Infinite/infinite analysis as a tool for an early oriented synthesis of a reactive pressure swing distillation

Jordi Bonet a,c, Raphaëlle Thery a, Xuan-Mi Meyer a, Michel Meyer a, Jean-Michel Renaeume b, Maria-Isabel Galan c,∗, José Costa c

a Laboratoire de Génie Chimique, UMR-CNRS 5503, INPT-ENSIACET, 5 rue Paulin Talabot, 3106 Toulouse Cedex 01, France
b UPPA/LATEP, Rue Jules Ferry, 64000 Pau, France
c Departament d’Enginyeria Química, Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain

Abstract

The study contributes to the characterization of an original reactive pressure swing distillation system. The methyl acetate (MeAc) transesterification with ethanol (EtOH) to produce methanol (MeOH) and ethyl acetate (EtAc) is shown as illustrative example. The streams outside the units are evaluated by the $\infty/\infty$ analysis to provide insights on the process behavior. Two simpler systems with recycling stream are also presented. The $\infty/\infty$ analysis allows checking the interrelation of the system streams without any column design consideration. Unfeasible regions, low limit values, multiplicity regions, discontinuities, control difficulties, recommendable operation conditions and column profile combinations are predicted and discussed. All these information are useful to establish an early and suitable system design strategy.

Keywords: Infinite/infinite analysis; Reactive distillation; Pressure swing

1. Introduction

Any sensibility analysis starts by the determination of the number of degrees of freedom. A continuous distillation column has two degrees of freedom when the pressure is fixed. These two variables can be manipulated to produce desired streams purity, e.g. reflux and distillate flow rate. To determine the distillate flow rate influence using rigorous simulation, fixing the feed flow rate and composition, it is necessary to choose the values for the number of stages for the stripping and rectifying sections and for the reflux. If any of these values are smaller than its minimal values, there will not be solution and neither convergence. So, instead of choosing any big enough values arbitrarily to assure the solution, it would be preferable to fix them to infinite and take advantage of the great simplifications provided. Thus the sensibility analysis can be performed without any column design considerations.

Infinite reflux and infinite number of stages are the simplifying hypotheses which have inspired the name of the $\infty/\infty$ analysis. This analysis was firstly proposed by Petlyuk and Avet’yan (1971), but without any significant impact on the scientific community. The potential of this analysis was rediscovered by Bekiaris, Meski, Radu, and Morari (1993) which lead it to a great grade of maturity (Bekiaris & Morari, 1996), it was extended to heterogeneous systems (Bekiaris, Meski, & Morari, 1996), kinetically controlled reactions (Gütinger & Morari, 1999) and its potential on process synthesis to find and rank feasible separation schemes (Ulrich, 2002). Potential control difficulties related to composition profile stability can also be investigated based on the $\infty/\infty$ analysis (Bonanomi & Morari, 2002; Dom & Morari, 2002a, 2002b).

The simplifying hypothesis of an infinite reflux reactive column enables to consider a packed column molar compositions profile as a section of a reactive residue curve (Ung & Doherty, 1995a). The simplifying hypothesis of an infinite length column implies that the column profile contains a pinch point. As the reflux is infinite, the pinch point must correspond to a singular point (pure component, azeotrope or reactive azeotrope). In reactive distillation, the Static Analysis uses also the infinite reflux hypothesis because it is easily checked via the reactive residue curve map whether there is a curve from the distillate to the bottom and therefore a feasible column pro-
The $\infty/\infty$ analysis is by itself a powerful tool but its potential can be increased by being coupled to other additional calculations for completing the design information, e.g. stage by stage calculations. Thery (2002) and Thery, Meyer, and Joulia (2004) proposed a sequential study for the feasibility, synthesis and design of reactive distillation process based on equilibrium reaction. Firstly, the streams outside the units are evaluated by the $\infty/\infty$ analysis. Secondly, the last results are used to fix the variables outside the units and focus on the evaluation of the streams and parameters inside the units (stage by stage calculation). And thirdly, all the parameters and streams of the entire system are evaluated together to assess their influence on the energy, costs, security and/or environmental factors. The information and insights obtained in each step are used on the subsequent calculations. A fast to rigorous calculations direction is followed and the exactness and complexity of the model can be increased at each step.

