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Industrial design of multifunctional supercritical extraction plant for agro-food raw materials

Lourdes Casas, Casimiro Mantell, Miguel Rodríguez, Eva López,
Enrique Martínez de la Ossa
Department of Chemical Engineering, Food Technology and Environmental Technologies, Faculty of Science, University of Cadiz, Box 40, 11510 Puerto Real, Cadiz, Spain. lourdes.casas@uca.es

Supercritical fluid extraction (SFE) using carbon dioxide can replace traditional organic solvent extraction processes due to several inherent advantages: contamination of the product does not occur; mass transport is highly facilitated owing to favourable transport properties (high mass and thermal diffusivities coupled with low viscosities); and the solvent parameters are tuneable by the operating conditions employed. One of the most promising applications of supercritical fluids is the extraction of high value natural compounds from residues in the food, pharmaceutical and cosmetics industries. The work described here concerns the industrial design of a multifunctional supercritical extraction plant for the recuperation of colorants and antioxidants (anthocyanins, resveratrol, catechin and epicatechin) from grape skin, tocopherol from olive leaves, bioactive compounds with herbicidal properties from sunflower leaves, and carotenoids from microalgae. The proposed plant consists of three extraction vessels that can operate up to 300 bar and 80 ºC. The extractors are connected in series in order to allow the recovery of the solvent after the extraction process and to minimize the pressure loss. The high pressure extractions enable several fractions with diverse properties to be obtained. All parts of the plant that are in contact with CO_2 are stainless steel (SS-316). The dimensions of the extraction plant are sufficient to enable the processing of approximately 200 to 1500 kg/day of raw material. The selected extraction solvent is carbon dioxide under high pressure, with the possibility of adding cosolvents (water or ethanol).

1. Introduction

The application of SFE is now a viable approach, as evidenced by the large number of papers published annually in this field (Bruner, 2005). Nevertheless, it is necessary to study the scale up of this process and to analyze its industrial viability. In this respect, the work described here concerns the design of an industrial plant for the supercritical fluid extraction of solids. An analysis of the economic viability of the process is presented based on its application in the extraction of a range of interesting substances in the agro-food sector. The application of supercritical technology to these raw materials has been reported in numerous papers in the literature (Lucas et al., 2002;

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Mantell et al., 2002; Casas et al., 2005; Macías-Sánchez et al., 2005). The multifunctional capacity of the proposed plant allows the extraction process to be carried out in a seasonal way, thus minimizing the need to stop production.

The first of the raw materials selected was red grape pomace, which is a by-product obtained during the vinification process. This raw material gives a concentrate that is rich in anthocyanins. The concentrate is also well known as a food dye and presents anticancer and antioxidant properties. Red grape pomace is also a source of resveratrol, which is a compound of great interest in the pharmaceutical sector. This by-product of the vinification process is available for extraction in the period September–December (after the vintage).

The second raw material investigated comes from agricultural waste of the sunflower and olive cultivars. From sunflower leaves it is possible to obtain a concentrate of bioactive substances with herbicidal properties, whereas olive tree leaves can provide a tocopherol (vitamin A) concentrate that is recognised as a food additive for its antioxidant properties. Sunflower leaves would be available in the period May–August after the harvest and olive tree leaves are available in the period January–March, i.e. coinciding with the ending of the pruning period.

Finally, as a non-seasonal raw material we studied microalgae that were specially cultivated and prepared for this purpose. The microalga are traditionally considered as authentic cellular factories and constitute an exceptional source of pigments, chlorophylls, carotenoids and ficobilines. These compounds are of great commercial interest in the food, pharmaceutical and cosmetics industries. They are also rich in polyunsaturated fatty acids (PUFA), vitamins and minerals that are indispensable for health.

In the following sections a description of the proposed industrial plant is presented along with a breakdown of the cost of production of the extract. In an effort to obtain the seasonal production of the plant, a simulation program capable of predicting the mass extraction yields of the SFE process was used.

2. Description of the industrial plant

A simplified diagram of the proposed supercritical extraction process proposed is presented in figure 1. The feed is loaded into a system of baskets and these are introduced into one of the extractors (E-1, E-2, E-3). The use of three extractors allows charge/discharge operations to be carried out in two of them while the extraction process is carried out in the third. The solvent flows through the extractor (passing through the raw material) for the appropriate time and exits the extractors – with the solute dissolved (extract) – through a filter to remove any remaining solids. After this step the flow of solvent in this extractor is stopped and the CO_2 remaining in this vessel is directed to the second extractor. When the pressure in the system is too low, the remaining carbon dioxide is redirected to the solvent recovery tank by the compressor C-2. The whole process is developed in a cyclic way for the three extractors.

