Simulation of an Industrial Plant for Supercritical CO_2 Fractionation of Omega-3 Fatty Acid Ethyl Esters from Fish Oil

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In this work a multistage continuous fractionation process was simulated. The process was intended to fractionate with supercritical CO_2 a mixture of fatty acid ethyl esters (FAEEs) from trout oil, with the aim of obtaining a fraction rich in omega-3 FAEEs.

The plant was simulated by means of a model on the purpose developed. In the model the mixture of FAEE was simplified as consisting on five ethyl esters (ethyl esters of C14, C16, C18, C20 and C22 fatty acids) representing the fish oil composition. The model, based on Peng-Robinson equation of state, was at first validated with literature data.

The plant was fed with 60 kg/h of FAEEs from trout oil, i.e. the potential oil production of ASTRO, a trout processing company located in Trentino, Italy. The target of the process was obtaining a high molecular weight stream composed of 85% EPA and DHA ethyl esters.

Several simulations were performed around the best operational conditions claimed in the literature (T=60°C, P=14,5 MPa) resulting, according to our simulation results, in a column of 20 theoretical plates. The pressure was varied in the range 13,5-15,5 MPa, the temperature in the range 52-70 °C. Through a preliminary cost-analysis, accounting for the whole plant (with pumps, heat exchangers, condenser), the best operational conditions resulted T=52 °C and P=14,5 MPa: even if in this case 40 theoretical plates were necessary, the CO_2 to feed ratio was minimal and the operational costs sensibly reduced.

1. INTRODUCTION

The primary source of natural omega-3 is fish oil, although the use of omega-3 fatty acids, in particular EPA and DHA, as active compounds in pharmacology or functional ingredients requires a previous concentration step into a chemical form easily metabolized by human organism and with a good stability against oxidation, like ethanol esterified form.

The path from crude fish oil to omega-3 concentrates can be accomplished in different ways: through crystallization, molecular distillation, chromatographic methods, enzymatic reactions, finally supercritical fluid fractionation (SFF). SFF seems particularly interesting given that it allows utilizing low temperatures (well below 100°C), it can be performed also at industrial scale and, finally, the performance of the process (in terms of omega-3 concentration) can be tuned opportunely by proper plant design.

SFF of fish oil can be achieved only after a preliminary reaction step where fish oil is esterified with ethanol to form fatty acid ethyl esters. Eventually, prior to feed the FAEE mixture to the SFF plant, the FAAE mixture can be partially enriched in polyunsaturated fatty acids (PUFA) by means of urea clathration. Urea clathration allows to precipitate saturated and monounsaturated FAEEs which can thus been separated from the FAEE mixture.

The SFF continuous process applied to fish oil foresees to operate in a counter-current packed column where the supercritical CO_2 (SC-CO_2) is fed to the bottom of the column and the FAEE mixture is fed at an intermediate level in the column. A reflux at the head of the column allows to control the extract composition (rich in light components such as the ethyl esters of the fatty acids C16, C18, C20), while the bottom product, or raffinate, results enriched in the heavy FAEEs, among which the ethyl esters of EPA and DHA are present.

The SFF process applied to fish oil has been the subject of a number of studies.

Fleck et al. [1] designed an automated countercurrent column which utilized SC-CO_2 for fractionating the FAEE mixture. In their work, the authors showed as the separation efficiency can be improved by adding automatic control to the column.

Riha and Brunner [2] studied phase equilibrium between SC-CO_2 and many FAEEs derived from fish oil, proving that it is possible to fractionate them according to their carbon number. Based on these results, the same authors developed a method to separate FAEEs from fish oil by countercurrent multistage extraction with CO_2 in a pilot-scale column [3]. According to their experimental results, a pressure of 14.5 MPa and a temperature of 60 °C were selected as the best performing. Furthermore, Riha and Brunner simulated the fractionation process [3]. They lumped all the components of the FAEE mixture into a set of five pseudo-components as a function of their chain length. The partition coefficient of each component was calculated through an empirical correlation the authors developed based on the equilibrium data previously obtained [2].

Espinosa et al. [4] studied phase equilibrium between a mixture of FAEE and SC-CO_2 based on a group contribution equation of state (GC-EoS). Moreover, they performed a simulation of the SFF process, and optimized the experimental conditions. Finally, they proposed a method to obtain a high yield of high purity fractions of EPA and DHA respectively, using a high pressure countercurrent system with three columns. Alternatively, to increase the purity of the product, they proposed a preparatory step based on urea complexation.

