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Process simulation of organic liquid products fractionation in countercurrent multistage columns using CO_2 as solvent with Aspen-Hysys

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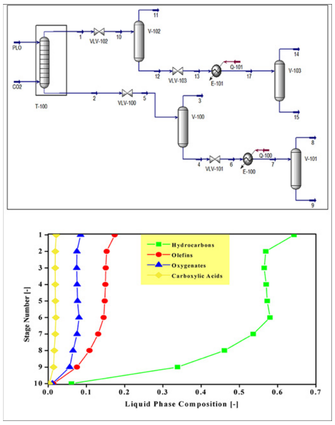
GRAPHICAL ABSTRACT



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ABSTRACT

Fractionation of liquid phase products (OLP), obtained by thermal catalytic cracking of palm oil, simulated in multistage countercurrent absorber/stripping columns using SC-CO_2 as solvent with Aspen-Hysys, at 333 K, 140 and 180 bar, and (S/F) = 12, 15, 17, 25, 30, 38. RK-Aspen EOS applied to correlate equilibrium data of binary systems (OLP)-i/CO_2. Composition of OLP used to predict thermophysical properties and acentric factor of OLP compounds by group-contribution methods. The effect of pressure and (S/F) on process performance evaluated by computing the yield and recoveries of hydrocarbons, olefins, oxygenates, carboxylic acids. The regressions show that RK-Aspen EOS describe well phase equilibrium data, showing AAD between 0.8% and 1.25% and 0.01%– 0.66% for the liquid and gaseous phases. The best deacidifying conditions obtained at 333 K, 140 bar, and (S/F) = 17. Simulations show that SC-CO_2 was able to deacidify OLP and to obtain fractions with lower olefins content.

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1. Introduction

Pyrolysis and/or catalytic cracking is one of the most promising process to convert triglycerides, the major compounds of vegetable oils and animal fats [1,2], into liquid biofuels [3], as reported in the literature [3–25]. Both have the objective to obtain hydrocarbons for use as fuels [3,4,6–24]. The reaction products obtained by pyrolysis and/or catalytic cracking of oils, fats, grease, and fatty acids mixtures include gaseous and liquid fuels, water and coke [6–8,14,15,17,21,7–24]. The physicochemical properties and chemical composition of OLP depends on the selectivity of the catalyst used [6,7,10,14–17,20,4–25]. The organic liquid products (OLP) consist basically of alkanes, alkenes, ring-containing alkanes, ring-containing alkenes, cycle-alkanes, cycle-alkenes, and aromatics [8,11,12,16,17,21,7–24], corresponding to the boiling point range of gasoline, kerosene and diesel fossil fuels, as well as and carboxylic acids, aldehydes, ketones, fatty alcohols, and esters [6–8,11,12,15,15,16,17,21,4–25]. The OLP can be refined and/or upgraded by applying physical (filtration, decantation, and centrifugation) and thermal separation processes (distillation, liquid-liquid extraction, and adsorption) to produce high quality green fuel-like fractions with potential to substitute partially fossil fuels [6,11,16,21,7–24,26–29]. The disadvantages and/or drawbacks of OLP obtained by pyrolysis and/or catalytic cracking of oils, fats, greases, and fatty acid mixtures remains on the high acid values [8,11,14,19,22], and high concentrations of olefins, making it a corrosive and unstable fuel [9,21].

In the last years, processes have been proposed to remove and/or recover oxygenate compounds from OLP, particularly fractionation by using single stage and multistage distillation to obtain hydrocarbons-like fuels in the temperature boiling point range of gasoline, kerosene, and diesel-like fractions [6,7,11,14,15,21–24,26–29]. In addition, biomass-derived bio-oils have been upgraded to remove oxygenate by applying several separation/purification processes including molecular distillation to separate water and carboxylic acids from pyrolysis bio-oils [30–32], fractional distillation to isolate/enrich chemicals and improve the quality of bio-oil [33–38], liquid-liquid extraction using organic solvents and water to recover oxygenate compounds of OLP and bio-oils [26,39], and until non- bio-oils have been also applied [39]. However, until the moment no study has been reported in the literature concerning the simulation of supercritical CO_2 fractionation of organic liquid products (OLP) using the commercial process simulator Aspen-Hysys.

Multistage gas extraction in countercurrent columns, a process identical in concept, to absorption [40] and/or liquid-liquid extraction [41–45], is an alternative separation technique for the extraction and fractionation of liquid mixtures [41–45]. In recent years, emphasis has been focused on the separation of real systems such as tocopherols from soya oil [46] and palm oil deodorizer distillates [41], among other applications [42–45].