The solvent that is rich in extract is directed to the separator S-1, where the pressure is decreased by a back pressure regulator BPR valve and the temperature is adjusted in the heat exchanger CC-2. The plant has a second separator (S-2) and second heat exchanger (CC-3) to allow fractionation of the resulting extract. All of the material decanted into

the separators is conducted to a tank or is packed directly, depending on the particular case.

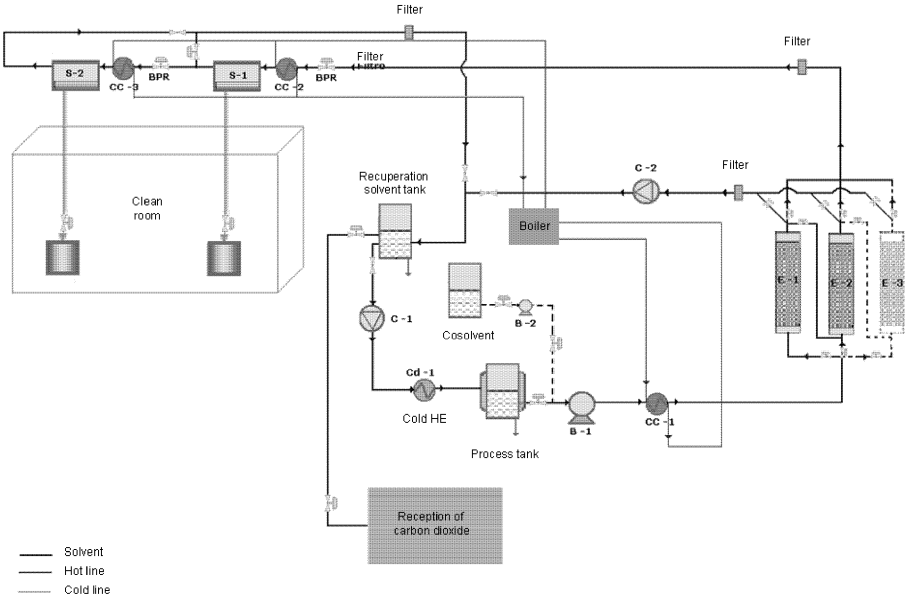

Figure 1. Schematic diagram of the proposed industrial plant

The gasified CO_2 from the separator flows through another filter and then on to the solvent recovery tank. This tank receives the residual CO_2 from the extractors, previously filtered, and the necessary supplement of CO_2 from the receptor tank. This amount of solvent is needed due to the loss of CO_2 that occurs during the extraction process. Compressor C-1 is used to pressurize the CO_2 up to 60 bar and this is cooled to 5 ºC to feed to the process tank, where it is stored under these conditions.

Finally, the CO_2 is transported from the process tank to the extractors, where it is combined with the cosolvent (if required), under the selected operation conditions, using pumps B-1 and B-2, respectively. The operating temperature is reached in the heat exchanger CC-1.

In order to provide a level of versatility to the plant, it is designed to work with a flow of 1500 Kg CO_2/h at a pressure of 300 bar and temperature of 80 ºC. In addition, the system is designed to allow about 6–7 bar and ambient temperature in the separators. The whole plant will be made of stainless steel (SS-316 L).

2.1 Auxiliary units

The plant will contain three auxiliary units that are of vital importance for correct operation: a cooler, a boiler and an installation for the reception of fresh CO_2.

The saturated vapour generated in the boiler is used in two different areas inside the plant: on the one hand, the vapour facilitates the process by which the solvent reaches the operating temperature in the heat exchanger CC-1 and, on the other hand, it provides

the operating temperature in the separators through heat exchangers CC-2 and CC-3. The condensed vapour at the exits of these processes is returned to the boiler for the generation of new vapour.

The cooler R-134A is to be used to condense the solvent in the condenser CD-1. This solvent is introduced directly into the process tank.

Finally, in order to compensate for the loss of CO_2 during the supercritical extraction process, it is necessary to have an installation with a cryogenic tank for storage of CO_2 at –64 ºC and 20 bar. This installation will be the property of the company that supplies this solvent.

2.2 Economic study

A description of the investment cost for the construction of the proposed plant is presented in table 1. Regarding the cost of the raw materials, it is necessary to consider that most of these are agrarian by-products without any value at present. The evaluation of the cost of this raw material includes an estimation of the collection, transport and pre-treatment for the extraction process. Only in the case of the microalgae is it necessary to include the cost of production.

