocity allows reducing the CPU time.

## Comparison of optimisation approaches

The purpose of the present study lies in the comparison between a traditional (dissociated) and a global optimisation approach, on a standard synthesis example. Thus, a simple reaction-separation process of propylene glycol production has been successively optimised according to each approach.

### Propylene glycol production

Industrially, propylene glycol is obtained by hydration of propylene oxide to glycol. In addition to monoglycol, smaller amounts of di- and triglycols are produced as by-products, according to the following reaction scheme:



Water is supplied in large excess in order to favour propylene glycol production. The reaction is catalysed by sulfuric acid and takes place at room temperature. In order to dilute the feed and to keep the propylene oxide soluble in water, methanol is

also added. The reaction is carried out in a 5 litre stirred-jacketed glass reactor. Initial conditions described by Furusawa et al.<sup>23</sup> have been applied: an equivolumic feed mixture of propylene oxide and methanol is added to the reactor initially supplied by water and sulfuric acid, for a propylene oxide concentration of  $2.15 \text{ mol} \cdot \text{L}^{-1}$ . In agreement with previous works reported in literature<sup>23–25</sup>, kinetic parameters of the reaction model are summarised in table 2.

Table 2 – Kinetic model of propylene glycol formation

Reaction	Pre-exponential factor ( $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )	Activation energy ( $\text{Kcal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )	Reaction apparent order		Heat of reaction ( $\text{Kcal} \cdot \text{mol}^{-1}$ )
			A	B	
1	$1.22 \cdot 10^8$	18.0	1	1	-20.52
2	$1.39 \cdot 10^{10}$	21.1	1	1	-27.01
3	$9.09 \cdot 10^{11}$	23.8	1	1	-25.81

Arrhenius law  $r = k \cdot \exp\left(\frac{-Ea}{RT}\right) [A]^{O_A} [B]^{O_B}$

According to components bubble point (table 3), separation of propylene glycol involves the distillation of the methanol and the resultant reactants (for the most part water). Propylene glycol and by-products are then recovered from the boiler. The process overhead batch distillation column consists of a packed column of 50 cm in length and 10 cm in diameter. A condenser equipped with a complex controlled reflux device completes this process. A heat transfer fluid supply reactor jacket with a temperature varying from 10 to 170 °C according to the operating steps. The geometric characteristics of the column are the same as the esterification column ones. Hence, the behaviour of the column is assumed to be represented by 6 theoretical stages with constant volume holdup.

### Reaction optimisation

Optimal control problem of reactions generally involves two contradictory criteria: the operating time and the reactants conversion. Thus, in the case of the present work, the optimisation study amounts in the determination of the optimal profiles of temperature and reactants addition, for an operating time objective function with an acid conversion constraint set up to 95.5 %. Within the con-

Table 3 – Components separation characteristics

Component	Bubble point temperature (°C)
Propylene oxide	34
Methanol	65
Water	100
Propylene glycol	182
Dipropylene glycol	233
Tripropylene glycol	271

text of an industrial reactor, the considered temperature consists in the heat transfer fluid temperature.

Two different optimal control problems have been studied with or without a production constraint on the by-products amount: by-products amount inferior to 3.5 % of the total produced amount. In these problems, the temperature profile of the heat transfer fluid is discretised in five identical time intervals. Piecewise constant parameterisation of the temperature has then been adopted. Reactant addition flow rate has also been discretised in five intervals, but only the four last ones have the same size. Then, the time of the first interval and the value of the piecewise constant constitute the optimisation variables of the feed flow rate. The optimisation results are given on figures 5 and 6.

Optimisation results show that a batch addition of the reactant constitutes the best feed profile. According to the reaction scheme (consecutive-competitive reactions) these profiles could be a priori determined.<sup>26,27</sup> The configuration of the activation energies implies that a temperature increase favours the production of by-products. Thus, it appears that, in optimal profiles, the temperature is maintained low and particularly with a by-products constraint.

