

# COUNTERCURRENT PACKED COLUMN FOR SUPERCRITICAL CO<sub>2</sub> SEPARATION OF WATER-ISOPROPANOL MIXTURES

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## ABSTRACT

The aim of this study is to evaluate the separation performances of a counter-current packed column, in the case of the purification of a water-isopropanol mixture using supercritical carbon dioxide. Experiments were performed on a 2m height and 17 mm diameter packed column. Variation of pressure, solvent to feed ratio and composition of the feed were investigated. Experimental results were compared to results obtained by simulation using Prosim Plus® process simulation software, where the column modeling is based on the concept of theoretical equilibrium stages. For fractionation of a diluted feed mixture containing 5w/w% of IPA at 10 MPa and 40°C, increase of the solvent ratio (S/F) from 2 to 10 has shown a beneficial effect on the water purification. For a S/F ratio of 10, water purity at the column bottom achieved 99.38% with a recovery rate of 88.69% of IPA in the column heading. Experimental results were shown reproducible and good agreement is observed between experiments and simulation results when only one theoretical stage is considered in that case. This result emphasizes the quite poor performances of the column (HETS=2m) for this kind of separation. Nevertheless, significantly better performances have been obtained in the case of the fractionation of concentrated solutions of IPA (60%w/w), which could be explained by the modification of phases physical properties leading to an improvement of mass transfer. Finally, preliminary results indicated that separation performances can be improved by using metallic foam as the packing.

## INTRODUCTION

As compared to supercritical extraction of solids, liquid fractionation by using a supercritical solvent is for the moment only slightly developed at industrial scale. In the case of CO<sub>2</sub> as the fractionating agent, the implementation of a "green" solvent is a decisive advantage over conventional processes using organic solvents having drawbacks in terms of pollution and contamination of the treated products by solvent residues. The potential for industrial development of these processes is thus significant.

Available literature studies on this type of devices are mainly experimental results obtained at laboratory scale. They are usually compared with simulations based on different approaches such as the conventional theoretical stages equilibrium models or rate based models [1, 2, 3]. The main objective of this study is to experimentally and theoretically evaluate the separation performances of a packed contactor in the case of the purification of aqueous solution of isopropanol (IPA). This model system was selected because the separation of alcohols from an aqueous phase is a potentially interesting application. Indeed, the separation of these mixtures by distillation is complicated by the presence of azeotropes. Previous work has thus shown that these mixtures can be efficiently separated with this supercritical technology that

overcomes azeotropic limits encountered in distillation operations, similarly to implementation of liquid-liquid extraction with a conventional organic solvent. Indeed, the analogy of fluid-liquid extraction and liquid-liquid extraction should be emphasized. Among the systems studied using this supercritical technology, ethanol-water [4] and 1-butanol/Eau [5] binary mixtures can be quoted. In this study, the water-isopropanol mixture was chosen because its thermodynamic behavior in the presence of CO<sub>2</sub> is known and easily modelled using the thermodynamic models available in commercial simulation softwares. Our work proposes an experimental part to assess the mass transfer capacity of the pilot column, available in the laboratory. A simulation study was then used to determine the values of the characteristic mass transfer parameter of our equipment in respect to the system considered.

## MATERIALS AND METHODS

### Materials

Carbon dioxide was supplied by Air Liquide ( $\geq$  purity 99.98%) and isopropanol is from Sigma-Aldrich ( $\geq$  purity 99.8%).

### Experimental set-up

The experimental set up (Fig. 1) was built by the Separex Company (France). This device consists of a 2 m high column with a 17 mm internal diameter, basically filled with random packing elements consisting of stainless steel "springs" (Fig. 2 (a)) whose dimensions are 5 mm length and 3 mm diameter. The wire diameter of the spring is 0.55 mm and its extended length is 62 mm. The specific surface of this packing was theoretically evaluated from the number of elements per unit volume (experimentally determined by counting) and calculating the surface of an element. If we consider the entire surface of the wire constituting the spring, the value of the specific surface of the packing is obtained as  $a = 1184 \text{ m}^2/\text{m}^3$ . If we only consider the outer and inner surface of an equivalent cylinder, the value  $a = 745.75 \text{ m}^2/\text{m}^3$  is obtained. The void fraction  $\varepsilon$  was experimentally measured at  $\varepsilon = 0.751$ . Original packing made of metallic (FeCrAlY) foam, consisting in open cellular structures materials (5 Pores Per Inches) has been used in this work. Cylindric pieces of 17 mm diameter have been cut in 5 cm thickness blocs of foam (Figure 2 (b)) and stacked inside the column. Void fraction of this packing is 92% and specific surface is equal to  $a = 610 \text{ m}^2/\text{m}^3$ .

