Supercritical Fractionation: Experimental Measurements and Modeling

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ABSTRACT

In the search of a continuous method for the separation and purification of natural products obtained from the oil extracted from microalgae *Dunaliella salina*, supercritical fractionation by carbon dioxide appears as an environmentally-friendly alternative to classical operations. However, reliable models for the conception of fractionation equipment are scarce. In this work, experimental data on raffinate and extract compositions and pressure drop along the column is presented and compared to model predictions.

INTRODUCTION

The work presented here is part of the French research and development project Salinalgue, whose goal is to convert underexploited salt fields in southern France for the culture and complete valorisation of the microalgae *Dunaliella salina* including its use as a 3rd generation biofuel source. In the development of an economically viable process, the recovery and purification of neutral lipids and carotenoids (particularly ß-carotene) is of upmost importance. Given the low vapour pressure and thermal sensitivity of these products, supercritical fractionation appears as good candidate for their treatment.

The supercritical fractionation process relies on the difference of solubility of the feed components in a solvent beyond its critical point. The operating temperature must be below the mixture critical point since the biphasic (or multiphasic) nature of the process is what allows the desired separation. A counter-current column set-up allows for a continuous operation. In this set-up, the lightest solvent-rich extract is recovered by depressurization of the overhead current whereas the raffinate, which corresponds to the highest density phase, is recovered directly from the column bottom [1,2].

Although the feasibility of the enrichment of several oil components has been previously attested in literature [3-7], the prediction of the throughput capacity of a continuous supercritical fractionation counter-current column has received less attention [2]. The operation utterly depends on the relative solubility of the targeted compounds, but its transfer capacity must also be taken into account. The factors to be considered include the absence or presence of packing elements and their characteristics, the superficial velocities and the fluid properties such as densities, viscosities, individual component diffusivities and interfacial tensions. As a necessary step towards the application of supercritical fractionation to microalgae oil, the influence of such variables was studied.

Firstly, in order to focus the effort into the engineering aspects of the operation rather than the thermodynamic modeling of the equilibrium concentrations, a widely studied system was chosen to determine the limits and working range of the column and validate the experimental procedure for further studies. The ethanol-water fractionation by supercritical carbon dioxide was selected, being the most studied operation of its kind. This process drew the attention of the scientific community as a mean to overcome the thermodynamic restraints on distillation processes to obtain pure ethanol in a single step imposed by the existence of the water-ethanol azeotrope [8-12]. The same reasoning imposed the working temperature and pressure to be chosen at 333 K and 10.1 MPa, respectively.

Modeling of the steady-state extract and raffinate compositions was done using equilibrium stage models. Equilibrium stage models were first developed for distillation processes in plate towers. Although the principle of clearly differentiated equilibrium stages does not stand in the case of packed towers, the experience has shown that equilibrium stage model predictions are still widely used for packed column design applications [13]. In the case of an isothermal fractionation column with a binary feed, the mass balances are equivalent to those found in liquid-liquid extraction processes, and by extension, mathematically equivalent to those encountered on binary distillation columns [14-16]. It is thus possible to employ models developed for distillation processes to the supercritical fractionation process by a simple change of variables. The Ponchon-Savarit method applied to supercritical fractionation was presented by Budich and Brunner [12] to predict water-ethanol extract and raffinate compositions. The McCabe-Thiele method was also portrayed by Brunner and Machado [7] for the fractionation of edible oils, and a good agreement between experimental and simulated data was found.

Secondly, a study of the pressure drop along the column for a non-wetted packing was conducted using a differential pressure transducer. Stockfleth and Brunner [17] measured pressure drop values for 5x0.5 mm wetted Raschig Rings for the water–carbon dioxide system at 313 K and 12 MPa on a special apparatus conceived for flooding point measurements. Their experiments show that the evolution of the pressure drop as a function of the feed and solvent flowrate under supercritical conditions for a counter-current contactor follows the same tendency than atmospheric pressure gas-liquid contactors. Hence, prediction of the pressure drop using gas-liquid correlations appears as an interesting possibility. As a first step to validate this approach the non-wetted pressure drop for carbon dioxide at 333 K and 10.1 MPa was measured and compared to the prediction of the widely used Ergun equation [18].