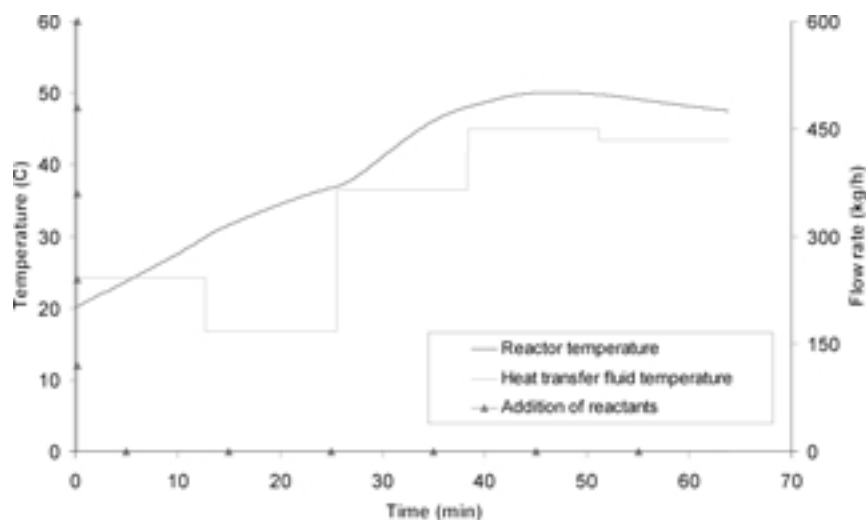


Fig. 5 – Optimal reaction profiles without by-products constraints

At the end of the reaction step, the reactor temperature increases in order to respect the conversion constraint (95.5 %).

### Distillation optimisation

Optimal control of a batch distillation column consists in the determination of the suitable reflux policy with respect to a particular objective function (e.g. profit) and set of constraints (e.g. product purity). In the purpose of the present work, the optimisation problem is defined with an operating time objective function and purity constraints set on the recovery ratio (90 %) and on the propylene glycol final purity (80 % molar). Different basis functions have been adopted for the control vector parameterisation of the problem: piecewise constant and linear with five identical time intervals and a hyperbolic tangent function. Optimal reflux profiles are determined with the final conditions of the previous optimal reactions as initial conditions. The optimal profiles of the resultant distillations are presented on figures 7 and 8.

The determination of the optimal reflux profiles leads to equivalent results in the case of propylene glycol production with or without by-products constraint. In fact, due to a reaction step carried out with large water excess, the compositions at the beginning of the separation step are quite identical, independently of the considered production.

For a given production (with or without by-products constraint), independently of the considered profile, the optimal solution appears to be the same, with an accurate representation by continuous profiles (figures 7 and 8). This equivalence highlights the strong non-linearity of the optimisation problem and the difficulty to find suitable optimal solutions. Moreover, in the cases of piecewise linear and hyperbolic