This column is equipped with several temperature and pressure sensors and is held in temperature by an electrical heating device at the wall. At the column bottom, the pilot is equipped with a set of valves allowing steady recovery of the raffinate. Two separators in series at the top of the column allow recovering the liquid extract free of CO<sub>2</sub>. The pilot can be operated with CO<sub>2</sub> recycling. However, for easier interpretation of results, it has been operated in open loop for most of our experiments. The extraction procedure is as follows: the output liquid from the CO<sub>2</sub> bottle (about 5.5 MPa) is subcooled in a heat exchanger up to 5°C and then pumped using a high pressure positive displacement diaphragm pump (Milton Roy) with a maximum capacity of 5 kg/h. The pressurized liquid CO<sub>2</sub> is then heated to the desired temperature for the separation. The CO<sub>2</sub> is fed at the bottom of the column and flows countercurrently with the water-IPA mixture feed which is introduced at the top of the column using a membrane pump (Milton Roy Dosapro ®), having a maximum capacity of 2.4 kg/h. The purified water is recovered at the bottom of the column at atmospheric pressure and room temperature. The CO<sub>2</sub> rich mixture at the top of the column flows through the two cyclone separators ( $V = 40 \text{ mL}$ ) in series. The pressures in the extractor and in the separators are regulated by a backpressure regulator (TESCOM). The extract was recovered at 60 bar and 25

°C in the first separator and 1 bar and 25 °C in the second one. A water trap (*i.e.*, micro-bubbling gas in a capacity filled with water), placed at the output of the second separator allows maximum recovery of isopropanol still present in the output gas. Analyses of the compositions of the different liquid phases were performed by refractometry.



**Figure 1.** Experimental set-up



(a) Inox springs



(b) Metallic foam

**Figure 2.** Packings

## MODELING

### Phase equilibria of the ternary mixture CO<sub>2</sub> - IPA - water

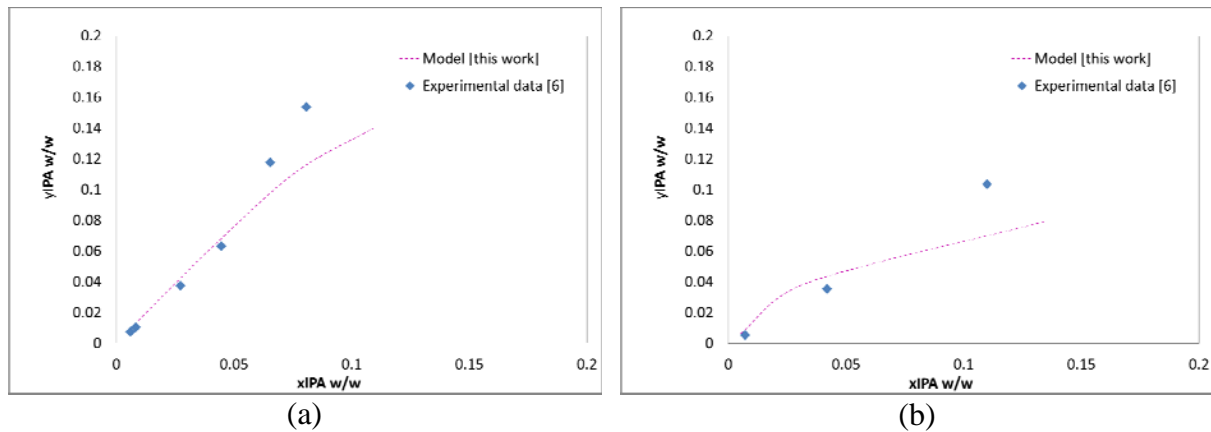
Knowledge of phase equilibria of the ternary mixture is essential to understand and analyse the process of fractionation. Furthermore, in view of simulation, a model capable of representing the phase equilibria must be selected and validated. Experimental data exist in the literature for this mixture for pressures ranging from 68.9 to 172.23 bar and temperatures between 15 and 70°C [6]. These thermodynamic experimental data were modelled using the Simulis Thermodynamics software (ProSim SA) in the Excel environment (Windows). Given the pressure zone and the highly polar nature of water and isopropanol, the combined approach equation of state / activity coefficient (EoS/G<sup>E</sup>) model using a suitable mixture rule was chosen. In this approach, the behaviour of the fluid mixture is represented by an equation of state over the entire range. The combined approach allows to increase the field of application of original equations of state (high pressure but low polar compounds) to polar compound containing mixtures, by incorporating the excess Gibbs energy G<sup>E</sup> in the calculation of the energy term  $a$  of the equation of state. The excess Gibbs energy is calculated using an activity coefficient model. Huron and Vidal [7] were the first to propose this approach, and several models based on this concept were then developed, such as Wong-Sandler, MHV1, MHV2, PSRK...and have been successfully applied to describe high pressure phase equilibria for mixtures containing polar compounds. The equation of state chosen in this study is the Soave-Redlich-Kwong equation [8] with the modification proposed by Boston-Mathias [9], which is suitable for mixtures containing compounds above their critical temperature. The co-volume  $b$  of the SRK equation is obtained from a standard mixing rule (arithmetic mean of the parameters  $b_i$  of the pure substances). The mixing rule PSRK [10] was chosen here to compute the energy term  $a$  of the SRK equation of state:

$$q_1 \left( \alpha - \sum_i z_i \alpha_i \right) = \frac{g_0^E}{RT} + \sum_i z_i \ln \left( \frac{b}{b_i} \right) \quad (1)$$

$$\text{with } a_i = 0,457235529 \cdot \frac{R^2 T_{c,i}^2}{P_{c,i}} \cdot \alpha_i(T) \quad (2)$$

and  $q_1 = -0,64663$  for SRK.

The PSRK UNIFAC model for activity coefficients [10] was then adopted to calculate the excess energy at zero pressure  $G^{0E}$ , involved in Equation 1. This version of the UNIFAC predictive model takes into account a temperature dependence of the interaction between functional groups. The chosen approach has the advantage of being fully predictive. No binary interaction coefficient should be calculated. This model was used to model the entire set of data of the experimental work of Chun and Wilkinson [6]. An example of comparison of experimental data and values calculated by the model at different temperatures and pressures is shown in Figure 3.



**Figure 3.** Experimental phase equilibria (symbols) [6] and computed (solid lines) for the CO<sub>2</sub>-IPA-water system  
(a): 70<sup>o</sup> C and 172 bar ; (b) : 40<sup>o</sup>C and 100 bar

The results presented in Figure 3 show an acceptable matching between the experimental results and the results obtained by the thermodynamic model. So, the approach has been used to represent the thermodynamic behaviour of the mixture in the process simulator.

### Modeling of the supercritical extraction column

Simulation of the multi-component mixture separation is useful to analyze the influence of operating conditions (pressure, temperature) on the separation efficiency and also to optimize parameters, such as the number of theoretical stages, the solvent to feed ratio and optionally the extract reflux ratio. Commercial process simulator softwares are useful tools, capable of simulating this type of unit operation. The ASPEN+ software for example has been used successfully by Brunner [11], and Riha and Brunner [12] to predict the concentration profiles in a column separating a mixture of ethyl esters of fatty acids. Similarly, the HYSIS software was used by Moraes et al. [13] in order to optimize a process for dehydration of ethanol using supercritical propane. Typically, with these approaches, counter-current contactors are represented by a succession of equilibrium theoretical stages. It is considered that the column consists of a set of fictitious stages where the output of the two fluids are in thermodynamic

equilibrium (same pressures and temperatures and equalities of fugacities of components in the two phases).

