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Supercritical CO_2 fractionation of omega-3 lipids from fish by-products: Plant and process design, modeling, economic feasibility

L. Fiori[a,*], M. Manfrini[b], D. Castello[a]

[a] Department of Civil, Environmental and Mechanical Engineering, University of Trento, via Mesiano 77, 38123 Trento, Italy
[b] ASTRO, via Galilei 43, 38015 Lavis Trento, Italy

ABSTRACT

Biopharmaceutical, nutraceutical and food sectors are experiencing an increasing market interest in omega-3 concentrates. Fish and fish processing by-products represent the major source of lipids rich in omega-3. The present work focuses on the supercritical CO_2 fractionation of fish oil derivatives for obtaining omega-3 concentrates, which seems a promising process given that it allows utilizing low temperatures (well below 100 °C) and it can be performed also at industrial scale. The process was conceived, modeled, and evaluated in terms of the main parameters affecting its performances: solvent to feed ratio, reflux ratio, temperature, and pressure of both the fractionation column and the column head separator.

The process was further optimized minimizing its operating costs. The optimum foresaw operating the column at high temperature (80 °C) and pressure (19.5 MPa), which allowed for a reduced reflux ratio (=0.92) and solvent to feed ratio (=63). At these conditions, the process cost per unit product (omega-3 concentrate) turned out to be of about 2.3 €/kg.

Finally, the plant was designed for three different throughputs: 10, 100, and 300 kg/h. This allowed estimating the investment costs, in order to outline a preliminary process feasibility evaluation.

Keywords: Fish oil; Omega-3; FAEEs; Supercritical fluid fractionation; Process optimization; Plant costs

1. Introduction

The healthy value of omega-3 is well recognized. The major source of omega-3 is fish, more precisely fish oil. It is decades that refined cod liver oil is found in specialty stores and pharmacies and drunk as it is. Nowadays, fish oil and more often omega-3 concentrates from fish oil are added to a large portion of daily food advertised in the market as omega-3 enriched food products: milk, yogurt, cheese, bakery products, baby food, etc. Omega-3 concentrates from fish oil are important components in many nutraceutical products and are sold in pills in pharmacies. Recent reviews concerning omega-3 benefits and production are available in the literature (Sahena et al., 2009; Rubio-Rodríguez et al., 2010).

Fish oil production occurs mainly by the so called wet reduction process: whole fish or fish by-products (mainly viscera, heads and bones) are processed through mincing, heating, and one- or two-stage centrifugation. Fish oil and fish meal (i.e. dried fish proteins) are the final products of the wet reduction process. Fish oil can be refined to a marketable product or can be utilized as raw material for obtaining omega-3 enriched oily formulations. Fish oil production seems well established in technological terms. The same cannot be said regarding the omega-3 concentration step: different options can be envisaged.

Omega-3 are a particular kind of fatty acids (FAs), and are almost randomly distributed in the triglycerides which constitute the oil even though, actually, they are in greater

* *Corresponding author*. Tel.: +39 0461 282692.
E-mail address: luca.fiori@unitn.it (L. Fiori).
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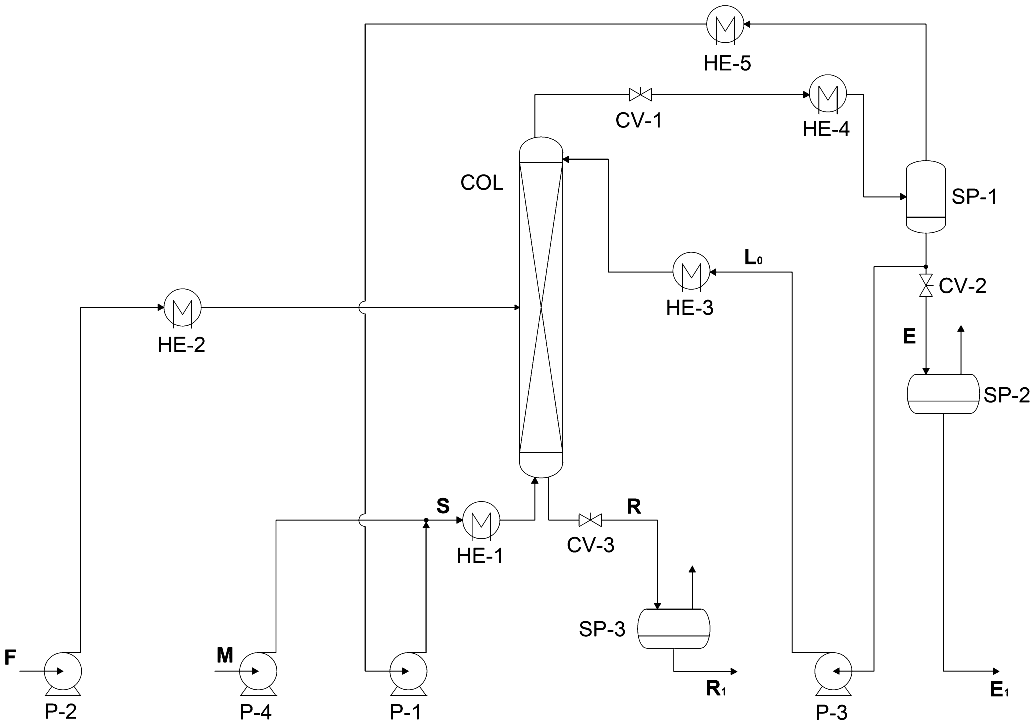