Despite the wide range of application of multistage gas extraction in countercurrent packed columns, particularly in the food industry [42,43], only a few number of works are devoted to simulation of multistage gas extraction using self-made computer codes or commercial chemical process simulators such as Aspen-Hysys, including the simulation of the separation of mono-glycerides from a mixture of oleic acid + glycerides as well as fatty acids from palm oil in countercurrent columns [47], simulation of the separation of tocopherol from a synthetic mixture of tocopherol + squalene + carboxylic acids using supercritical carbon dioxide as solvent within a flowsheet consisting of an one stage extractor and a flash separator and the PR-EOS with the LCVM mixing rule using the commercial simulator ASPEN+ [48], simulation of deterpenation of lemon essential oil using supercritical carbon dioxide as solvent by considering a one stage extractor using a self-made academic computer code and the commercial simulator ASPEN+ to simulate the fractionation in multiple stages represented by a flowsheet consisting of a series of flash separators using the PR-EOS with quadratic mixing rules [49], simulation process to recover provitamin A (β-carotene) from palm oil (esterified) using carbon dioxide/ethanol as the supercritical mixed solvent with the commercial simulator HYSYS™ [50], fractionation of esterified olive oil deodorizer distillates, enriching of squalene from trans-esterified olive oil deodorized distillates, separation of esters and sterols of soya oil deodorizer distillates esterified enzymatically and until the de-acidification of crude olive oil using supercritical carbon dioxide as solvent in countercurrent columns using an academic self-made computer code written in FORTRAN [51–53] with the CG-EOS [54]. In addition, the literature reports a dynamic model to simulate a supercritical fluid extraction plant coupled to a countercurrent fractionation column, whose flowsheet was modularly organized into a set of sub-models, including the extraction packed column, the supercritical solvent heat exchanger, the product recovery and solvent regeneration column, and the solvent make-up, being the model validated against experimental data for the fractionation of edible oil mixtures using supercritical carbon dioxide as the solvent [55]. Recently, the modeling and simulation of the fractionation of liquid streams from natural products, particularly vegetable oils, in countercurrent columns absorber/stripping columns using SC-CO2 as solvent with Aspen-Hysys, has been systematically investigated [40].

The objective of this work was to apply the commercial simulator Aspen-Hysys 8.6 (Aspen One, 2015) to simulate the supercritical CO_2 fractionation of organic liquid product (OLP), obtained by catalytic cracking of palm oil at 450 °C, 1.0 atm, using 10% (wt.) Na_2CO_3 as catalyst. The simulations were carried out by selecting the multistage countercurrent absorber/stripping unit operation column. The Redlich-Kwong Aspen (RK-Aspen) equation of state (EOS) was used as the thermodynamic fluid package, applied to correlate the experimental phase equilibrium data of binary organic liquid products (OLP) compounds-i/CO_2 systems available in the literature. The RK-Aspen temperature-independent binary interaction parameters were obtained using the Aspen Properties computational package from Aspen Plus 8.6 (Aspen One, 2015). The effect of pressure and the solvent to feed ratio (S/F) on process performance were evaluated by analyzing the yield, recovery of hydrocarbons, olefins, oxygenates, carboxylic acids in the top and bottom streams, as well as the feasibility to obtain deacidify OLP fractions with lower content of olefins.

2. Modeling and simulation methodology

2.1. Thermodynamic modeling

2.1.1. Prediction of thermo-physical properties of organic liquid products compounds

Predictive methods were selected considering their applicability to describe the chemical structure of molecules and ease of use, including effects of the molecular weight of hydrocarbons. To perform a comparison and evaluation of all the methods applied to predict the thermo-physical properties of organic liquid products compounds described in Table 1, experimental data of normal boiling point (T_b) and critical properties from Yaws [56], as well as vapor pressure data from Boublik [57], were used.

Based on the composition of OLP described in Table 1, experimental data of critical properties available in the literature were selected to the following hydrocarbon functions: normal alkanes from C_2 to C_{30}, cyclic from C_3 to C_{17}, alkenes with only one unsaturation C_4 to C_{20} and aromatics from C_6 to C_{15} [58]. The predictive methods by Joback and Reid [59], Constantinou and Gani [60], Marrero-Marejón and Pardillo-Fontdevila [61] and Marrero and Gani [62] were applied to estimate the normal boiling temperature and critical properties of all the compounds present in the OLP. In addition, the methods by Costantinou et al. [63], Han and Peng [64], were applied to predict/estimate the acentric factor directly, as well as an indirect method in which the acentric factor is calculated using its definition from vapor pressure data, based on Araújo and Meireles [65]. In this case, the correlation by