Gironi and Maschietti [5] proposed a thermodynamic model which assumes the oil being composed of five FAEEs, each of them representing a specific acid chain length, similarly as Riha and Brunner [3]. The model was based on Peng-Robinson EoS, assuming van der Waals mixing rules for the mixture parameters. They validated the model with some experimental data obtained in a semi-continuous single-stage fractionation process and then applied it to simulate a multistage continuous process. They demonstrated that this process enables to produce a raffinate with 95% by weight of EE-EPA and EE-DHA, together with 95% recovery of these compounds.

Martín and Cocero [6] developed a comprehensive mathematical model for the SFF of liquids with SC-CO_2 by including the differential mass and energy balances in the column, and the coupled mass and heat transfer at the interface between the two fluid phases. Phase equilibrium and volumetric and thermal properties were described by using Peng-Robinson EoS; the mass transfer coefficient was estimated applying correlations available in the literature. The authors validated this model with the SFF of fish oil FAME mixtures and found it to be able to predict the trends of variation of the composition of extract and raffinate with the different operating parameters.

Perretti et al. [7] confirmed the possibility of modifying the FAEE concentration of a mixture by using SC-CO_2.

Antunes-Corrêa et al. [8] investigated the concentration of omega-3 PUFA in their natural form (triglycerides) instead of as ethyl esters. They measured fish oil solubility in SC-CO_2 and calculated the distribution coefficients of several oil components. The distribution coefficients they found were very close to unity, giving little expectation to SFF of the crude

triglycerides to concentrate omega-3 PUFA. Similar conclusions were reached also by Davarnejad et al. [9].

Research on fish oil SFF is still open with the aim of achieving production at large scale. A fundamental point for scaling up the process is the knowledge of phase behavior of the mixtures involved in SFF and the development of reliable models to describe it. As it has been detailed previously, models to describe SFF process can be developed once phase equilibrium can be well described.

In this work a multistage continuous fractionation process was simulated and designed at a preliminary level. The process model contained a thermodynamic phase-equilibrium model based on Peng-Robinson EoS. At first the equilibrium model was validated with equilibrium data available in the literature [2]. Then, the process model was validated with the experimental data of Riha and Brunner [3], that are the only experimental data available in the literature concerning continuous supercritical fractionation column.

In the equilibrium model the mixture of FAEE was assumed as composed of five fatty acid ethyl esters, each of them representing a specifically fatty acid chain length, in accordance with Riha and Brunner [3] and Gironi and Maschietti [5].

2. MODELLING

2.1. The phase equilibrium model

The mixture of FAEEs deriving from fish oil was simplified as consisting of the ethyl esters (EE) of the fatty acids C14, C16, C18, C20 and C22. The system was thus composed by CO_2 and 5 pseudo-components representing the FAEE mixture. Phase equilibrium can be expressed through eq.s (1-4):

$$f_i^L = f_i^V \tag{1}$$

$$f_i^L = P\varphi_i^L x_i \tag{2}$$

$$f_i^V = P\varphi_i^V y_i \tag{3}$$

$$y_i/x_i = \varphi_i^L/\varphi_i^V \tag{4}$$

Apex L refers to the phase rich in FAEEs (heavy phase, liquid phase); apex V refers to the phase rich in CO_2 (light phase, supercritical phase).

φ_i^L and φ_i^V can be calculated through an EoS. The Peng-Robinson EoS was chosen, which has been extensively used [3,5,6] on account of its capability of dealing effectively with supercritical fluids.

Peng-Robinson EoS describes the link between system pressure, temperature and molar volume by resorting to parameters derived from critical properties of the substances, such as critical temperature T_c, critical pressure P_c and acentric factor ω. For a pure substance, it has the following form:

$$P = \frac{RT}{\tilde{V} - b} - \frac{a}{\tilde{V}^2 + 2b\tilde{V} - b^2} \tag{5}$$

Parameters a and b depend on T_c, P_c and ω of the compound considered.