MATERIALS AND METHODS

A simplified schematic diagram of the fractionation set-up used for the first part of this study is shown in Figure 1. The liquid fractionation unit provided by Separex (France) consists on a packed column of 19 mm internal diameter and 2 m height with a viewing cell located at the bottom of the column, below the solvent injection tube level. The column is able to withstand a pressure up to 35 MPa, and its temperature is controlled by means of two independent heating jackets. The column is filled with 10 mm Interpack® random packings from VFF (Germany), with a measured apparent density of 588 kg/m^3, a specific surface area of 580 m^2/m^3 and a void fraction of 0.917. A high pressure piston pump with a top capacity of 15 L/h of liquid carbon dioxide and a maximum attainable pressure of 35 MPa delivers the supercritical solvent. The liquid mixture is fed by a Gilson 307 HPLC Pump, with a 20 mL/min (roughly 1.2 kg/h) maximum piston capacity. The carbon dioxide flowrate is controlled by a Rheonik RHE 14 mass flowmeter, while the liquid feed flow is directly controlled by the pump.

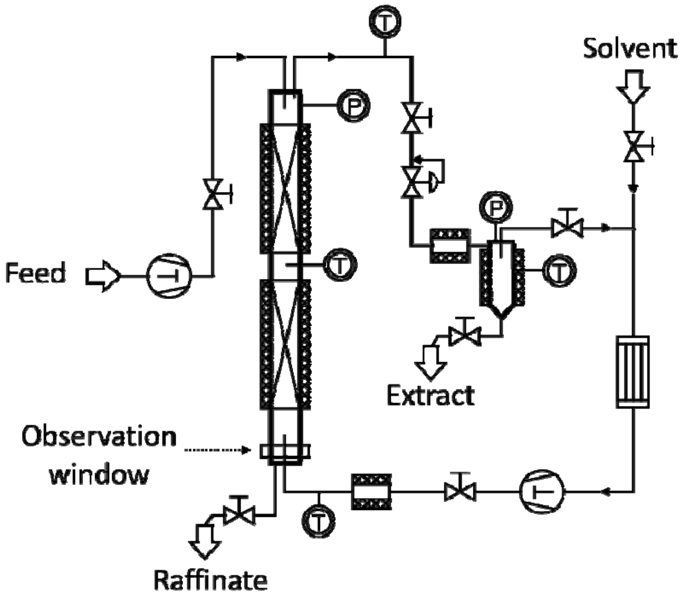

Figure 1. Schematic diagram of the fractionation column.

Through all experiments, the fractionation column was kept at 333 K and under 10.1 MPa. According to the solvent-to-feed ratio, the liquid feed was selected as the dispersed phase. At steady-state conditions, the pressure was kept within 0.1 MPa of the targeted value and temperatures at both thermocouples in the column were kept within 1 K of the desired value. Because of the alternative nature of the piston pump, solvent flowrate varied within ±0.06 kg/h at 12 kg/h according to the mass flowmeter. Double-distilled water and technical-grade anhydrous ethanol (>99.8%) purchased from A.P.I. were used for the experiments. Technical grade carbon dioxide (>99.8%) was provided by Air Liquide Méditerranée (France).

During operation, carbon dioxide under roughly 4.5 MPa was cooled to 275 K in a double tube heat exchanger before being pumped and then heated to the working temperature. Once the supercritical solvent left the column, it was depressurized through a backpressure regulator to recover the extract in a pressurized cyclonic separator. The solvent was recycled into the cooler to reduce carbon dioxide consumption. For all runs, the cyclonic separator was kept roughly under 4.5 MPa and at 293 K to avoid ethanol entraining by the recycled solvent.

Extract and raffinate samples were recovered regularly and steady-state conditions were assumed to be reached when the standard deviation among three successive samples was less than 0.5% (w/w) of ethanol.

In a typical run, the column was heated at 343 K before the introduction of carbon dioxide. Then, the column was pressurized up to 4.5 MPa. After, the solvent pump was set at the desired flow rate and the pressure was progressively increased up to the operating pressure by means of the back-pressure regulator. The introduction of carbon dioxide chilled the column, so the heating jackets were regulated to maintain the desired temperature. Once a steady temperature regime was reached, the liquid feed pump was turned on.

Finally, the extract and raffinate were collected from the bottom of the cyclonic separator and column respectively, by manual regulation of the corresponding valves. Under high feed rates, the liquid was continuously withdrawn, while an accumulation and purge method was preferred for small liquid rates.

In order to maintain a constant flowrate and for a continuous withdrawal of raffinate, the liquid level in the column was kept constant by adjustment of the corresponding valve and observation through the windows on the bottom of the column.