The mathematical model used in this paper for the $\infty/\infty$ analysis is composed by the mass balances around the units and the chemical equilibrium equation. For instance, the $\infty/\infty$ analysis is by itself a powerful tool but its potential can be increased by being coupled to other additional calculations for completing the design information, e.g. stage by stage calculations. Thery (2002) and Thery, Meyer, and Joulia (2004) proposed a sequential study for the feasibility, synthesis and design of reactive distillation process based on equilibrium reaction. Firstly, the streams outside the units are evaluated by the $\infty/\infty$ analysis. Secondly, the last results are used to fix the variables outside the units and focus on the evaluation of the streams and parameters inside the units (stage by stage calculation). And thirdly, all the parameters and streams of the entire system are evaluated together to assess their influence on the energy, costs, security and/or environmental factors. The information and insights obtained in each step are used on the subsequent calculations. A fast to rigorous calculations direction is followed and the exactness and complexity of the model can be increased at each step.

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2. Methodology

The $\infty/\infty$ analysis proceeds as follows. Thanks to the hypothesis of infinite number of stages and infinite reflux and, therefore to the presence of a singular point on the column profile, the sensibility analysis cannot be performed.

Considering continuous non-extractive distillation, when a column profile contains an unstable node, the distillate, all residue curves start from it and can reach any bottom molar composition in the same distillation region, fulfilling the mass balance. Also when the bottom is at the stable node, all residue curves of the distillation region converges to it and start at any distillation composition in the same region fulfilling the mass balance. Graphically, the fulfillment of the mass balance corresponds to distillate, feed and bottom molar compositions set on straight line, with the flow rates set according to the lever rule (Fig. 1).

A four component system with one reaction has only two independent molar fractions, the other two are related by the chemical equilibrium constant and the summation of the four molar fractions to one. Reactive compositions are defined by these relations, and they can be used as the real compositions (Ung & Doherty, 1995b).

3. Evaluation of systems with recycling streams by the $\infty/\infty$ analysis

The aim of this paper is to contribute to the characterization of an original reactive pressure swing distillation system (Bonet et al., 2004). This new system leads to the process intensification and therefore it drives to energy savings with lower costs (Charpentier, 2005). The reaction and the pressure swing are used in synergy to overcome four azeotropes, two are eliminated by the reaction and the pressure swing is used to cross the boundary line that the other two form. The illustrative example is the methyl acetate (MeAc) transesterification with ethanol (EtOH) to produce methanol (MeOH) and ethyl acetate (EtAc) (España, 1996):

$$\text{MeAc} + \text{EtOH} \Leftrightarrow \text{EtAc} + \text{MeOH}$$
This example is of industrial interest and beneficial for the environment. The polyvinyl alcohol is a non-flammable, non-toxic and biodegradable polymer but, for each tonne of polyvinyl alcohol, around 1.68 tonnes of residual stream composed by MeAc and MeOH at the molar composition of atmospheric pressure azeotrope are produced (xMeOH = 0.35).

A non-reactive pressure swing distillation and a reactor followed by a distillation column to recycle the reactants are also shown for a better understanding of the reactive pressure swing presented. The reactor followed by a distillation column has been studied by Kiss, Bildea, Dimian, and Iedema (2002) and Kiss, Bildea, Dimian, and Iedema (2003). They focused on the reactor influence while the distillation column was considered as a black box where the products where separated completely from the reactants. They concluded that stirred and plug flow reactors have the same behavior.

Ramirez and Gani (2004) point out that the high sensitivity to changes or disturbances in the operating variables for the reaction-separation-recycle configurations are due the nonlinearity of process and kinetic models, the specified performance of the separation units and/or the amount of purge from a recycle stream. A systematic resolution approach is proposed. Firstly, the reactor design, the kinetic rate constant, the reactor volume and the feed flow rate are grouped into the dimensionless parameter known as the Damkohler number (Da) and the distillation column is a black box with the recycling of all unreacted components, removal of the entire product and no purge as in Kiss et al. (2003). Secondly, the parameters are ungrouped and the recovery factor of the column and the reactants feed ratio becomes variables of design. From a controllability point of view for a reaction of type \( A + B \leftrightarrow C \), it can be stated that as the reactants flow rate ratio approaches the stoichiometry, a high sensitivity to this ratio is observed and the possibility of the “snowball-effect” therefore increases. Finally, the last results were verified by rigorous simulation.