To deal with a mixture, rather than a pure compound, van der Waals' binary mixing rules were introduced. These rules enable to calculate a_m and b_m, which are the a and b parameters appearing in eq (5) but with reference to a mixture of N components, each having the molar fraction z, in the following way:

$$a_m = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j a_{ij} \tag{6}$$

$$b_m = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j b_{ij} \tag{7}$$

Where:

$$a_{ij} = a_{ji} = \left(1 - k_{ij}\right)\sqrt{a_i a_j} \tag{8}$$

$$b_{ij} = b_{ji} = \left(1 - \eta_{ij}\right)\frac{b_i + b_j}{2} \tag{9}$$

$$a_{ii} = a_i; \quad a_{jj} = a_j; \quad b_{ii} = b_i; \quad b_{jj} = b_j \tag{10}$$

Parameters k_{ij} and η_{ij} are called interaction parameters and express the interaction between species i and j. They are equal to zero in the case $i = j$ and, for the present study, they were let equal to zero also in the case i and j were both ethyl esters, given the similarity between these compounds. Consequently, the only interaction parameters different from zero are those relevant to the couples FAEE/CO_2, i.e. EE-C14:0/CO_2, EE-C16:0/CO_2, EE-C18:0/CO_2, EE-EPA/CO_2 and EE-DHA/CO_2.

According to Riha and Brunner [3] and Gironi and Maschietti [5], it is worth to introduce the dependence of k_{ij} on the temperature as reported in eq. (11):

$$k_{ij} = \alpha_{ij} + \beta_{ij}T \tag{11}$$

The values of critical temperature, critical pressure and acentric factor were taken from ref. [5], while the values of the interaction parameters were optimized to best fit experimental data from literature (see later). For completeness, they are reported in Table 1.

Table 1: Critical properties, acentric factor (from Gironi and Maschietti [5]) and interaction parameters (this study, optimized).

	P_C [MPa]	T_C [K]	ω	α_{iCO_2}	β_{iCO_2}	η_{iCO_2}
EE-C14:0	1.454	735.8	0.855	0.008810	0.00012700	0.000
EE-C16:0	1.315	757.9	0.928	-0.028536	0.00025799	0.030
EE-C18:0	1.200	778.2	0.998	-0.037786	0.00031592	0.030
EE-EPA	1.269	817.1	1.046	-0.060565	0.00037023	0.020
EE-DHA	1.194	837.3	1.108	-0.0096899	0.00024260	0.012
CO_2	7.376	304.2	0.225	0.000	0.000	0.000

The thermodynamic equilibrium model above detailed was implemented as a Fortran code. The model predicted equilibrium data available in the literature very well.

In Fig. 1 equilibrium data for mixtures of FAEEs and CO_2 are reported. Experimental data are from Riha and Brunner [2] and refer to three different FAEE mixtures (referred in Fig. 1 as EE-2, EE-7 and EE-9 like in the original manuscript [2]). The data reported in Fig. 1 refer to the temperature of 333K and to the heavy phase. Fig. 1 evidences that the model predictions are extremely reliable.
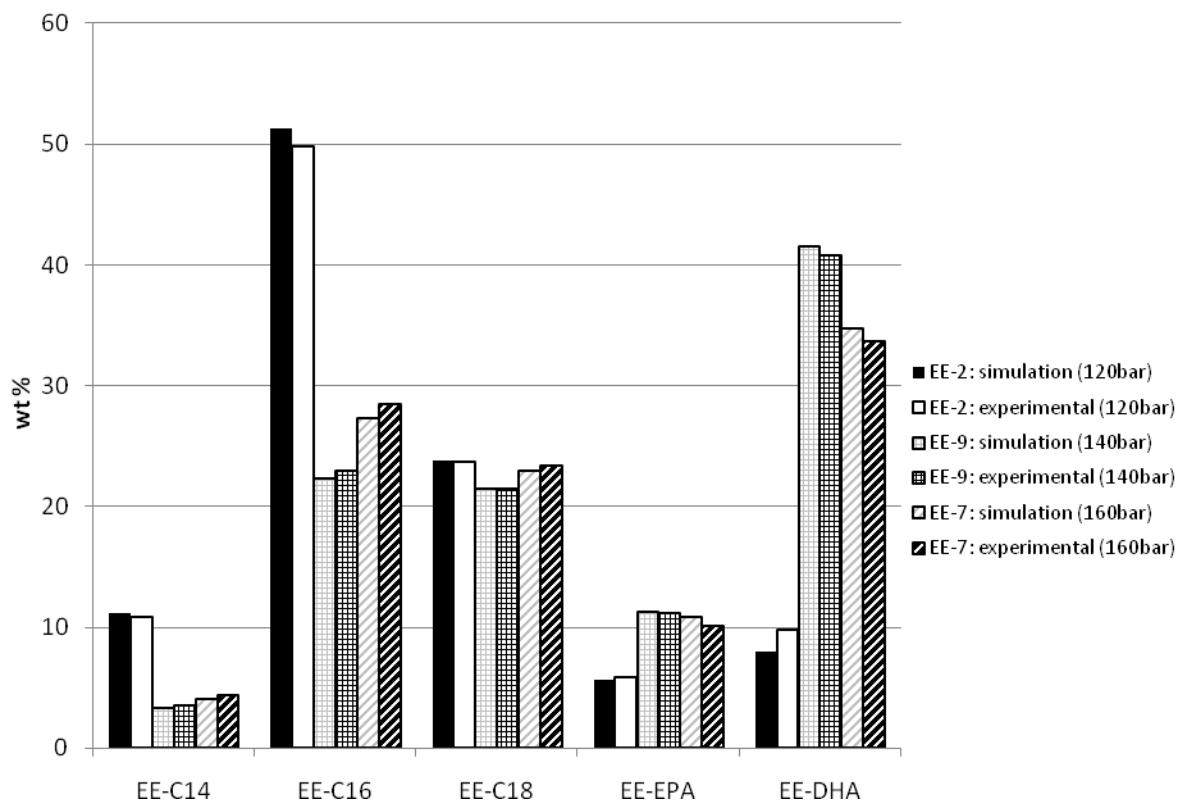
Fig. 1. The phase equilibrium model: comparison among experimental data (Riha and Brunner [2]) and model predictions.