All water-ethanol mixture compositions were determined by densimetric measurements on a DMA 5000M unit from Anton Paar. Each sample was treated by use of a sonicator to desorb the excess carbon dioxide prior to analysis. Ethanol mass fraction was determined from literature density tables [14].

For modeling purposes, the biphasic equilibrium compositions were predicted by the empirical relations proposed by Budich and Brunner [12] to describe the water-ethanol-carbon dioxide equilibrium compositions at 333 K and at 10 MPa.

For the second part of this study, a Fuji Electric RKCT48 differential pressure gauge was installed with a range of 50 kPa and a 0.065% precision. In order to reduce pressure and temperature fluctuations that would affect the differential pressure on the column, several modifications were introduced as shown in Figure 2. Compared to the previous set-up, the feed went through a spiral tube in a heated bath before entering the column in order to minimize the thermal impact upon the column temperature. On the solvent side, a 4 m double tube heat exchanger connected to an external water bath was used to stabilize the temperature fluctuations on the solvent. Also, a 500 mL vessel with a filter was introduced between the two solvent heaters to minimize pressure fluctuations.

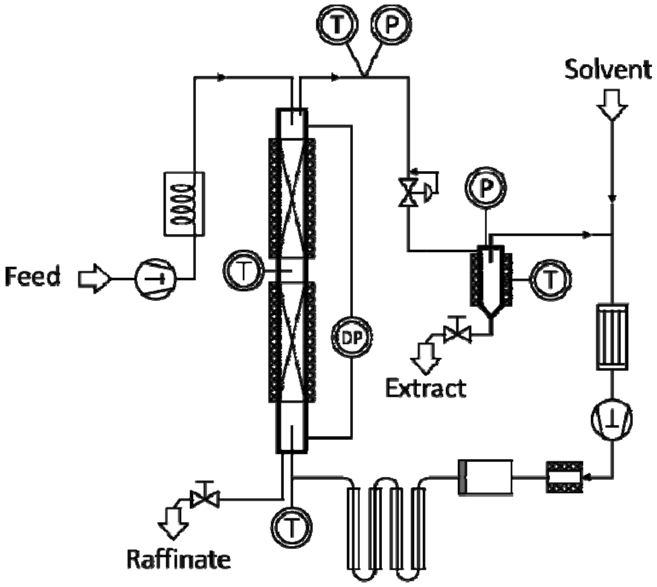

Figure 2. Experimental set-up for pressure drop measurements.

Given the vertical set-up used and due to the lack of temperature control between the column pressure taps and the differential pressure gauge, a static pressure difference is imposed upon the differential pressure gauge. This static pressure depends on the density difference in the column and on the pressure conducts. The global system was isobaric, but the column temperature was kept at 333 K under working conditions while the tubes were at ambient temperature. At 10.1 MPa, this static pressure varied between 8 and 13 kPa depending on the ambient temperature. This static pressure could not be measured directly with enough accuracy and its value was determined by extrapolation of the differential pressure as a function of the solvent apparent velocity.

For modeling purposes, the Ergun equation [19] was used as follows:

$$\left(\frac{\Delta P}{H}\right)_{measured} = \left(\frac{\Delta P}{H}\right)_{static} + \frac{150(1-\varepsilon)^2\mu}{\varepsilon^3\phi_s^2 D_p}v + \frac{1.75\,(1-\varepsilon)\rho}{\varepsilon^3\phi_s D_p}v^2 \tag{1}$$

where $\Delta P/H$ is the pressure drop divided by the packing height; v is the solvent apparent velocity; μ is carbon dioxide viscosity, taken as 2.82 x10^{-5} Pa.s; ρ is its density, taken as 291.6 kg/m^3; ε is the packing void fraction calculated as 0.917; D_p is the particle diameter, taken as 0.86 mm and ϕ_s is the packing sphericity calculated at 0.2795. Packing characteristics were determined from packing dimensions while viscosity and density data for carbon dioxide were obtained from literature [19, 20].

RESULTS

For the study of the fractionation process, the stability and reproducibility of the extract and raffinate composition were investigated. Figure 3 shows a comparison between two typical runs at the same operating conditions. It can be seen that the extract and raffinate compositions stabilize quickly and remain constant. It has to be noted that there is a residual liquid volume that cannot be purged from the bottom of the column or cyclonic separator. Therefore, the dynamic concentration profiles should not be considered as an exact representation of the evolution of the extract and raffinate composition in the column.