In the present paper the reaction kinetics are not considered and the Damkohler number is taken as infinite, only the nonlinearity of the process by itself is evaluated. The column is considered under the \( \infty/\infty \) hypothesis instead as a black box.

\[ D1 = \frac{1}{4Kz(1-z)} \]

3.1. Reactor followed by a distillation column to recycle the reactants

A simple situation where a reactant is converted to a product by an equilibrium reaction \( (K = 0.63) \) is considered. The reactant is more volatile than the product and can be separated by distillation. The \( \infty/\infty \) analysis is applied to the system composed by an infinite volume reactor, a distillation column under the \( \infty/\infty \) hypothesis and a distillate recycle stream to the reactor (Fig. 2). Fc and \( xFc \) are fixed. The system has only one degree of freedom, e.g. D1.

The results of the \( \infty/\infty \) analysis are shown in Fig. 3. The flow rates for each stream and for each component are proportional to the plotted thickness of the stream. D1 is chosen as the manipulated variable. On the left side (0) of the graphic, D1 is zero and increases uniformly until infinite. Too higher values for D1 are not interesting and they are not graphically represented above an arbitrary value (+). The energetic costs increase in proportion to D1. As there is not mole generation, Fc is equal to B1 according to the overall mass balance. Then, at steady state, it is not possible to manipulate B1 because it would produce an accumulation or loss of moles closed inside the system.

When D1 is zero, all the other streams have the same flow rate value equal to Fc. F is pure reactant and F1 is at chemical equilibrium. As D1 increases, then F and F1 also increase. When D1 goes from zero to the optimal value, then \( xD1 \) is at pure reactant (fulfilling the \( \infty/\infty \) hypothesis), while B1 increases its product content. The optimal D1 is the minimal D1 which produces pure product at B1. For D1 bigger than the optimal, B1 is assured as pure product (fulfilling the \( \infty/\infty \) hypothesis). The distillation energetic costs increase according to the distillate flow rate.

If there are two reactants which produce two products \( (R1+R2 \leftrightarrow P1+P2) \), the \( \infty/\infty \) analysis is similar (Fig. 4). It has also only one degree of freedom, e.g. D1. The two reactants ratio on the distillate R1/R2 can be at any value “\( z \)” when there are not azeotropes. This ratio is more a design variable than a manipulated variable. The optimal D1 depends on “\( z \)” according to

Fig. 2. Sketch for the reactor and distillation system.

Fig. 3. \( \infty/\infty \) analysis for the reactor and distillation system (R \( \leftrightarrow \) P).
The excess of one reactant closed inside the system is set by the system start up: it is not manipulated by D1. In this paper, we are not talking about dynamic behavior, just about steady state. From a dynamic point of view, it would be possible to adjust the ratio of reactants closed inside the system by changing the feed composition. But at steady state, when the system has a high quantity of one of the reactants, the second reactant introduced by a stoichiometric feed will be always at low concentration inside the system. The optimal flow rate ratio of reactants inside the system depends on the reaction stoichiometry. When the reactants are not in a stoichiometric ratio, a higher D1 is necessary to achieve its optimal value (Fig. 5).

3.2. Pressure swing distillation without reaction

A non-reactive pressure swing distillation for breaking the azeotrope MeOH/MeAc is considered (Fig. 6). This azeotrope is enough pressure sensitive to make the pressure swing distillation feasible (Appendix A). An increase in pressure, leads to azeotropic molar composition richer in MeOH. A constant Fc, at the azeotropic molar composition at atmospheric pressure, is feed to the system. In a first higher pressure column (877,470 Pa), an azeotropic molar composition richer in MeOH, due the pressure, is obtained by D1 and then xB1 becomes richer in MeAc. D1 is fed to a second column at atmospheric pressure (101,320 Pa), obtaining a xD2 richer in MeAc and xB2 becomes richer in MeOH. D2 is recycled, mixed with Fc and this resulting stream F1 is fed to the first column. The system has two degrees of freedom, e.g. B1 and D2.