2.2. The fractionation column model

A schematic drawing of the column with the ancillary equipments is reported in Fig. 2. The FAEE mixture enters the column at the center, while the supercritical solvent enters at the bottom. A reflux is foreseen to recycle to the column head a portion of the light phase and to allow the coexistence of a biphasic system in all the column height. The FAEE mixture flows downward and enriches itself in its heavy components (EE-C20 and EE-C22) because the light components (EE-C14 and EE-C16) tend to pass in light phase, rich in CO_2, which flows upward.

From the column a light phase and a heavy phase are obtained. The CO_2 released in the expansion vessel at the top of the column is recycled to the column, after being liquefied. CO_2 consumption is thus related to the initial pressurizing of the column and to the CO_2 released from the expansion of the heavy phase.
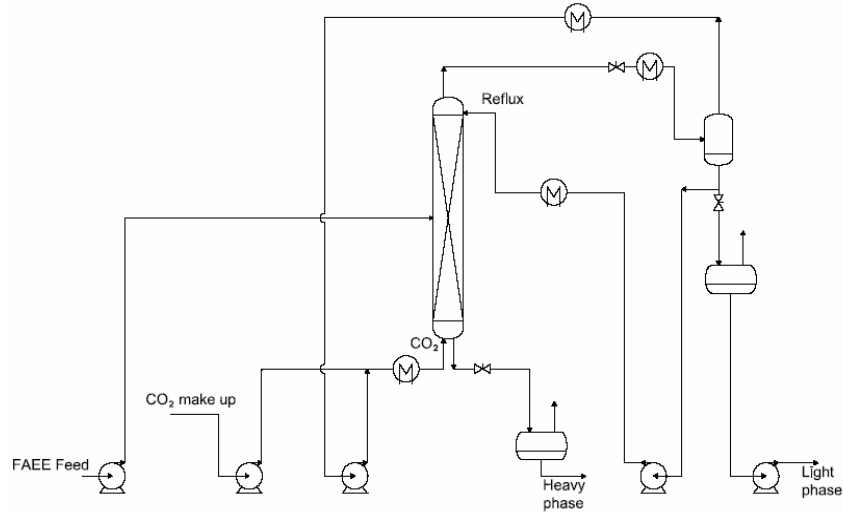
Fig. 2. Schematic drawing of the column with the ancillary equipments.

The fractionation column was assumed to be isothermal and isobaric. Thus, the column was modeled by means of mass balances and phase equilibrium relationships. The packed column was modeled as consisting of a number of theoretical plates where phase equilibrium was achieved. They were numbered from the top plate, number 1, to the bottom plate, number n. The hold up of each plate was fixed at t=0.