Under steady state conditions, the mean standard deviation over all runs for the extract and raffinate ethanol mass fraction was 0.38%.

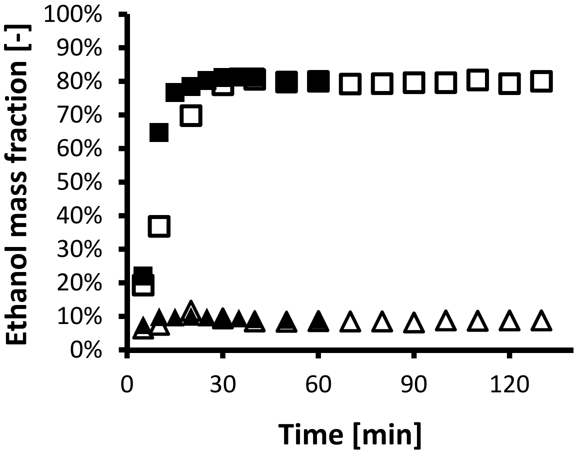

Figure 3. Evolution of the raffinate (▲,△) and extract (■,□) composition for two runs under the same conditions.(Feed rate = 0.576 kg/h; Solvent rate = 9.6 kg/h; Feed ethanol mass fraction = 26.7%; Solvent superficial velocity =32 mm/s)

A comparison between the predictions of the McCabe-Thiele and the Ponchon-Savarit model varying the solvent-to-feed ratio, feed composition and number of stages was carried to determine the impact of the model assumptions on the predicted extract and raffinate compositions. The maximum deviation found was less than 2.5% ethanol for a two-stage column and a solvent-to-feed ratio of 20. Furthermore, the influence of the number of theoretical stages on the predicted extract and raffinate compositions was also studied. It was found that the compositions predicted for a single stage and the maximum allowable compositions were similar, especially at high ethanol concentration in the feed. Considering these facts, a single stage model was chosen for the prediction of extract and raffinate compositions for its simplicity. Model equations are:

$$E = \dot{m}_E\left(1 - w_E^{CO_2}\right) \tag{2}$$

$$R = \dot{m}_R\left(1 - w_E^{CO_2}\right) \tag{3}$$

$$X = \frac{w_R^{Eth}}{1 - w_R^{CO_2}} \tag{4}$$

$$Y = \frac{w_E^{Eth}}{1 - w_E^{Eth}} \tag{5}$$

$$Z = \frac{w_F^{Eth}}{1 - w_F^{CO_2}} \tag{6}$$

$$N = \frac{w_R^{CO_2}}{1 - w_R^{CO_2}} \tag{7}$$

$$M = \frac{w_E^{CO_2}}{1 - w_E^{CO_2}} \tag{8}$$

$$M = \frac{S}{Z} + \left(\frac{Y - Z}{Z - X}\right)\left(\frac{S}{Z} - N\right) \tag{9}$$

$$M = 426 - 1290\, Y^{1.5} + 884\, Y^2 \tag{10}$$

$$\frac{1}{N} = 426 - 36.7\, X + 13.7\, X^{2.5} \tag{11}$$

$$Y = \frac{X(28.1\exp(-2.65X) - 0.73)}{1 - X(28.1\exp(-2.65X) - 1.73)} \tag{12}$$

where $\dot{m}_A$ represents the mass flowrate of the current *A*; w_A^B stands for the mass fraction of species *B* in the current *A*; *S* represents the solvent mass flowrate; *F* is the feed mass flowrate; the *E* and *R* subscripts stand for the extract and raffinate respectively, and the *Eth* superscript stands for ethanol. Equations (2-7) represent the conversion of mass flowrates and compositions to Janecke coordinates (X and Y are the solvent-free mass fractions of ethanol in the liquid and solvent respectively; N and M are the solvent to non-solvent ratios for the liquid and solvent and E and R are the solvent-free mass flowrates of extract and raffinate) [16]; Equation (9) represents the ethanol mass balance and Equations (10-12) represent the equilibrium relations from Budich and Brunner [12].

As can be seen in Figure 4, model predictions agree well with experimental data from fractionation runs.

Finally, non-wetted single flow dynamic pressure drop values were determined as a function of the solvent apparent velocity. The results from two independent runs are presented in

Figure 5 and compared to the predictions of the Ergun equation. The static pressure term in Equation (1) was calculated from the lowest solvent velocity pressure drop value.