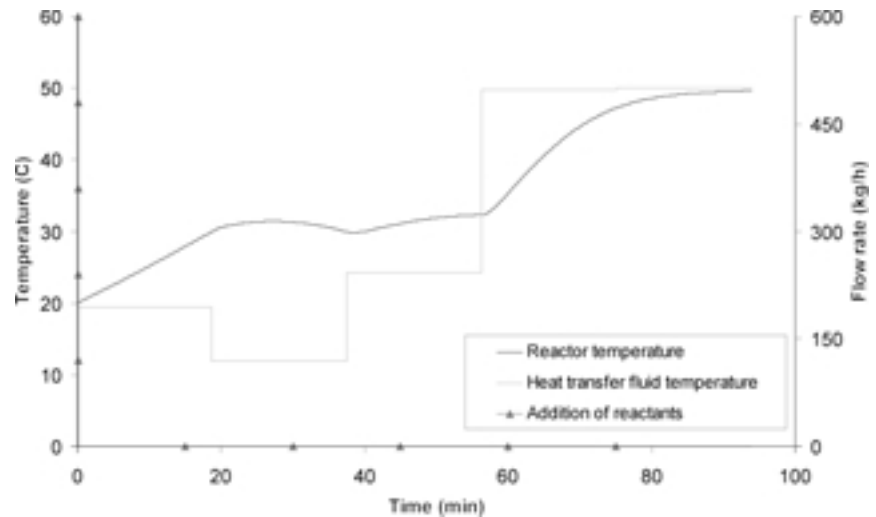


Fig. 6 – Optimal reaction profiles with a by-products constraint

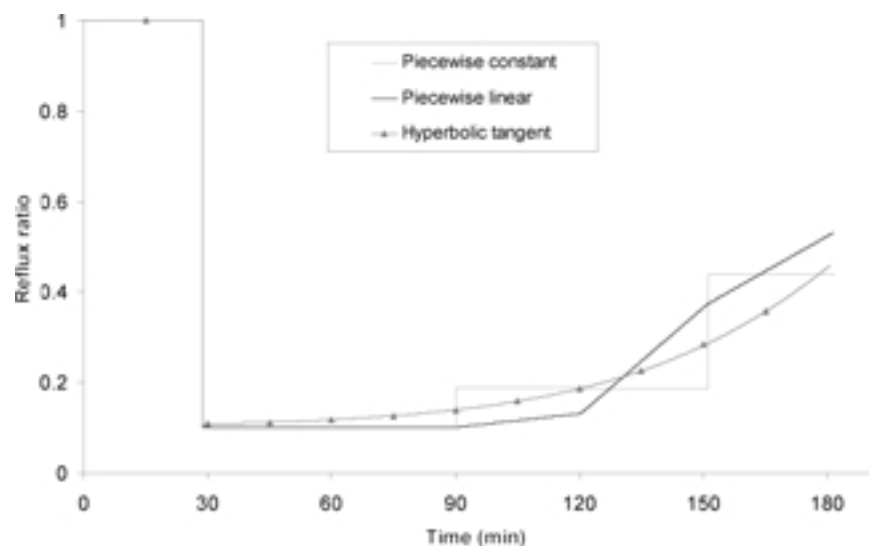


Fig. 7 – Optimal reflux profiles resultant from a reaction without by-products constraints

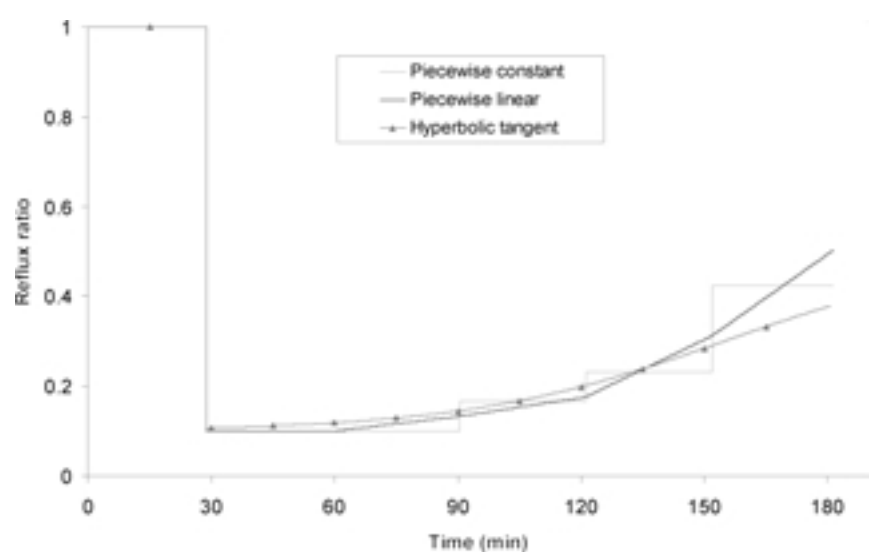


Fig. 8 – Optimal reflux profiles resultant from a reaction with a by-products constraint

tangent reflux profiles, initials conditions (initial value of optimisation variables) are extrapolated from the optimal piecewise constant profile. This procedure contributes to the obtaining of optimal profiles close to the piecewise constant one. Specific initial conditions according to the considered parameterisation profile should probably lead to different solutions and then to conclude in the continuous profiles superiority (hyperbolic tangent, piecewise linear).