In this study we used the ProSim Plus software based on the concept of theoretical equilibrium stages to simulate the whole process of separation. The column was simulated by using an ABSORBER module, representing the steady state operation of a multi-constituent absorption counter-current column by resolution of mass and energy balances and thermodynamic equilibrium. The difference with actual operation can be accounted for by using the concept of Murphree efficiency ( $E_M$ ) which quantifies the overall efficiency of the stage.

## RESULTS

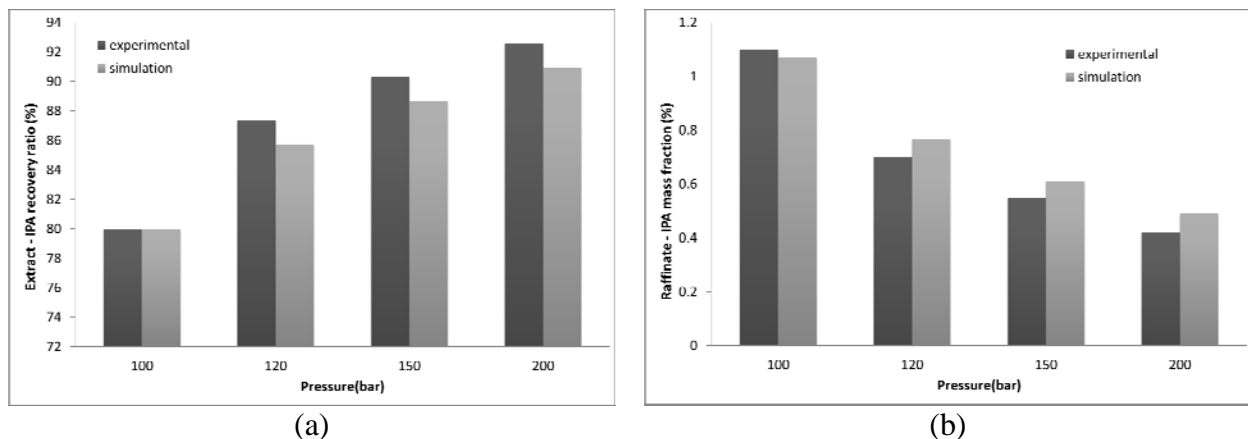
CO<sub>2</sub>-free extract and raffinate compositions are analyzed after steady-state establishment (about 40 minutes). Reproducibility of experiments has been evaluated and shown to be acceptable with a standard deviation around 1%.

To purify and separate the water-IPA mixture using CO<sub>2</sub>, several tests have been run by varying operating parameters such as pressure, solvent to feed ratio, and IPA composition of the feed. Results have been analysed, based on the measured composition and flowrate of the raffinate, because of an incomplete recovery of the light phase (extract). Consequently, composition and recovery ratio of IPA in the extract has been obtained by mass balances, based on experimental characterisation of the raffinate phase.

Simulations are performed by fitting number of theoretical stages and/or Murphree efficiency to experimental results.

### Influence of extraction pressure

Figure 4 represents influence of the pressure in the range 100-200 bar, on the fractionation of a 5%w/w IPA aqueous solution at 40°C, with a feed flowrate equal to 0.48 kg/h and a solvent to feed ratio equal to 6 (inox spring packing). Recovery ratio of IPA in the extract and residual IPA mass fraction in the raffinate are plotted. Simulation of the process have been done with a column with one theoretical stage only ( $E_M=1$ ).



**Figure 4.** Influence of the pressure on (a) recovery ratio of IPA at the extract and (b) mass fraction of IPA in the raffinate (40°C, feed flowrate 0.48 kg/h and S/F=6)