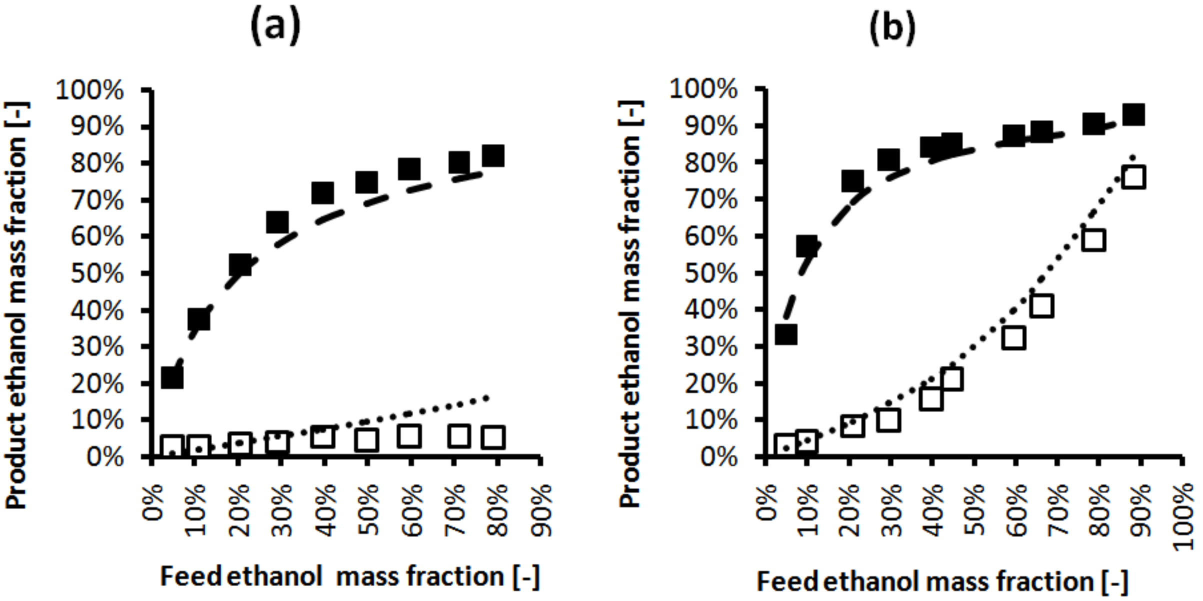

Figure 4. Comparison between extract (■) and raffinate (□) experimental compositions and model predictions for the fractionation of water-ethanol mixtures with carbon dioxide at 333 K and 10.1 MPa. Solvent mass flowrate = 12 kg/h; **(a)** Solvent-to-feed ratio = 66.7**(b)** Solvent-to-feed ratio = 20.