The results of the ∞/∞ analysis when B1 is chosen as manipulated degree of freedom and D2 is fixed are shown in Fig. 7. There is an optimal B1 which produces pure MeAc at xB1 and pure MeOH at xB2 when their distillates are at xDP1 and xDP2 respectively (see Appendix A). When B1 is between zero (0) and the optimum, the first column profile contains the singular point of pure MeAc at xB1 and the second column profile contains the singular point of xDP2. When B1 becomes smaller than the optimal, xD1 becomes closer to xF1 and xB2 becomes closer to xFc.

When B1 is between the optimal and the maximal values, the first column profile contains the singular point xDP1 and the
second column profile contains the singular point of pure MeOH at \( x_B2 \). As \( B1 \) becomes larger than the optimum, \( xD2 \) becomes closer to \( xDP1 \) and \( xB1 \) becomes closer to \( xFc \).

The results of the \( \infty/\infty \) analysis when \( D2 \) is chosen as manipulated degree of freedom and \( B1 \) is fixed are shown in Fig. 8. There is a minimal \( D2 \) corresponding to the situation of both distillate molar compositions (0.650 and 0.455 in MeOH) at their azeotrope, respectively, at pressure \( P1 \) (101,320 Pa) and \( P2 \) (877,470 Pa). For our example, when products are collected pure at the bottoms, this minimal \( D2 \) is 1.3 times \( B1 \). \( D2 \) has no influence on both column bottoms. A \( D2 \) increase leads to multiple possibilities according the lever rule on the second column mass balance. Then the lever section from \( xD1 \) to \( xD2 \) must become smaller than the lever section from \( xD1 \) to \( xB2 \). This diminution can be achieved by increasing the MeOH content of \( xD2 \) or by increasing the MeAc content of \( xD1 \). A complete range of solutions are feasible, from fixing \( xD1 \) at \( xDP1 \) (0.650 MeOH) to fix \( xD2 \) at \( xDP2 \) (0.455 MeOH).

3.3. Reactive pressure swing distillation

A reactive pressure swing to increase the value of the residual azeotrope MeOH/MeAc by transesterification with EtOH is proposed (Fig. 9). This transesterification produces a quaternary mixture with four azeotropes (MeOH/MeAc, EtOH/MeAc, MeOH/EtAc, EtOH/EtAc) and the traditional scheme of a reactor followed by a train of columns to recycle the reactants becomes a very complex and expensive alternative. When a reactive distillation column is used, a total conversion of the reactants is possible and the reactant recirculation could be avoided. But, in this example, the MeAc is a reactant that forms an azeotrope with a product, the MeOH, and its recirculation is not avoided. The EtOH conversion is complete and it is not recycled. Another advantage from the reactive distillation is that two of the four present azeotropes disappear by the reaction: the MeOH/MeAc and the EtOH/EtAc azeotropes. The two remaining azeotropes (MeOH/MeAc, EtOH/EtAc) form a boundary line which divides the reactive residue curve map in two distillation regions (Fig. 10). Because there is not a reactive residue curve from one to the other product, a single distillation column at high reflux is not able to recover both products. But, as the remaining azeotropes are pressure sensitive, a pressure swing distillation with a reaction on the first column can be used to overcome the boundary line. The system has two degrees of freedom, e.g. \( B1 \) and \( D2 \).

The results of the \( \infty/\infty \) analysis for the reactive pressure swing distillation are similar to the non-reactive results. As the non-reactive pressure swing distillations are used industrially and are technically viable, then the reactive should be also viable and the same points stressed for the non-reactive are also applicable to the reactive. Figs. 11 and 12 show the results of the \( \infty/\infty \)
analysis when D2 is fixed and B1 is chosen as manipulated variable. There is an optimal B1 that produces pure products at both column bottoms. D2 has no influence on product purities and its value should be fixed from the performance point of view to minimize the process costs.

The attainable values of molar compositions and flow rates for the second column distillate depend on the pressures on both columns. A higher pressure difference decreases the minimal distillation flow rate but increases the column costs. For a fixed B1, the minimal D2 is obtained when both distillate molar compositions are at the azeotropic value. When the minimal D2 is represented versus a variation of the first column pressure a clear slope change appears corresponding to the optimal value for this high pressure (Bonet et al., 2005). For this transesterification operation the optimal pressure interval is between 600,000 and 1,100,000 Pa (Fig. 13). An experimental value of 877,470 Pa from the literature is used (Nagahama & Hirata, 1971).