### Global synthesis optimisation

In this part of the study, optimisation of the production is carried out according to a global approach. The reaction step and the successive distillation step intervene simultaneously in the evaluation of the optimal operating conditions. In order to compare these results with the classical approach ones, like in the previous studies, an operating time criterion has been chosen. Thus the optimisation problem lies in the minimisation of the operating time required for the propylene glycol synthesis.

According to the previous optimisations, two kinds of propylene glycol production have been studied: a production with yield and purity constraints and a production with in addition a by-products constraint. In order to compare the different optimisation approaches, the same constraints have been adopted. Thus, the constraints on the final conditions for the global approach are the following:

- yield  $\geq 86\%$  (Conversion  $\geq 95.5\%$  during reaction and recovery ratio  $\geq 90\%$  during distillation),
- propylene glycol final composition  $\geq 80\%$  molar,
- by-products amount recovered  $\leq 3.8\%$  of total produced amount recovered (only for synthesis with a by-products constraint).

Control variables of the global synthesis optimisation problem consist of the different control variables of reaction and distillation steps extended to the total operating time: heat transfer fluid temperature, reactants addition flow rate and reflux ratio. Thus, except for the reactants addition, discretisation of the control variables differs from previous sections. The temperature is represented by a piecewise constant profile with six time intervals and a variable size for the last one. This discretisation offers an accurate temperature profile (with five intervals) in the beginning of the synthesis, when temperature vari-

ations have the most influence on the propylene glycol production. The last interval appears to be dedicated to the separation, when heat transfer fluid temperature reaches its maximal value. Reflux is assumed to be total during the reaction step and the column startup, with a constant volume holdup for each theoretical stage. Then, reflux ratio is represented by piecewise constant or linear (5 identical intervals) or by a hyperbolic tangent function.

Because of the configuration of the propylene glycol reaction scheme (consecutive-competitive reactions), a batch profile also constitutes the optimal solution of reactants introduction in the case of a global approach. Thus, in order to simplify results presentation, optimal profiles of reactants addition are not given. The optimal temperature conditions lead to a temperature profile of the heat transfer fluid divided in two parts. The first part represents a pure reaction step in which temperature is maintained low in order to favour propylene glycol production. The second part consists of a separation step with a maximal heat transfer fluid temperature. As opposition to a classical approach, in this case, these reaction and separation steps are not dissociated, separation beginning before the end of propylene glycol formation.

During the optimisation study, the influence of different reflux profiles (piecewise constant or linear, hyperbolic tangent function) has been evaluated. Like in distillation optimisation and for the same reasons, variation of reflux policy leads to the same optimal reflux profile and does not affect the other optimal operating conditions. Nevertheless, hyperbolic tangent profiles appear better allowing slightly reduction of the operating time. Consequently, only reflux optimal profiles based on hyperbolic tangent function are described in results graphical representations: figures 9 and 10.