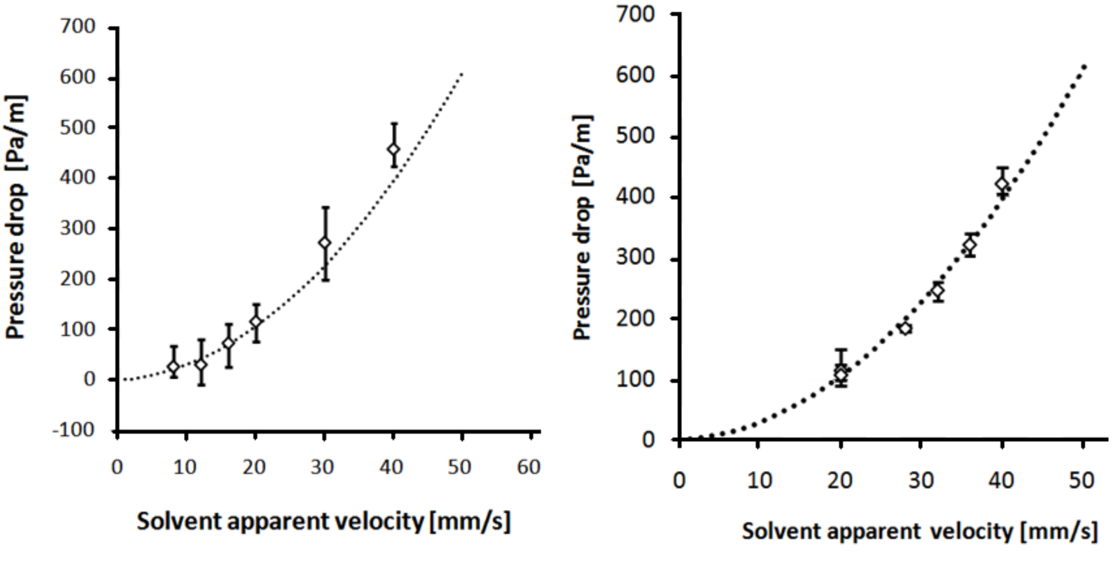

Figure 5. Comparison between experimental and predicted pressure drop values for two independent runs along non-wetted VFF® packing for an upflow of carbon dioxide at 333 K and 10.1 MPa as a function of the solvent apparent velocity.

CONCLUSION AND PERSPECTIVES

Firstly, the results presented here show that equilibrium-stage models are capable of predicting the extract and raffinate compositions within acceptable accuracy without parametric adjustments for a pilot scale set-up. A single-stage model was found to be acceptable for the simulation of the experimental extract and raffinate concentrations. However, conception of a supercritical fractionation column requires knowledge of the value of the Height Equivalent to a Theoretical Stage (HETS). The determination of HETS values will be addressed in a demonstration scale column.

Secondly, the pressure drop values obtained for a non-wetted packing show good agreement with those predicted by the Ergun equation. Future research will address the wetted packing pressure drop values and its prediction. Ultimately, prediction of pressure drop values can give a better understanding on the influence of hydrodynamics on the column throughput capacity.

REFERENCES

[1] KING J. W., LIST G. R. , Supercritical Fluid Technology in Oil and Lipid Chemistry, 1996 , Ed. AOCS Press
[2] BRUNNER G., J. Supercrit. Fluids, Vol. 47, **2009**,p. 574
[3] RIHA V., BRUNNER G., J. Supercrit. Fluids, Vol. 17,**2000**, p. 55
[4] DUNFORD N. T., TEEL J. A., KING J. W., Food Res. Int, Vol. 36, **2003**,p. 175
[5] GAST K., JUNGFER M., SAURE C., BRUNNER G., J. Supercrit. Fluids, Vol. 34, **2005**, p. 17
[6] PERRETTI G., MOTORI A., BRAVI E., FAVATI F., MONTANARI L., FANTOZZI P., J. Supercrit. Fluids, Vol. 40, **2007**,p. 349
[7] BRUNNER G., MACHADO N. T., J. Supercrit. Fluids, Vol. 66, **2012**, p. 96
[8] KUK M. S., MONTAGNA J. C., In Chemical Engineering at Supercritical Fluid Conditions, **1983**, Ed. Ann Arbor Science
[9] KREIM K.. Doctoral Thesis, **1983**, Technical Universität of Hamburg – Harburg.
[10] BRIGNOLE E. A., ANDERSEN P. M., FREDENSLUND A., Ind. Eng. Chem. Res, Vol. 26,**1987**,p. 254[11] LIM J. S., LEE Y.-W., KIM J.-D., LEE Y. Y., CHUN H.-S., J. Supercrit. Fluids, Vol. 8,**1995**, p. 127
[12] BUDICH M., BRUNNER G., J. Supercrit. Fluids, Vol. 25,**2003**,p. 45
[13] HENLEY E. J., SEADER J. D., Equilibrium-Stage Separation Operations in Chemical Engineering, **1981**, Ed. Wiley.
[14] PERRY J. H., CHILTON C. H., KIRKPATRICK S. D., Chemical Engineers' Handbook, **1963**, Ed. McGraw-Hill
[15] McCABE W. L., SMITH J. C., HARRIOTT P., Unit Operations of Chemical Engineering,**1985**, Ed. McGraw Hill
[16] TREYBAL R. E., Mass-Transfer Operations, **1980**, Ed. McGraw-Hill
[17] STOCKFLETH R., BRUNNER G., Ind. Eng. Chem. Res.,Vol. 40,**2001**,p. 347
[18] ERGUN S., Chem. Process Eng. Vol. 48, **1952**,p. 89
[19] HEIDARYAN E.,HATAMI T.,RAHIMI M.; MOGHADASI J., J. Supercrit. Fluids, Vol. 56, **2011**,p. 144
[20] AIR LIQUIDE, Division Scientifique, Gas Encyclopedia, **1976**, Ed. Elsevier.