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Supercritical carbon dioxide separation of fish oil ethyl esters by means of a continuous countercurrent process with an internal reflux

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ABSTRACT

The continuous countercurrent fractionation of fish oil ethyl esters using supercritical carbon dioxide is studied, modelling a process with internal reflux generated by a thermal gradient at the top stage. A methodology for process design is proposed and applied to determine the relationships between the temperature at the top stage (T_1), the number of theoretical stages (N), and the solvent to feed ratio (S/F), with the aim of providing a quantitative comparison with the external reflux process. The internal reflux process is viable and, for stated process specifications (mass fraction and recovery of C20 + C22 ethyl esters of 95%), provides comparable or better results than the external reflux process. For example, operating at 13.3 MPa and 50 °C, and keeping T_1 in the range (66–70) °C, the specifications are attained with N and S/F in the range 16–30 and 88–120, respectively.

1. Introduction

In the last two decades, the production of oils rich in polyunsaturated fatty acids (PUFA) of the omega-3 series has gained increasing attention, due to valuable applications of these compounds in the nutraceutical and pharmaceutical industry. Many anthropological, epidemiological, clinical and biochemical studies emphasize the nutritional value of omega-3 PUFA in the prevention of several diseases and indicate that typical Western diets are well below adequate daily intakes of these compounds [1–3]. In particular, the nutritional and pharmacological value of eicosapentaenoic acid (EPA, C20:5) and docosahexaenoic acid (DHA, C22:6) in the prevention of cardiovascular diseases [4,5] and the reduction of hypertriglyceridemia [5] has been well ascertained. As a result of these issues, many nutraceutical products based on oils with EPA + DHA mass fraction from 30% to 80% are currently marketed as dietary supplements. Furthermore, mixtures with EPA and DHA (in the form of ethyl esters) over 80%, with stated values of EPA/DHA ratio (typically in the range 1–1.6) are recognized by several Pharmacopoeias as Active Pharmaceutical Ingredient (API) against hypertriglyceridemia and myocardial infarction.

The raw material for the production of omega-3 oils is typically represented by fish oils. Most of the fatty acid chains in fish oil triglycerides have a number of carbon atoms ranging from 14 to 22, being PUFA more abundant in the longest chains. By simply selecting fish naturally rich in omega-3 (e.g., sardine, anchovies, mackerel, herring, menhaden, etc.), crude oil containing EPA + DHA from 10% to 25% can be obtained [6]. Since a considerable enrichment in a specific fatty acid cannot be achieved on a triglyceride feedstock, fractionation processes are usually performed on fish oil ethyl esters (FOEE), preliminary obtained by transesterification of fish oils.

In order to increase EPA and DHA concentration starting from FOEE, the shortest fatty acid chains (C14–C16–C18) must be separated from the longest (C20–C22), as well as saturated and monounsaturated esters from polyunsaturated ones. Separation on the basis of the degree of unsaturation is typically attained by means of crystallization processes, which may be performed in conventional solvents (e.g., methanol, acetone) or in the urea-adduction process [7]. With regard to the separation on the basis of chain length, short alkyl esters are classically separated by distillation processes. However, when dealing with the long polyunsaturated fatty acid chains of fish oils, the conventional vacuum distillation is not feasible, because the high temperatures required (well above 200 °C) unacceptably degrade PUFA [7,8].

Until now, only two processes have proven to be feasible for FOEE fractionation on chain length basis: short path distillation and supercritical fluid extraction. Short path distillation is a particular kind of distillation, performed at a pressure much lower (0.1–100 Pa) than conventional vacuum distillation, thus with lower operating temperatures and with very short residence time.

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This process is currently applied in some industries for producing omega-3 oils with EPA + DHA mass fractions typically around 50–60%. However, even operating at extremely low pressures (0.1 Pa), required temperatures are moderately high (in the range 140–170 °C) and process selectivity is relatively low. In addition, to achieve further increase of EPA + DHA mass fractions with this technology more passages are required, causing a substantial reduction in recovery and an increased residence time of EPA and DHA at the process temperatures [9].

A potential alternative to the short path distillation process is the fractionation using supercritical carbon dioxide ($SCCO_2$). A number of seminal studies dealing with semicontinuous processes demonstrated that this solvent is capable of separating FOEE at temperatures below 100 °C and pressures below 20 MPa, showing a selectivity that mainly depends on the length of the carbon chain, being the short chain esters preferentially solubilized. In these processes, a batch of oil is charged in an extraction vessel and $SCCO_2$ is then passed through the charge. Since the solvent extracts preferentially the short chain esters, the EPA and DHA esters are concentrated in the raffinate oil remaining in the extraction vessel [7,10–13]. In order to improve recovery and concentration of EPA and DHA esters, the use of a rectification column combined to the extraction vessel was proposed. In these studies, the reflux in the rectification column was generated by means of a temperature increase at the top of the column (or along the column), which causes re-condensation of part of the extracted oil (retrograde condensation) [11–13]. Although these original processes allow the production of fractions highly concentrated (mass fractions up to 95%) in specific chain length classes, they require very high solvent to feed ratios (from 200 to 400) [13]. More recently, Riha and Brunner [14] showed that it is possible to obtain C20 and C22 ethyl esters (EE-C20 and EE-C22) at mass fraction above 95%, together with 95% recovery, operating a continuous countercurrent process in a column provided with external reflux of extract and using reasonable solvent to feed ratios (in the range 60–130). This process was modelled and simulated by Gironi and Maschietti [15], who obtained a good agreement with experimental data using a thermodynamic model based on the Peng–Robinson Equation of State (PREOS). In the same work, relationships between solvent to feed ratio (S/F), number of theoretical stages (N), and external reflux ratio were investigated in order to find out optimal operating conditions.