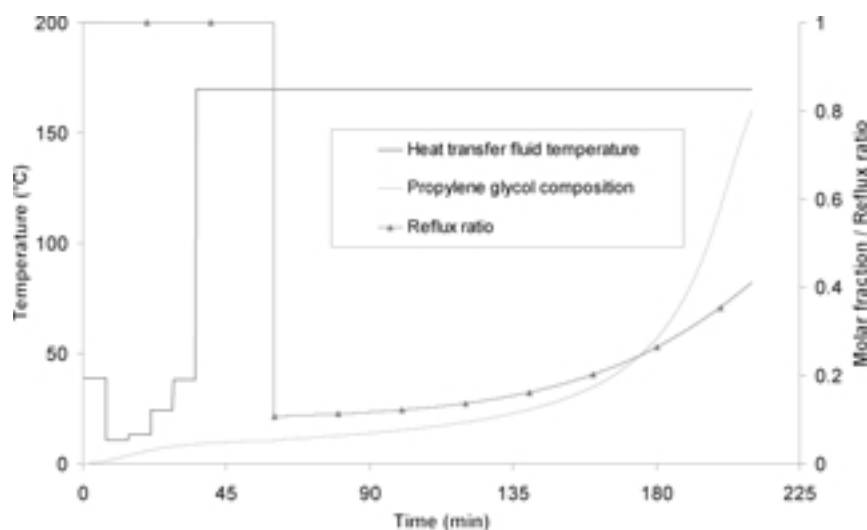


Fig. 9 – Optimal profiles for global synthesis without by-products constraints



### Comparison of optimisation approaches

The different optimisation approaches are compared in terms of optimal control variables (figures 11 and 12) and in terms of objective function (operating time, table 4). Propylene glycol synthesis involves three control variables: reactants introduction, heat transfer fluid temperature, reflux policy. Whatever the optimisation approach is, a batch profile always constitutes the optimal solution of reactants introduction. Hence, the comparison of control variables is reduced to the comparison of temperature and reflux policy.

In the case of a global approach, the optimal temperature profile of heat transfer fluid involves a shorter pure reaction step. The beginning of distillation (maximal value of the heat transfer fluid temperature) occurs earlier, before the total conversion of propylene oxide, revealing a coupling between the reaction and the separation steps. Optimal solutions based on a classical approach, because of the dissociated consideration of the operating steps can not integrate such a coupling. This coupling involves a particular temperature profile, lying during pure reaction step, initially in an increased reaction temperature and then in an enhanced cooling in order to compensate the by-products formation during the separation beginning and to obtain the desired final production.

The global approach improves the determination of the optimal operating conditions, resulting in an operating time reduction, from 9 to 14 %. This reduction appears as the consequence of the coupling between reaction and separation steps resulting in a faster reaction and an earlier separation. Nevertheless, an addition of constraints to the synthesis optimisation problem, by restricting