The mass balance for a generic component (indicated with the subscript 'i') at a generic plate (indicated with the subscript 'j') at a certain time (indicated with the subscript 'k') consists of the following equation:

$$\frac{dN_{i,j,k}}{dt} = V_{j+1,k} y_{i,j+1,k} + L_{j-1,k} x_{i,j-1,k} - V_{j,k} y_{i,j,k} - L_{j,k} x_{i,j,k} \tag{12}$$

Where $y_{i,j,k}$ and $x_{i,j,k}$ have to respect eq. (4), that is the streams leave the plate at thermodynamic equilibrium.

Also in this case the model was written as a Fortran code.

The model was tested utilizing the experimental data reported by Riha and Brunner [3]. Table 2 reports experimental data (referred as test P8, P9 and P10 like in the original manuscript [3]) and simulation results. The simulations were performed fixing temperature, pressure, reflux flow rate, extract (light phase), feed, raffinate (heavy phase), feed composition, number of theoretical plates (45), plate where the feed enters the column (22). The model furnished as output the composition of both extract and raffinate and the solvent flow rate. Experimental data and model predictions were in satisfactory agreement (Table 2).

Table 2. The fractionation column model: comparison among experimental data (Riha and Brunner [3]) and model predictions.

		P8		P9		P10	
		Experimental	Simulated	Experimental	Simulated	Experimental	Simulated
Temperature	K	333.15	333.15	343.15	343.15	353.15	353.15
Pressure	MPa	14.5	14.5	17	17	19.5	19.5
Solvent	kg/h	303	307	269.6	276.21	209.3	223
Reflux	kg/h	11.6	11.6	12.7	12.7	14.9	14.9
Extract	kg/h	1.6	1.6	1.8	1.8	2.1	2.1
C14	wt%	12.55	12.89	12.65	12.89	13.2	13.49
C16	wt%	50.54	49.74	50.93	49.89	52.01	52.33
C18	wt%	32.89	36.88	32.88	36.81	32.28	33.64
EPA	wt%	3.99	0.32	2.1	0.25	2.44	0.37
DHA	wt%	0.04	0.16	1.44	0.16	0.07	0.17
Feed	kg/h	2.4	2.4	2.7	2.7	3.3	3.3
C14	wt%	8.38	8.38	8.38	8.38	8.38	8.38
C16	wt%	33.73	33.73	33.73	33.73	33.73	33.73
C18	wt%	22.26	22.26	22.26	22.26	22.26	22.26
EPA	wt%	21.23	21.23	21.23	21.23	21.23	21.23
DHA	wt%	14.4	14.4	14.4	14.4	14.4	14.4
Raffinate	kg/h	0.8	0.8	0.9	0.9	1.2	1.2
C14	wt%	0.01	0	0	0	0	0
C16	wt%	0.02	0	0	0	0	0
C18	wt%	0.94	0.11	1.44	0.18	2.57	2.64
EPA	wt%	55.82	57.10	58.75	56.49	56.9	56.77
DHA	wt%	43.22	42.59	39.81	43.33	40.53	40.59
S/F		126.25	127.9	99.9	102.3	63.4	67

3. TROUT OIL FRACTIONATION

The fractionation model above detailed and validated on literature data was intended to model and design a SFF plant for the fractionation of a FAEE mixture from trout oil.

Trout oil composition was previously measured [10]. It is reported in Table 3 where, moreover, the fatty acids have been lumped according to their chain length.

According to the potentiality for oil production of ASTRO, a trout processing company located in Trentino, Italy, the SFF plant foresaw a feed consisting of 60 kg/h of FAEE mixture. The aim of the process was obtaining a stream (raffinate) containing 85% by weight of EPA and DHA.

Table 3. Trout oil: fatty acids analytic composition [10] and 'pseudo-components' composition.