An alternative to external reflux in countercurrent fractionation processes using $SCCO_2$ is the application of a thermal gradient along the column, leading to an internal reflux [16]. The internal reflux can be generated if the solubility of the mixture to be fractionated in $SCCO_2$ exhibits a substantial variation with temperature. Focusing on continuous processes, experimental data on the fractionation of liquid mixtures using $SCCO_2$ and exploiting the internal reflux are reported in a few studies, such as in the case of the refining of lampante olive oil [17], the recovery of squalene from vegetable oil deodorizer distillates [18,19], and the deterpenation of citrus oils [20]. In these studies, a positive effect of the internal reflux on the separation process efficiency is reported but no process modelling is provided. In addition, to our knowledge, there are no modelling studies in the literature where the relationships between the thermal gradient, generating the internal reflux, and the other process parameters (e.g., N, S/F) are studied. In particular, there is a lack of research works where the internal and external reflux processes are quantitatively compared with respect to stated process specifications, thus allowing the potential for application of the internal reflux process to be assessed.

In the present work, the continuous countercurrent separation of FOEE using $SCCO_2$ is studied modelling a process which exploits retrograde condensation to generate an internal reflux in the column. In particular, the reflux for the enriching section is generated operating the top stage at a temperature (T_1) higher than the temperature of the body of the column (T), which is isothermal. The relationship between the main process parameters, such as S/F, N, T and T_1, is investigated, allowing a quantitative comparison with the external reflux process.

2. Thermodynamics of the system CO_2–FOEE

Experimental data on phase equilibria of binary systems composed of carbon dioxide (CO_2) and long chain ethyl esters at high pressures are reported in several literature works [21–26]. Some experimental data are also available on synthetic multicomponent mixtures of relevant FOEE [22,27] or natural mixtures of FOEE [7,15,22,28–32]. When thermodynamic modelling is available, models based on cubic equations of state are selected in most of the cases [15,21,22,26,27,32]. In particular, satisfactory results were obtained using the Peng–Robinson Equation of State in association with the van der Waals mixing rules, including two binary interaction parameters [15,21,27].

Thermodynamic modelling of FOEE natural mixtures requires the preliminary selection of appropriate key components, being the oil composed of a huge number of compounds. Considering that supercritical carbon dioxide is a solvent selective on the basis of chain length, the typical choice is to group the components of the oil in five classes of ethyl esters (EE) on the basis of the acid chain length (C14, C16, C18, C20, C22). Each class is then considered as composed of its most abundant component only. A model scheme based on the following ethyl esters can be employed: myristate (EE-C14:0), palmitate (EE-C16:0), oleate (EE-C18:1), eicosapentaenoate (EE-EPA), and docosahexaenoate (EE-DHA). Adopting such description of the natural oil, a good representation of phase equilibrium experimental data on the system $SCCO_2$ + FOEE was obtained by Gironi and Maschietti [15], who utilized a thermodynamic model based on the Peng–Robinson Equation of State [33]. In the proposed model, the mixture parameters are calculated by means of the van der Waals mixing rules, corrected by two binary interaction parameters (k_{ij} and η_{ij}). Null k_{ij} and η_{ij} for EE couples were shown to be a reasonable approximation. In addition, it was shown that it is necessary to allow k_{ij} varying with temperature in order to fit the data in the whole experimental temperature range (42–70) °C. In the proposed model, k_{ij} varies according to the following equation:

$$k_{ij} = \alpha_{ij} + \beta_{ij} T \quad (1)$$

On the whole, the thermodynamic model employs three regression parameters (α_{ij}, β_{ij}, η_{ij}). A detailed description of the model, comprising data and procedure used both for pure component and binary parameter calculations, is reported in the original work [15].

Besides validation on phase equilibrium data, the proposed thermodynamic model was also used to simulate the separation of FOEE carried out by Riha and Brunner [14] using a 12 m countercurrent column. The thermodynamic model proved reliable in predicting the relationships between column separation factors, solvent to feed ratio, and reflux ratio, for temperatures in the range (40–70) °C, pressures in the range (9.6–17.0) MPa, and for two different feed oil composition, which is to say for different composition profiles in the column [15].

Prior to applying the thermodynamic model to the study of the internal reflux multi-stage process, some interesting features of the thermodynamic behaviour of the system CO_2 + FOEE at high pressure are discussed here, analysing the results obtained in a series of single-stage flash calculations. A typical composition of the oil, suitable for EPA and DHA production (see Table 1), was considered both in these calculations and in the rest of this work [15]. S/F was set equal to 60 g/g, which is a realistic value for the industrial supercritical separation process of FOEE [14,15]. The flash calculations were