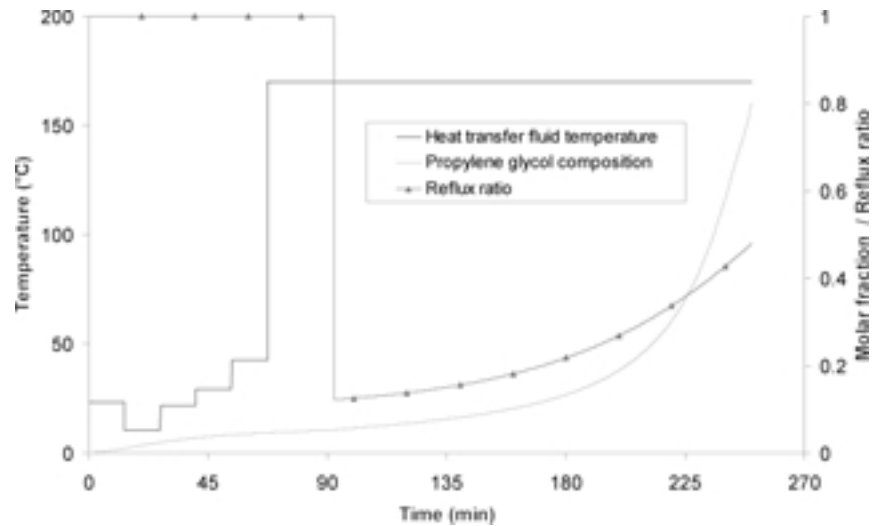


Fig. 10 – Optimal profiles for global synthesis with a by-products constraint

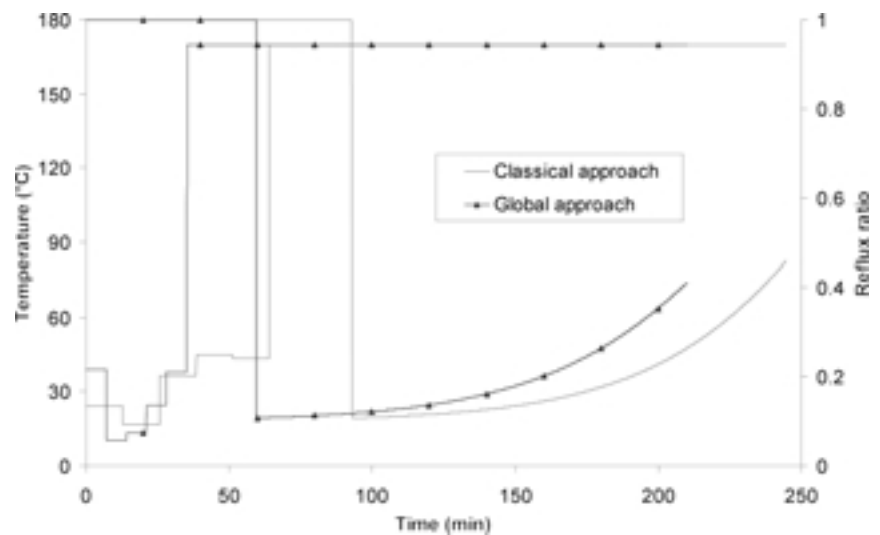


Fig. 11– Comparison of the optimal operating conditions according to the optimisation approach in the case of propylene glycol synthesis without by-products constraints

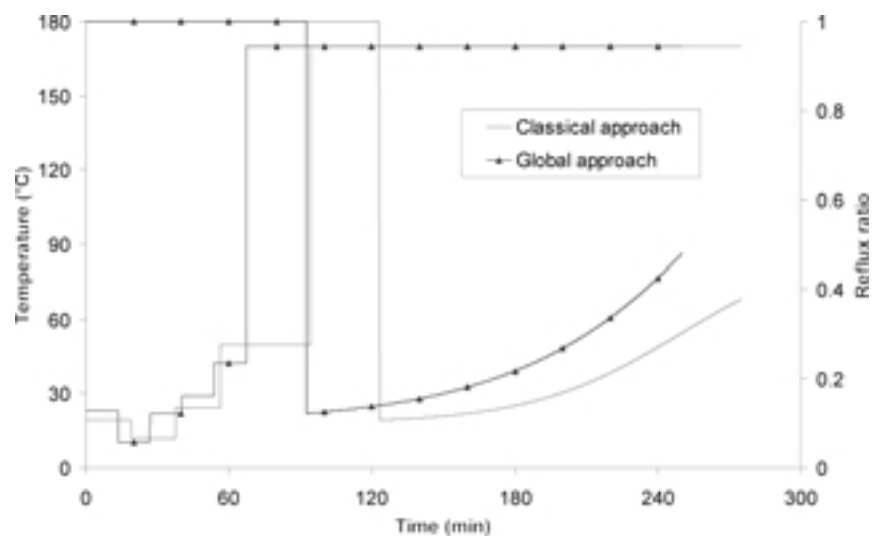


Fig. 12– Comparison of the optimal operating conditions according to the optimisation approach in the case of propylene glycol synthesis with a by-products constraint

Table 4 – Comparison of operating times according to the optimisation approach

		Classical approach			Global approach		
		Variables	Constraints	Op. Time	Variables	Constraints	Op. Time
Synthesis without by-products constraint	Reaction	12	2	1 h 04 min			
	Separation	4	2	3 h 02 min			
	Global	16	4	4 h 06 min	17	2	3 h 30 min
	Gain						14 %
Synthesis with by-products constraint	Reaction	12	3	1 h 34 min			
	Separation	4	2	3 h 02 min			
	Global	16	5	4 h 36 min	17	3	4 h 11 min
	Gain						9 %

the coupling influence, leads the global approach nearer a dissociated approach and so reduces the possible benefits. Consequently, global optimisation approach appears attractive in the case of high coupling synthesis (e.g. synthesis capable to be performed by reactive distillation processes) and offers only few improvements in high constrained synthesis problems.