The mass balances for a fixed feed with stoichiometric ratio reactants, pure products collected at bottom and distillates compositions at azeotropes provides the next expression for the minimal D2 in front of the MeOH concentrations:

\[
D_{2\text{min}} = \frac{F_c (1 + x_{\text{Fc}})(1 - x_{\text{DP1}})}{2(x_{\text{DP1}} - x_{\text{DP2}})}
\]

\[
= B_1 \frac{(1 + x_{\text{Fc}})(1 - x_{\text{DP1}})}{(1 - x_{\text{Fc}})(x_{\text{DP1}} - x_{\text{DP2}})}
\]

The minimal D2 for this example is 3.3 times B1 when P1 is 877,470 Pa \((x_{\text{DP1}} = 0.650)\) and P2 is 101,320 Pa \((x_{\text{DP2}} = 0.455)\). For any D2 bigger than the minimum, the distillate molal compositions can change while all the input Fc and output B1 and B2 streams flow rates compositions are constant and, hence, all the flow rates. When a sensibility analysis of B1 is performed with a D2 bigger than the minimum, a sharp change of distillate purities is observed at the pure bottom molal composition (Fig. 14). A continuous range of distillation molar compositions are valid at
Fig. 14. Sensitivity analysis of B1 by simulation (D2/Fc = 1.75). Lines are from ∞/∞ analysis and points by simulation by ProSim Plus.

Fig. 15. Sensitivity analysis of D2 by simulation using ProSim Plus (B1/Fc = 0.39).

this fixed B1 as has been illustrated by the non-reactive pressure swing.

The resolution of the same problem by steady state MESH equation based simulation using ProSim Plus verifies the ∞/∞ results (Appendix B). The simulator exhibits an excellent performance and it is able to reach D2 bigger than the ∞/∞ analysis D2 minimum without providing any column profile for initialize the calculations. Sometimes, xD1 converges near xDP1 (877,470 Pa); sometimes xD2 is near the xDP2 (101,320 Pa) and a few times at profiles between both results (Fig. 15). Fig. 16 shows the first column profile depending on the distillate purity.

3.4. Implications on control

For the systems with recirculation streams, the ∞/∞ analysis results leads to recommend constant flow rates for the strategies of control.

For the reactor followed by the distillation column, a reboiler duty manipulation to collect pure bottom is an undesirable control strategy. B2 is fixed by the overall mass balance and it is not an available degree of freedom. The degree of freedom at steady state that defines the streams purities must assure that the output and input molar flow rates fulfill the mass balance and that D2 is high enough to produce pure products. Setting B2 for this system could be desirable on the control strategy.

For the pressure swing distillation, an independent control of both column bottom purities by manipulation of their reboiler heat duty is an undesirable control strategy. Both bottom purities are linked by the overall mass balance and this fact can lead to conflicting controller behaviors. To control the product purities is enough to manipulate one variable; for instance, the reboiler duty of the first column can be manipulated by measuring both bottom purities. These are general considerations, obviously a faster control could be obtained in measuring the defilement of

Fig. 16. First column profile simulations using ProSim Plus (P1 = 877,470 Pa; P2 = 101,325 Pa; D2/Fc = 5.9).
the first column distillate by EtAc and it would be also cheaper if temperatures are measured instead of concentrations. D2 does not affect to the product purities, only to the process performance. According the \( \infty/\infty \) analysis, the minimal recycling stream D2 is the optimum. In a real column, setting D2 on the low limit is not desirable for the risk to become at the infeasible D2 range.

From the \( \infty/\infty \) analysis, the system behavior for the reactive pressure swing is not so much different than for a non-reactive pressure swing. There are not additional difficulties predicted at this stage of study for the reactive pressure swing and this system can open new possibilities at the industry as for the illustrative example of the MeAc transesterification.

4. Conclusions

For a system of reactor, distillation column and recycle stream, the output stream flow rate from the system is given by the input stream. If there are two reactants, a design variable corresponds to the recycle stream reactant ratio.