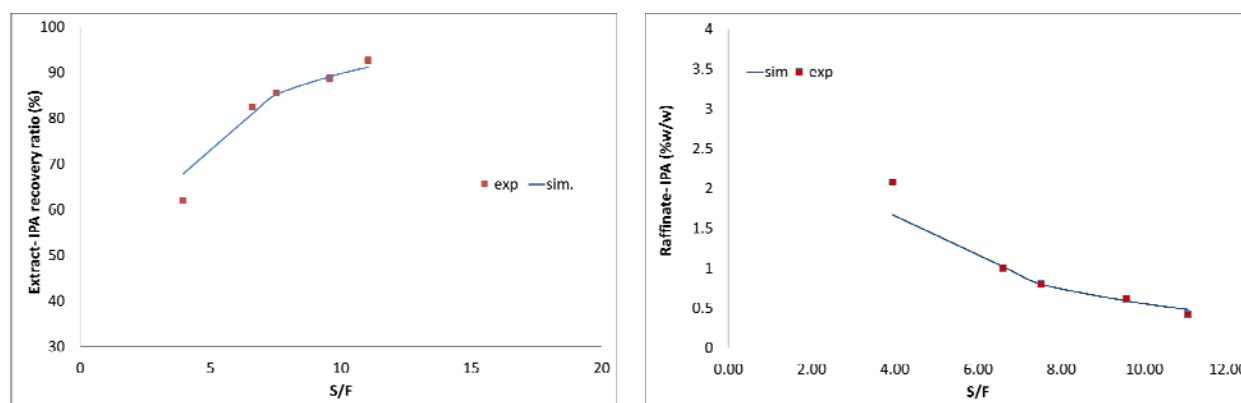
For these experimental conditions, an improvement of performances of the separation is observed when pressure is increased. At 200 bar (which corresponds to the maximum pressure of our experiments) the purity of the water at the raffinate reached 99.58% with a

92.23% recovery of IPA in the extract, which corresponds to a theoretical purity of the extract equal to 73.7%. Experimentally we obtain a difference of about 18% for IPA recovery in the extract (about 74% IPA recovered, at a purity of 72%), due to incomplete actual recovery of the extract in the separators and in the water trap. This is explained by the small amounts of extract. The positive influence of the pressure is a consequence of the better solvent power of CO<sub>2</sub> when increasing the pressure.

These results establish that under these conditions, the column is equivalent to one theoretical stage, which yields a height equivalent to a theoretical stage (HETS) equal to 2m. This value may seem surprisingly high, but the literature shows that the HETS values in such devices are often high, typically of the order of 1 m [14]. In our case, the very high value could be due to poor wetting of the packing by the liquid phase, leading to low efficiency of contact between the phases. Indeed in very small diameter columns, it is suspected that a substantial portion of the liquid film flows preferentially along the inner walls of the contactor.

### Influence of solvent to feed ratio

The influence of the solvent to feed ratio (S/F) has been studied for operation at 100 bar and 40°C with a 5% w/w IPA feed and spring packing. The solvent to feed ratio was chosen according to the technical limits of the pumps but also in order to avoid flooding of the column (detectable by the presence of a large amount of water in the separators, due to entrainment of the liquid to the head of the column). The theoretical and experimental results in terms of recovery ratio and IPA purity in the extract are presented in Fig. 5.



**Figure 5.** Influence of S/F on the recovery ratio of IPA in the extract and content of IPA in the raffinate (100 bar, 40°C, F=0.48 kg/h, 5% w/w IPA, spring packing).

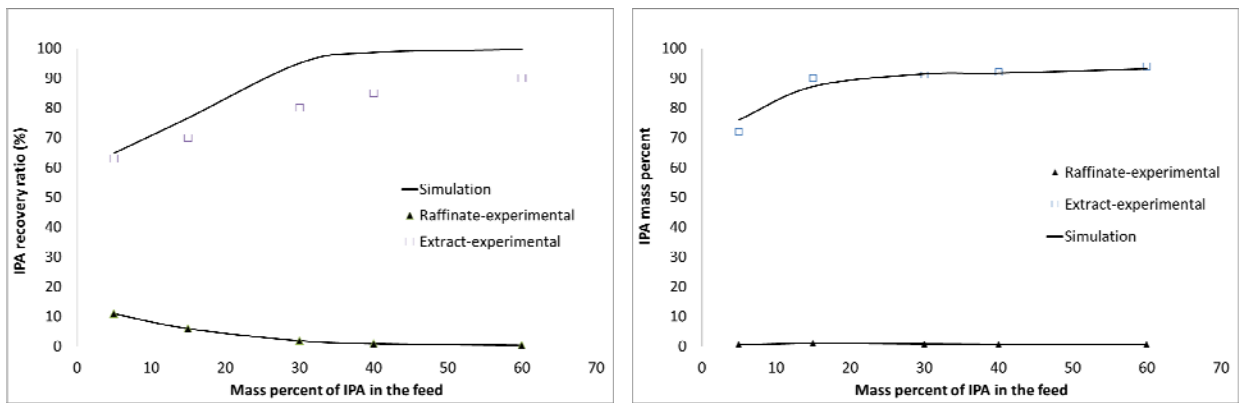
A good agreement is observed between the experimental results and the simulation results using a single theoretical stage. However, improved separation performance is observed when the solvent to feed ratio increases from 2 to 11. Actually, Figure 5 shows that an increase of the solvent to feed ratio increases the IPA recovery ratio in the extract, and purity of water in the raffinate is slightly increased. However, mass balance on both IPA and water show a slight influence of S/F on IPA purity at the extract, which is equal to around 50% at large solvent to feed ratio because of co-extraction of water.