## Conclusion

The study reported in this paper lies in the use of a general optimisation framework dedicated to global syntheses and based on a global approach. In contrast with a classical approach, a global approach simultaneously integrates all operating steps in the determination of a process optimisation conditions and so takes into account possible coupling between steps. The resultant benefits of this methodology have been clearly demonstrated in an example of reaction solvent choice.<sup>28</sup>

The dynamic simulation aspects of this framework have been validated through the study of a reactive batch distillation process of methyl acetate production. In spite of the strong coupling between reaction and separation (i.e. between kinetic and VLE modelling aspects) of the reactive distillation, the framework successfully provides accurate and reliable representations of various experiments.

The developed framework presents the capability of solving optimal control problems by a global and also a classical approach. The application of this characteristic to a propylene glycol synthesis provides a relevant comparison leading to strategic conclusions about global approach advantages. Thus, outwards cases of global process (e.g. reactive distillation process) in which a global approach constitutes the only optimisation alternative, global approach appears more favourable in cases of low

constrained processes. Such “freedom” provides the possibility to couple operating steps and so to realise resultant benefits. Introduction of constraints in the optimisation problem restricts this possibility and then reduces the influence of a global approach. For high constrained processes, unfortunately the majority of fine chemistry processes, the global approach tends towards a classical dissociated approach and then provides few improvements. Nevertheless, in such cases our framework offers the advantage of an estimation of these improvements.

## Notation

$A$	– heat transfer area, $m^2$
$C$	– concentration, $mol \cdot l^{-1}$
$C_p$	– specific heat, $J \cdot kg^{-1} \cdot K^{-1}$
$C_s$	– stoichiometric coefficient
$D$	– heat transfer fluid flow rate, $m^3 \cdot s^{-1}$
$E_a$	– activation energy, $J \cdot mol^{-1}$
$e$	– Murphree efficiency
$F$	– molar flow rate of feed, $mol \cdot s^{-1}$
$h$	– liquid molar enthalpy, $J \cdot mol^{-1}$
$H$	– vapour molar enthalpy, $J \cdot mol^{-1}$
$K$	– VLE constant
$L$	– molar flow rate of liquid, $mol \cdot s^{-1}$
$m$	– mass, kg
$Q$	– rate of heat transfer, $J \cdot s^{-1}$
$r$	– reaction rate, $mol \cdot m^{-3} \cdot s^{-1}$
$R$	– reflux ratio
$S^L$	– liquid side stream coefficient
$S^V$	– vapour side stream coefficient
$t$	– time, s
$T$	– temperature, K
$U$	– heat transfer coefficient, $J \cdot m^{-2} \cdot K^{-1} \cdot s^{-1}$
$u$	– molar holdup, mol
$V$	– molar flow rate of vapour, $mol \cdot s^{-1}$
$v$	– volume, $m^3$

- $x$  – liquid mole fraction  
 $y$  – vapour mole fraction

### Greek letters

- $\Delta H_c$  – molar condensation heat,  $J \cdot mol^{-1}$   
 $\Delta H_r$  – formation enthalpy,  $J \cdot mol^{-1}$   
 $\rho$  – density,  $kg \cdot m^{-3}$

### Subscripts

- amb – ambient medium  
 c – condenser  
 cf – condenser cooling fluid  
 hf – heat transfer fluid  
 jw – jacket wall  
 k – plate index  
 n – total number of plates  
 r – reactor  
 rw – reactor wall