FA	Analytic composition	Pseudo-component composition
14:0	5.45	5.488
15:0	0.34	-
16:0	16.54	
16:1	7.27	
16:2 ω-6	1.14	27.862
16:3 ω-3	1.15	
16:4 ω-1	1.57	
17:0	0.27	-
18:0	3.65	
18:1	18.4	
18:1	3.3	
18:2 ω-6	15.46	
18:2 ω-6	0.49	46.259
18:3 ω-6	0.26	
18:3 ω-6	0.47	
18:3 ω-3	1.65	
18:4 ω-1	1.43	
18:4 ω-1	0.83	
20:1	1.14	
20:2 ω-6	0.45	
20:3 ω-6	0.28	11.110
20:4 ω-3	0.55	
20:4 ω-6	0.8	
20:5 ω-3	7.89	
21:5 ω-6	0.6	-
22:5 ω-3	2.61	8.932
22:6 ω-3	6.26	

3.1. Modeling results

The first simulations were performed at the conditions proposed by Riha and Brunner [3], that is operating the column at 60 °C and 145 bar and with a reflux ratio equal to 7.25. By basic mass balances, the extract and raffinate flow rates were set equal to 46 and 14 kg/h, respectively. Various simulations were performed varying the number of theoretical plates, maintaining the feed inlet at half of the column height. The results are reported in Table 4. By working with 20 theoretical plates (simulation S2), the desired target (85% EPA and DHA in the raffinate) was achieved.

Table 4. Results from simulations

		S1	S2	S3	S4
N° plates	-	25	20	18	16
Feed inlet	-	12	10	9	8
S/F	-	174	174	174	174
Extract	kg/h	46	46	46	46
C14	wt%	7.07	7.07	7.07	7.06
C16	wt%	36.8	36.7	36.7	36.7
C18	wt%	55.69	55.72	55.65	55.52
EPA	wt%	0.28	0.35	0.42	0.55
DHA	wt%	0.16	0.16	0.16	0.17
Feed	kg/h	60	60	60	60
C14	wt%	5.42	5.42	5.42	5.42
C16	wt%	28.22	28.22	28.22	28.22
C18	wt%	46.09	46.09	46.09	46.09
EPA	wt%	10.99	10.99	10.99	10.99
DHA	wt%	9.27	9.27	9.27	9.27
Raffinate	kg/h	14	14	14	14
C14	wt%	0	0	0	0
C16	wt%	0	0.01	0.02	0.03
C18	wt%	14.65	15.03	15.29	15.73
EPA	wt%	45.9	45.53	45.28	44.84
DHA	wt%	39.45	39.42	39.41	39.4

Considering that the values of parameters of simulation S2 represented a possible choice for conducting the SFF process, we decided to keep them as reference and to conduct other simulations by varying one value at a time, while maintaining fixed the target of the process.

So in simulations S5 and S6 the temperature was varied, in S7 and S8 the pressure was changed, in S9 and S10 the reflux ratio was varied. Table 5 reports the values used in the different simulations, Table 6 specifies the relevant results in terms of compositions of extract and raffinate. It is clear as, for maintaining fixed the concentration of EPA and DHA at 85% in the raffinate, for certain operative conditions the SFF column should foresee an increased number of theoretical plates, as is the case of simulations S5, S8 and S9.

Looking at Tables 5 and 6, an increase in temperature (S6) and a decrease in pressure (S7) improved the separation efficiency but caused a greater solvent consumption, while working at a lower temperature (S5) meant to increase the number of theoretical plates. At this stage, it was not obvious to state which was the best set of operative conditions for running the SFF process. Some economical evaluations could help to choose among S2 and S5–S10.

Table 5. Parameter used in simulations S2, S5, S6, S7, S8, S9, S10

		S2	S5	S6	S7	S8	S9	S10
S/F	-	174	75	450	315	110	126	231
T	K	333.15	325.15	343.15	333.15	333.15	333.15	333.15
P	MPa	14.5	14.5	14.5	13.5	15.5	14.5	14.5
Reflux ratio	-	7.25	7.25	7.25	7.25	7.25	5	10
Feed	kg/h	60	60	60	60	60	60	60
N°plates	-	20	40	20	20	25	25	20
Feed inlet	-	10	22	10	10	10	10	10