### Influence of IPA composition of the feed

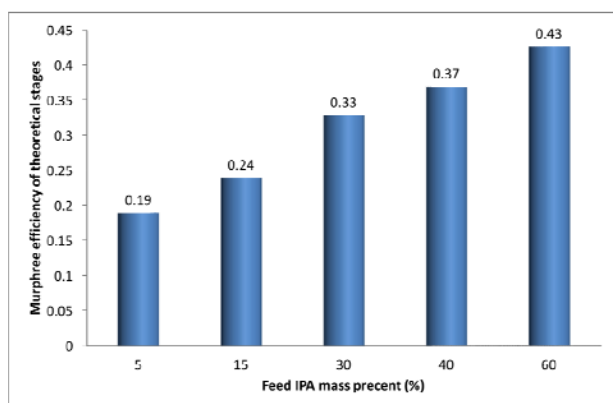
The composition of IPA in the feed was varied, at 100 bar and 40°C, and at a solvent to feed ratio equal to 10. Figure 6 shows experimental results and simulation results.

When the IPA percentage in the feed increases, it is observed that the composition of the raffinate remains almost constant but a decrease in the recovery ratio of IPA in the raffinate is noted. For a 60 % IPA feed, purity of water at the raffinate is equal to 99.4 % w/w with an IPA experimental recovery ratio at the extract equal to 90% and a IPA mass fraction of the extract equal to 94 % w/w.

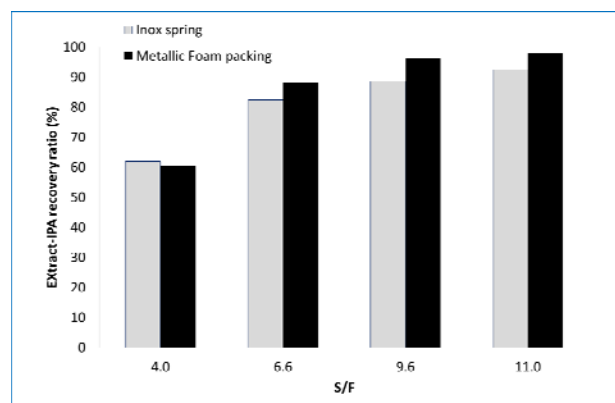
The simulation results were in this case obtained by adjusting the number of theoretical stages for every IPA feed composition. Specifically, to make this adjustment, as the software does not accept fractions of theoretical stages, we arbitrarily set the number of stages of the column to 4 and the mass transfer efficiency was accounted for through the adaptation of the value of the Murphree efficiency of the stages. This value was adjusted to match the experimental results. Figure 6 shows that the Murphree efficiency increases with the concentration of IPA in the feed. With this approach, the Murphree efficiency exhibited an almost 2-fold increase from 5% to 60% IPA in the feed. This result could be explained by changes of physico-chemical properties of the aqueous phase, such as interfacial tension, which would provide better wetting of the packing and thus an increase of the effective exchange surface in the column, when the liquid mixture is rich in alcohol



**Figure 5.** Influence of feed IPA content on the recovery ratio and purity of IPA in outlet flows (100 bar, 40°C, F=0.48 kg/h, S/F=10, spring packing).