For a system of pressure swing distillation with or without reaction, both bottoms purities depend only on one bottom flow rate. The distillation flow rate can be set according to optimize the performance of the process.

In opposition to the process without recycling streams, where flow rates changes accordingly to set the purities, for processes with recycling streams could be useful to fix some flow rates at a performable and constant value.

We have not observed multiplicities. When all the variables are fixed, a unique solution is obtained. But the component ratio in the recycle stream is a variable that it is not physically manipulable by the flow rates. Although all flow rates and input and output stream purities of the system are fixed, a continuous interval of compositions is feasible for the streams linked to the recycle.

The intensification of processes are able to simplify greatly the traditional process of reactor followed by a train of distillation columns, by the synergy of the reaction and pressure swing distillation to overcome azeotropes. The transesterification of the MeAc by EtOH in a reactive pressure swing distillation is an illustrative example.

Acknowledgement

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Appendix A. Thermodynamic data

The default conditions of the simulator are used (State equation: perfect gas. Molar liquid volume: Rackett modified Gunn-Yamada. Liquid fugacity at pure standard state: vapor tension law):

\[
\ln(p) = A - \left( \frac{B}{T + C} \right)
\]

Antoine constants (ProSim data base):

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Validity interval (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtAc</td>
<td>C4H6O2</td>
<td>7.10179</td>
<td>1244.950</td>
<td>217.881</td>
<td>269-349</td>
</tr>
<tr>
<td>EtOH</td>
<td>C2H6O</td>
<td>8.11220</td>
<td>1592.864</td>
<td>225.184</td>
<td>293-366</td>
</tr>
<tr>
<td>MeAc</td>
<td>C3H6O2</td>
<td>7.06524</td>
<td>1157.630</td>
<td>219.726</td>
<td>275-329</td>
</tr>
<tr>
<td>MeOH</td>
<td>CH4O</td>
<td>8.08097</td>
<td>1582.271</td>
<td>239.726</td>
<td>288-357</td>
</tr>
</tbody>
</table>

Binary interaction parameters—NRTL (calc/mol) (ProSim data base and DEHEMA):

\[
g_{ij} - g_{jj} = C_{ij}^0 + C_{ij}^T(T - 273.15)
\]

\[
a_{ij} = a_{ij}^0 + a_{ij}^T(T - 273.15)
\]

Pressure sensibility of the MeAc/MeOH azeotrope:

<table>
<thead>
<tr>
<th>P (kPa)</th>
<th>T (K)</th>
<th>xMeOH</th>
<th>xMeAc</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>xDP2</td>
<td>101.32</td>
<td>327</td>
<td>0.6500</td>
<td>0.3500</td>
</tr>
<tr>
<td>xDP1</td>
<td>877.47</td>
<td>398</td>
<td>0.4550</td>
<td>0.5450</td>
</tr>
</tbody>
</table>

Chemical equilibrium constant (España, 1996):

\[
K_{eq} = \frac{x_{MeOH}^{3}EtAc}{x_{MeAc}^{3}EtOH} = 0.63
\]

Appendix B. Data to the simulator

Feed stream to the system: temperature at boiling point, pressure equal to first column pressure (877.47 kPa), flow rate = 251.52 mol/s, stoichiometric reactants and MeAc/MeOH ratio near the azeotropic molar composition (FcMeOH = 0.2048, FcEtOH = 0.7952, FcMeAc = 0.3976).

Reaction: At the ProSim version available, the equilibrium constant could not be directly introduced and high enough parameters to assure it were used.

First column: entirely reactive, pressure at 877.47 kPa, number of stages = 72, feed stage = 42, molar reflux ratio = 2.41, total condenser, distillate flow rate D1 = 529.69 mol/s (flow rate given by the \( \infty/\infty \) analysis at each point).

Second column: non-reactive, pressure at 101.32 kPa, number of stages = 24, feed stage = 16, molar reflux ratio = 2, total condenser, distillate flow rate D2 = 378.18 mol/s (flow rate given by the \( \infty/\infty \) analysis at each point).

Stream D1 initialized according to \( \infty/\infty \) analysis results (molar composition: 0.4 MeOH, 0.6 MeAc; flow rate: 1350.00 mol/s; an approximated value is enough although it is not the same than at the evaluated point).
References