Fig. 1 – Flow scheme of the SFF process simulated. *Streams*: *F* = FAEE feed; *M* = CO_2 make-up; *S* = CO_2 to column; *E* = extract; E_1 = extract CO_2 free; L_0 = reflux; *R* = raffinate; R_1 = raffinate CO_2 free. *Equipment*: COL = fractionation column; SP = separator; P = pump; HE = heat exchanger; CV = control valve.

percentage in the sn-2 position. Because of that, only a few techniques – enzymatic methods – can accomplish the omega-3 enrichment path dealing directly with triglycerides. All the other technologies (i.e. chromatographic methods, urea clathration, molecular distillation, and supercritical fluid fractionation SFF) account for a preliminary reaction step: triglycerides are trans-esterified with ethanol to obtain fatty acid ethyl esters (FAEEs). FAEEs, as well as the original triglycerides, are edible.

FAEE mixtures can be enriched in poly-unsaturated fatty acids (PUFAs) through urea clathration, which precipitates saturated fatty acids (SFAs) and, to a limited extent, also mono-unsaturated fatty acids (MUFAs).

FAEE mixtures can be split in two fractions, long chain FAs and short chain FAs, by means of molecular distillation or SFF. Omega-3 FAs will concentrate on the long chain FA fraction given that the main fish oil omega-3, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), have a large number of carbon atoms.

Currently, the most utilized technology at industrial facilities seems to be molecular distillation. As for classical distillation, it is based on the different vapor pressure of the different constituents of the FAEE mixture. Because of that, it is a treatment based on temperature. Considering that high temperature is detrimental for highly unsaturated FAs, and thus for omega-3, molecular distillation operates under very high vacuum and with very low residence time. But, in any case, it operates in the range 140–170 °C and with only modest selectivity (Lembke, 2013). Conversely, SFF, which utilizes supercritical CO_2 ($SCCO_2$) as the fractionation medium, allows operating well below 100 °C, it is easily tunable in terms of omega-3 selectivity, and thus it seems to be a promising technique for fish oil omega-3 concentration ($SCCO_2$ is CO_2 at temperature and pressure greater than 31 °C and 7.38 MPa, respectively).

SFF of fish oil derivatives is based on the different solubility of FAEEs in $SCCO_2$: the solubility of short chain FAEEs is greater than the solubility of long chain FAEEs, while the solubility dependence on the number of unsaturated chemical bonds is almost negligible.

SFF occurs in a high pressure fractionation column, where the FAEE mixture flows in counter-current in respect to the $SCCO_2$. The liquid FAEE mixture flows downwards, while the $SCCO_2$ flows upwards (Fig. 1). Short chain FAEEs are preferentially solubilized into $SCCO_2$ and, consequently, the liquid FAEE mixture is enriched in long chain FAEEs, among which EPA and DHA.

The SFF of FAEEs has been experimentally tested in continuous apparatuses – packed towers – in only a few works in the literature. Fleck et al. (1998) utilized a column with inner diameter of 35 mm and a packing height (Sulzer, CY wire mesh packing) of 13.6 m. Riha and Brunner (2000) utilized a larger column (inner diameter of 68 mm and an effective height of 12 m packed with Sulzer CY) and reported a remarkable number of experimental data (analytical data, process data) related to different SFF process operating conditions. Both plants can be defined as pilot-scale plants: the feed (FAEE mixture) to the column was 0.35 kg/h (Fleck et al., 1998) and up to 4.2 kg/h (Riha and Brunner, 2000). The solvent to feed ratios were between 70–180 (Fleck et al., 1998) and 63–127 (Riha and Brunner, 2000). Correspondingly, Riha and Brunner utilized a $SCCO_2$ flow rate of about 300 kg/h. Despite the very interesting results obtained in these works, since then no other experimental work has been published dealing with similar apparatuses and FAEE fractionation process. This was most probably due to the cost of this kind of pilot plants: the one set and utilized by Riha and Brunner (2000) would cost several hundreds of thousands of euro today (see Section 3.4).

Thus, the research activity in the field focused on experimental tests with simpler apparatuses (Perretti et al., 2007)