The Manufacturing cost (COM) was calculated using the expression proposed by Rosa and Meireles (2005):

$$COM = 0.304\ FCI + 2.73\ COL + 1.23\ (CUT + CWT + CRM)$$

where FCI is the fraction of investment calculated as the product of the total investment and the depreciation rate, COL is the operational labour cost, CUT is the utility cost, CWT is the waste treatment cost, and CRM is the raw material cost. According to this expression, and with the data presented in tables 1 and 2, the manufacturing cost of the proposed plant is approximately one million euros per year.

3. Scale up and simulation

In the study of the extraction processes, and also of the chemical processes, one of the aspects that requires most attention is the extension and application of the results obtained on a laboratory scale to pilot plant and industrial scales. This process is in most cases very complex and it is known as scale up.

The methodology applied to the scale up requires the application of the theory of similarity and involves the use of systems of magnitudes and units.

In the work described here, we considered that the extractor is under isothermal conditions and chemical reaction does not take place. Consequently, the only similarity relationships that are considered are those corresponding to geometry and dynamics. For this reason, it is only necessary to keep constant in both scales, laboratory and industrial, the geometric factors and the dimensionless numbers related to the dynamic similarity.

The next factor that must be analyzed is the extraction time. In this case it is necessary to use simulation techniques developed in an existing model selected from the bibliography. The selected model is based on an analysis of the diffusivity within a particle (Mantell et al., 2003). The equation for this model depends on different parameters: internal diffusion coefficient, extraction time, and the solute concentration in the fluid and in the solid. These parameters are estimated by considering different factors:

Table 1. Estimation of the fixed cost

Symbol	Description	Estimated cost (Euros)
E-1, E-2, E-3	Extractors	1,200,000
-	Baskets	28,000
S-1, S-2	Separators	93,000
-	Tanks	379,000
CC-1, CC-2, CC-3, Cd-1	Heat exchangers	107,000
B-1, B-2, C-1, C-2	Pumps and compressors	380,000
-	Auxiliaries	52,000
Direct cost		2,239,000
Indirect cost		895,600
Fixed cost		3,134,600

Table 2. Estimation of operational cost

Concept	Description	Comments	€/year	€/h
Raw material	Grape pomace	By-product of vinification	9000	1
	Sunflower leaves	Agricultural by-product	6000	0.7
	Olive leaves	Agricultural by-product	6000	0.7
	Microalgae	Industrial production	45000	5
	SUBTOTAL		66000	7.4
Labour	Labour cost	30000€/man year		
		6 man/day	180000	20
	Supervision	(25% of MO)	45000	5
	SUBTOTAL		225000	25
Utility	Electricity	60 kwh; 0.1€/kwh	52560	6
	Cold water	3 m^3/h; 1€/m^3	26280	3
	Steam (LP)	150 kg/h; 0.05€/kg	65700	7.5
	CO_2	30 kg/h; 0.6 €/kg	157680	18
	SUBTOTAL		302220	34.5
Investment fraction	Depreciation rate	10%		
	Depreciation	10 years	30000	4
	Tax - insurance	1.5% of investment	45000	5
	Maintenance	4% of investment	120000	14
	SUBTOTAL		195000	23

Table 3. Raw material parameters

RAW MATERIAL	Solute composition	Apparent density
Grape pomace	150 mg of anthocyanins/100 g pomace	0.31 g/mL
Sunflower leaves	2 g of extract/100 g raw material	0.17 g/mL
Olive leaves	10 mg Tocopherol/100 g raw material	0.20 g/mL
Microalgae	1 mg carotenoids/100 mg of microalgae	0.15 g/mL

- ✓ The solute concentration in the fluid and in the solid only depends on the extraction time and the position in the extractor.
- ✓ The initial solute concentration in the solid and the maximum value of solute concentration in the fluid are known.
- ✓ The solvent flow rate does not vary along the bed of particles and there is no radial distribution and turbulence.
- ✓ The bed of particles is divided into differential elements of longitude and the extraction process in differential elements of time. It is possible to determine, for each differential element, the molar flow rate of solute and, from this data, to estimate the value of the concentration in the fluid and in the solid.

The final extraction yield of the process is determined on the basis of solute concentration in the solvent at the exit of the vessel. To obtain the curves for the global extraction yield, a simulation program has been developed in *MathLab*. This program can be used to obtain an average optimal extraction time of 8 hours for different raw materials.

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