ECCE12
The 12th EUROPEAN CONGRESS OF CHEMICAL ENGINEERING
Florence 15-19 September 2019

Continuous acetic acid extraction from dilute aqueous solutions with supercritical CO_2: experiments and simulation of external extract reflux

Astrid Novella*, Séverine Camy, Jean-Stéphane Condoret

Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

**astrid.novella@ensiacet.fr*

Highlights

- Supercritical fractionation of acetic acid-water mixtures was experimentally studied
- Performances of extraction of AA are low due to thermodynamic limitation
- Simulation of external reflux of extract was performed with Prosim Plus software
- Use of reflux significantly increased the mass fraction of AA in the extract

1. Introduction

Because of emergence of bio-refineries, recovery of valuable products from fermentation broths, such as carboxylic acids, is an important issue to deal with. Conventional purification processes like distillation or solvent extraction present drawbacks that could be alleviated by alternative processes such as supercritical carbon dioxide ($scCO_2$) extraction. $ScCO_2$ was already proposed for purification of alcohol-water mixtures[1] but rarely for recovery of organic acids[2]. Recovery of acetic acid (AA) from dilute aqueous solutions (5% w/w) using a $scCO_2$ countercurrent packed column was experimentally studied at laboratory scale and compared with modelling using a so-called rate-based model[3]. Experimentally, best results were obtained at 40°C and 15 MPa with a solvent-to-feed ratio S/F equal to 11 (according to experimental limits of the set-up), resulting in 43% w/w AA in the CO2-free extract with an AA recovery ratio equal to 36%[4]. This remains low as compared to performances of conventional processes and this is mainly due to the low partition coefficient of AA between CO_2 and water. However, for such systems with unfavorable thermodynamic behavior, use of reflux of extract is likely to allow significant increase of the extract composition. In the present work, performance of this configuration with reflux is assessed by using the commercial process simulation software Prosim Plus (ProSim SA, France), where the column is described as a set of theoretical stages. Thermodynamics of the CO_2-AA-water ternary system is described by an homogeneous approach with Boston-Mathias modified SRK equation of state with PSRK mixing rule and UNIQUAC coefficient activity model (EoS/G^E). For this system, depending on pressure and temperature conditions, so-called type I or type II ternary diagrams can be observed. In this study, design is proposed in terms of reflux ratio and number of theoretical stages for the recovery of AA from water with $scCO_2$, for two sets of operating conditions, corresponding to type I and type II ternary behavior.

2. Methods

Two sets of operating conditions were studied, 45°C and 10 MPa (type I diagram) and 65°C, 12.8 MPa (type II diagram) with and without external extract reflux. From ternary diagrams of figure 1, about 90% w/w of acetic acid in the extract could theoretically be reached at 45°C, 10 MPa, using external reflux (Fig.1 left) and 100% w/w at 65°C and 12.8 MPa (Fig.1 right). To reach these separation objectives, minimal reflux ratio was graphically determined. Then, value of operational reflux, CO_2 flow-rate and number of theoretical stages were varied to approach these high separation performances.

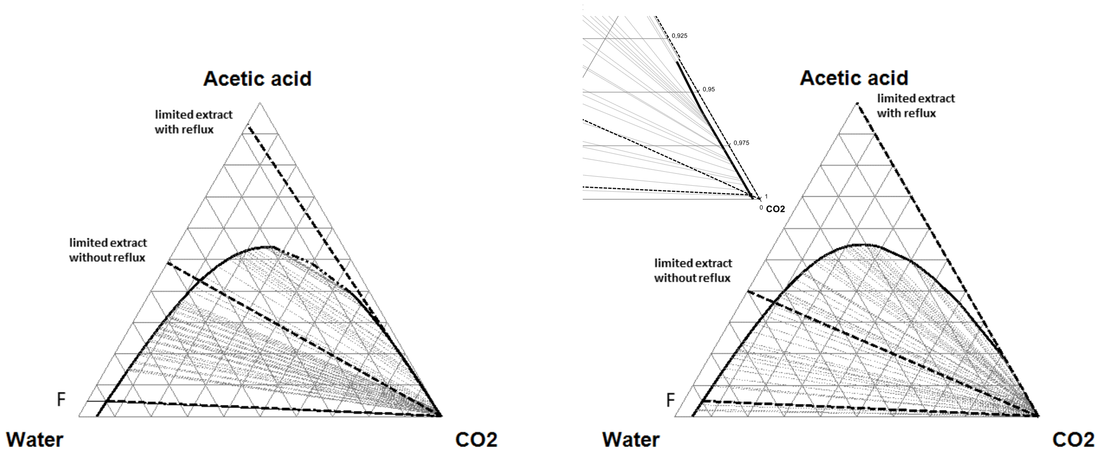

Figure 1. Left : 45°C 10 MPa (type I diagram) & Right : 65°C 12.8 MPa (type II diagram)
Equilibrium curves (solid lines), construction for limited extract in simple and reflux configurations (dotted lines)

3. Results and discussion

At 45°C and 10 MPa, using a S/F=10 with 10 theoretical stages and a reflux ratio=15.5, 87% w/w AA in the extract could be obtained, with a 23% recovery ratio whereas in the conventional extraction without reflux, only 30% w/w of AA in the extract are achieved. At 65°C and 12.8 MPa, 85% w/w AA (with a recovery ratio of 23%) in the extract could be obtained (same S/F and number of stage and with reflux ratio=18.2) whereas only 24% is reached without reflux. These results evidence the theoretical possibility to reach high separation performances for the recovery of dilute acetic acid in water.

4. Conclusions

In this work, supercritical CO_2 extraction for recovery of acetic acid, as an alternative to conventional processes, such as distillation or solvent extraction, was studied. Using conventional configuration of a packed column, *i.e.,* without extract reflux, high purity and high recovery ratio cannot be obtained due to thermodynamic barrier whereas modeling indicated that use of extract reflux could significantly improve separation performances. A larger range of operating conditions has to be considered now to find the optimal design of the contactor (S/F, number of stages, position of feed, reflux ratio). Nevertheless, these theoretical findings remain to be experimentally validated using a lab scale contactor[5]and this work is in progress in our lab.

References

1. M. Budich, G. Brunner, J. Supercrit. Fluid **2003**, 25, 45-55
2. B. G. Garrett, K. Srinivas, B. K. Ahring, J. Supercrit. Fluid **2014**, 95, 243-251
3. N. Gañán, J. Morchain, S. Camy, J.-S. Condoret, J. Supercrit. Fluid **2018**, 135, 168-179
4. A. Novella, N. Gañán, S. Camy, J.-S. Condoret, Proceeding for ISSF **2018**, http://supflu2018.fr/pdf/PF02.pdf
5. R. Lalam, S. Chamali, S. Camy, D. Rouzineau, R. Kessas, J.-S. Condoret, J. Supercrit. Fluid **2015**, 101, 24-35