Table 6. Results from simulations

		S2	S5	S6	S7	S8	S9	S10
Extract	kg/h	46	46	46	46	46	46	46
C14	wt%	7.07	7.093	7.07	7.17	7.25	7.21	7.31
C16	wt%	36.7	36.95	36.69	36.79	36.77	36.82	36.57
C18	wt%	55.72	55.18	55.8	55.60	55.46	55.32	55.50
EPA	wt%	0.35	0.52	0.2	0.28	0.35	0.48	0.43
DHA	wt%	0.16	0.19	0.14	0.17	0.17	0.17	0.16
Feed	kg/h	60	60	60	60	60	60	60
C14	wt%	5.42	5.42	5.42	5.42	5.42	5.42	5.42
C16	wt%	28.22	28.22	28.22	28.22	28.22	28.22	28.22
C18	wt%	46.09	46.09	46.09	46.09	46.09	46.09	46.09
EPA	wt%	10.99	10.99	10.99	10.99	10.99	10.99	10.99
DHA	wt%	9.27	9.27	9.27	9.27	9.27	9.27	9.27
Raffinate	kg/h	14	14	14	14	14	14	14
C14	wt%	0	0	0	0	0	0	0
C16	wt%	0.01	0	0	0	0.02	0.01	0
C18	wt%	15.03	14.69	14.2	14.56	14.99	15.05	14.48
EPA	wt%	45.53	45.75	46.24	45.94	45.59	45.85	45.69
DHA	wt%	39.42	39.55	39.57	39.49	39.4	39.09	39.83

3.2. SFF Colum sizing

Calculated the number of theoretical plates, the following step was to determine the column size, i.e. its diameter and height. An incorrect choice of the diameter could led to the occurrence of flooding. The formulas and the flow diagram proposed by Machado and Brunner [11] were thus utilized to calculate the diameter of the column for the various cases considered (simulations S2 and S5-S10).

About column height, as a first approximation and to be conservative, the value of the HETP was assumed equal to 0.6 m for all the simulated configurations (Riha and Brunner [3] reported HETP=0.3 m).

3.3. Economical evaluation

In order to evaluate the investment and operating costs, the main equipments of the plant were considered: the separation column, the solvent pump and the heat exchangers. Total cost (including piping, secondary pumps, automation, tanks, etc) was estimated multiplying the cost of the main equipments by a factor of 2.5.

The cost of the main equipments was calculated resorting to the formulas of Seider [12] and the cost of column was estimated using the correlation proposed by Woerlee [13]. Without entering into details, we report here only the total investment and operating costs.

Table 7. Investment costs.

	S2	S5	S6	S7	S8	S9	S10
CO_2 pump [$ at year 2000]	73,197	60,282	100,578	86,799	65,869	67,273	79,622
Heat exchangers [$ at year 2000]	370,357	131,900	890,906	656,85	241,172	272,869	485,176
Column [$ at year 1996]	271,425	260,608	345,623	310,224	264,403	287,577	312,724
Total with other utilities [$ at year 2011]	2,212,793	1,423,522	4,097,727	3,239,175	1,780,433	1,955,051	2,710,747
Total amount [€ at year 2011]	1,702,149	1,095,017	3,152,098	2,491,673	1,369,564	1,503,886	2,085,190

The costs for pump, heat exchangers and column were actualized using a factor 1.3 for the column and a factor 1.2 for pump and heat exchangers. The conversion value from € to $ was fixed to 1.3.

Table 8. Operating costs for the proposed configurations

		S2	S5	S6	S7	S8	S9	S10
Pumping	kW	75.2	45.1	142.63	103.22	61.97	62.34	89.5
	€/year	98,188	58,972	186,132	134,702	80,870	81,353	116,797
Heat exchange	kW	468	166	1211	840	298	339	621
	€/year	679,107	241,980	1,756,312	1,218,000	432,510	491,767	901,573
Cooling	kW	189	67	489	342	119	137	251
	€/year	246,623	87,877	637,819	446,473	155,911	178,589	327,414
Make up CO_2	€/year	12,180	15,138	5,220	6,960	13,920	14,442	11,136
Depreciation	€/year	243,000	152,000	468,000	366,000	190,000	209,000	300,000
Total	€/year	1,279,098	555,967	3,053,483	2,172,135	873,211	975,151	1,656,920

Looking at the data in Table 7 and 8, we observe that the investment and the operating costs for the simulation S5 and S8 are the lowest with a significant difference compared with S6 and S7 mainly due to lower flows of solvent in the column.

Simulation S5, despite the highest number of plates, is certainly the most advantageous economically: the reduced solvent flow in the column allows to reduce the SFF column diameter and the operating costs for solvent pumping and thermal conditioning.

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