### Superscripts

- in – inlet  
 f – feed  
 i – component index  
 j – reaction index  
 \* – vapour liquid equilibrium

### References

1. *Toulouse C.*, PhD Thesis, I. N. P. Toulouse, Toulouse, 1999
2. *Furlonge, H. I.*, PhD Thesis, Imperial College, London, 2000
3. *Ishikawa, T., Natori, Y., Liberis, L., Pantelides C. C.*, *Comput. Chem. Eng.* **21** (1997) S1239
4. *Furlonge, H. I., Pantelides, C. C., Sorensen, E.*, *AIChE J.* **45** (1999) 781
5. *Wajge, R. M., Reklaitis, G. V.*, *Chem. Eng. J.* **75** (1999) 57
6. *Hernandez, H., Zaldivar, J. M., Barcons, C.*, *Comput. Chem. Eng.* **18** (1993) S45
7. *Cézerac, J.*, PhD Thesis, I. N. P. Toulouse, Toulouse, 1995
8. *Gani, R., Ruiz, C. A., Cameron, I. T.*, *Comput. Chem. Eng.* **10** (1986) 181
9. *Albet, J., Le Lann, J. M., Joulia, X., Koehler, B.*, COPE-91, Barcelona, Spain (1991) 75
10. *Dream, R. F.*, *Chem. Eng. January* (1999) 90
11. *Le Lann, J. M., Joulia, X., Koehler, B.*, *Int. Chem. Eng.* **28** (1988) 36
12. *Sargousse, A., Le Lann, J. M., Joulia, X., Jourda, L.*, MOSIM'99, Annecy, France, 1999
13. *Elgue, S., Cabassud, M., Prat, L., Le Lann, J. M., Casamatta, G., Cézerac, J.*, ESCAPE 11, Kolding, Denmark, 2001
14. *Bonnaillie, L., Meyer, X. M., Wilhelm, A. M.*, ISMR2, Nuremberg, Germany, 2001
15. *Smith, H. A.*, *J. Am. Chem. Soc.* **61** (1939) 254
16. *Balland, L., Mouhab, N., Cosmao, J. M., Estel, L.*, *Chem. Eng. Proc.* **41** (2002) 395
17. *Ronnback, R., Salmi, T., Vuori, A., Haario, H., Lehtonen, J., Sundqvist, A., Tirronen, E.*, *Chem. Eng. Sci.* **52** (1997) 3369
18. *Popken, T., Gotze, L., Gmehling, J.*, *Ind. Eng. Chem. Res.* **39** (2000) 2601
19. *Vassiliadis, V. S., Sargent, R. W. H., Pantelides, C. C.*, *Ind. Eng. Chem. Res.* **33** (1994) 2123
20. *Farhat, S., Czernicki, M., Pibouleau, L., Domenech, S.*, *AIChE J.* **36** (1990) 1349
21. *Schittkowski, K.*, *Annals of Op. Res.* **5** (1986) 485
22. *Rosen, O., Luus, R.*, *Comput. Chem. Eng.* **15** (1991) 273
23. *Furusawa, T., Nishiura, H., Miyauchi, T.*, *J. Chem. Eng. Japan* **2** (1969) 95
24. *Xing, Y.*, Master of Engineering Thesis, Widener University, Chester, 1996
25. *Fogler, H. S.*, *Elements of chemical reaction engineering*, Third Edition, Prentice Hall PTR, 1998
26. *Burghardt, A., Skrzypek, J.*, *Chem. Eng. Sci.* **29** (1974) 1311
27. *Garcia, V.*, PhD thesis, I. N. P. Toulouse, Toulouse, 1993
28. *Elgue, S., Prat, L., Cognet, P., Cabassud, M., Le Lann, J. M., Cézerac, J.*, ISCRE17, Hong Kong, China, 2002