**Figure 6.** Fitted Murphree efficiency as a function of feed IPA content in the case of 4 theoretical stages.



**Figure 7.** Extract IPA recovery ratio in the case of random springs and foam packings (100 bar, 40°C, 5% w/w IPA feed, F=0.48 kg/h)

### **Influence of the packing of the column**

In an attempt to improve mass transfer efficiency of the column, random inox springs has were replaced by a type of structured packing, metallic foam, This type of packing has been shown to be very attractive in the case of counter-current gas-liquid operation, because of their specific properties such as high void fraction, leading to high liquid hold-up and low pressure drop [15]. An example of preliminary results is shown on Figure 7, where the IPA recovery ratio in the extract has been plotted as a function of the solvent to feed ratio, for experiments at 100 bar, 40°C and a IPA content in the feed equal to 5% w/w. Performances of the column in terms of mass transfer are slightly improved with this kind of packing for these operating conditions. We are currently under work to improve further mass transfer efficiency using these types of packing.

### **CONCLUSION**

This study has demonstrated the feasibility of the continuous purification of an aqueous phase containing isopropanol using supercritical CO<sub>2</sub> as the separation agent. We have evaluated the influence of operating conditions on the separation performance and a high degree of purification could be obtained (92% IPA recovery in the extract) with a solvent to feed ratio of about 11, at a pressure of 100 MPa and a temperature of 40°C. The predictive Soave Redlich Kwong model (SRK) modified by Boston Mathias with PSRK mixing rules and using the predictive UNIFAC-PSRK model for activity coefficients was used for the thermodynamic modelling of the CO<sub>2</sub> -IPA - Water system under pressure. The experimental results were compared with simulation results of the process. The simulation was based on a representation of the column by the concept of theoretical equilibrium stages. A low efficiency of mass transfer in the column was evidenced (one theoretical stage at 5 % IPA feed) which was improved as the IPA concentration in the feed was increased (up to 2 theoretical stages at 60 % IPA feed). This improvement is probably due to a better wetting of the column packing. The use of metallic foam as structured packing as replacement of random inox packing was shown to improve the column separation performances.

### **References**

- [1] BRUNNER, G., J. Super. Fluids, Vol. 47, **2009**, p.574
- [2] ZACCHI, P., CALVO BASTIDA, S., JAEGER, P., COCERO, M.J., EGGERS, R., J. Super. Fluids, Vol. 45, **2008**, p.238
- [3] DIAZ, M.S., BRIGNOLE, E.A., J. Super. Fluids, Vol.47, **2009**, p.611
- [4] IKAWA, N., NAGASE, Y., TADA, T., FURUTA, S., FUKUZATO, R., Fluid Phase Equ., Vol. 83, **1993**, p.167
- [5] LAITINEN, A., KAUNISTO, J., J. Super. Fluids, Vol.15, **1999**, p.245
- [6] CHUN, B.S., WILKINSON, G.T., Korean J. Chem. Eng, Vol. 16, **1999**, p.187
- [7] HURON, M.J., VIDAL, J., Fluid Phase Equ., Vol. 3, **1979**, p.225
- [8] SOAVE, G., Chem. Eng. Sci., Vol.27, **1972**, p. 1197
- [9] BOSTON, J.F., MATHIAS, P.M., Proceedings of the 2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Process Industries, West Berlin **1980**, p.823
- [10] HOLDERBAUM, T., GMEHLING, J., Fluid Phase Equ., Vol 70, **1991**, p.251
- [11] BRUNNER, G., J. Super. Fluids, Vol 13, **1998**, p.283
- [12] RIHA, V., BRUNNER, G., J. Super. Fluids, Vol.17, **2000**, p. 55
- [13] MORAES, E.B., VASCONSELOS, C.J.G., WOLF MACIEL, M.R., Proc. Of the 6<sup>th</sup> World Congress of Chemical Engineering, Melbourne, **2001**
- [14] PIECK, C.A., CRAMPON, C., CHARTON, F., BADENS, E., 6<sup>th</sup> International Sym. on High pressure processes technology, Serbia, **2013**, p 174
- [15] LEVEQUE, J., ROUZINEAU, D., PREVOST, M., MEYER, M., Chem. Eng. Sc., Vol. 64, **2009**, p. 2607