PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE
ESCUELA DE INGENIERIA

DEVELOPMENT OF A SIMULATION TOOL FOR THE ECONOMIC OPTIMIZATION OF AN EXTRACTION PLANT FOR VEGETABLE SUBSTRATES USING SUPERCRITICAL CO_2

GONZALO ALEXIS NÚÑEZ MONTOYA

Thesis submitted to the Office of Research and Graduate Studies in partial fulfillment of the requirements for the Degree of Doctor in Engineering Sciences

Advisor:
JOSÉ MANUEL DEL VALLE LLADSER

Santiago de Chile, (April, 2013)

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Dedicated to Daniela and Javiera, for all their love and support along all these years, and to my soon to be born daughter

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DESARROLLO DE UNA HERRAMEINTA DE SIMULACIÓN PARA LA OPTIMIZACIÓN ECONÓMICA DE UNA PLANTA DE EXTRACCIÓN PARA SUSTRATOS VEGETALES USANDO CO_2 SUPERCRÍTICO

Tesis enviada a la Dirección de Investigación y Postgrado en cumplimiento parcial de los requisitos para el grado de Doctor en Ciencias de la Ingeniería.

GONZALO ALEXIS NÚÑEZ MONTOYA

RESUMEN

La extracción con fluidos supercríticos de sustratos sólidos se ha aplicado comercialmente por mucho tiempo para aplicaciones como extracción de lúpulo, descafeinización de granos de café, extracción de sabores de hierbas y especias, extracción de oleaginosas, etc. A pesar de esto, en la literatura hay poca información sobre escalamiento y costeo de esta tecnología, lo cual generalmente es parte del *know-how* de fabricantes de plantas. El objetivo de esta tesis fue desarrollar una herramienta de simulación para estimar los costos en una planta de extracción con CO_2 supercrítico y evaluar el efecto de parámetros relevantes en el proceso a nivel industrial. Esta tesis presenta estimaciones para costo de operación y de producción de la extracción de oleaginosas preprensadas con CO_2 supercrítico, usando un nuevo algoritmo de simulación basado en un modelo predictivo. El costo de operación (rango estimado, 4,081-8,149 USD/kg de aceite) disminuye cuando el tamaño de partícula disminuye y la velocidad superficial del CO_2 aumenta. Los costos de producción (rango estimado, 5,881 a 12,74 USD/kg de aceite) tiene al costo de capital como el ítem de mayor incertidumbre en las estimaciones. Bajo las mismas condiciones de extracción, si relación de aspecto (L/D) de los extractores disminuye, el costo de

producción disminuye. En plantas de dos extractores, el costo de producción mínimo fue a 70 MPa. Sin embargo, en plantas de múltiples extractores, el costo de producción mínimo fue a 50 MPa. En todos los casos estudiados, el número de extractores y el volumen total de la planta tienen un efecto positivo sobre el costo de producción, lo que confirma se aplican economías de escala a este proceso. El tiempo óptimo de extracción, el grado de agotamiento del sustrato, y la productividad de la planta son factores a considerar al momento de tomar decisiones de inversión en esta tecnología.

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Santiago, Abril, 2013

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Thesis submitted to the Office of Research and Graduate Studies in partial fulfillment of the requirements for the Degree of Doctor in Engineering Sciences by

GONZALO A. NÚÑEZ

ABSTRACT

Supercritical fluid extraction of solid substrates has been applied comercially for a long time to several applications (including extraction of hops, decaffeination of coffe beans, extraction of flavors from herbs and spices, extraction of oilseed, among others). Despite of this, in literature there is little information about scaling-up and costing of this technology, which generally is part of the know-how of plant manufacturers. The objective of this thesis was to develop a simulation tool to estimate the costs in an industrial supercritical CO_2 extraction plant and to evaluate the effect of relevants parameters in the extraction process. Particularly, this thesis presents estimates for operational and production costs of the supercritical CO_2 extraction of prepressed oilseeds using a novel simulation algorithm based on the fully predictive shrinking core model for the inner mass transfer. Operational costs (estimated range of 4.081-8.149 USD/kg of oil) decrease when particle size decreases and superficial CO_2 velocity increases. Production costs (estimated range of 5.881-12.74 USD/kg of oil) include the capital cost, which is one of the items with major uncertainties in the estimates. Under the same extraction conditions, a decreasing of the aspect ratio (L/D) of the extraction vessels has a positive effect on

production cost. In two-vessel plant, the lowest production cost was reached at highest extraction pressure (70 MPa). However, in multi-vessel plants, the minimum production cost was at 50 MPa. In all cases studied, the number of extraction vessels and the total volume of the plant had a positive effect on production cost, confirming that economies of scale apply to this process. Finally, other factors (as optimal extraction time, exhaustion grade of the substrate, and productivity of the plant) should be take in count to make decisions about investment or to optimize the operation of an industrial plant.

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LIST OF PAPERS

This thesis is based on scientific papers published in ISI journals. The papers are the following:

- Núñez, G.A., Gelmi, C.A., and del Valle, J.M. (2011). Simulation of a supercritical carbon dioxide extraction plant with three extraction vessels. *Computers & Chemical Engineering*, 35(12), 2687-2695.
- del Valle, J.M., Núñez, G.A., and Aravena, R.I. (2012). Supercritical CO_2 oilseed extraction in multi-vessel plants. 1. Minimization of operational cost. *Journal of Supercritical Fluids* (submitted).
- Núñez, G.A. and del Valle, J.M. (2012). Supercritical CO_2 oilseed extraction in multi-vessel plants. 2. Effect of number and geometry of extractors on production cost. *Journal of Supercritical Fluids* (submitted).
- Núñez, G.A. and del Valle, J.M. (2012). Supercritical CO_2 oilseed extraction in multi-vessel plants. 3. Effect of extraction pressure and plant size on production cost. *Journal of Supercritical Fluids* (in progress).

1. INTRODUCTION

The SuperCritical Fluid Extraction (SCFE) of solid substrates has been carried out on a commercial scale for more than two decades (Brunner, 2005). Large-scale implementation of the SCFE include coffee beans decaffeination (extraction vessels ≥ 20 m^3) and the extraction of hops (extraction vessels ≈ 5 m^3) (Brunner, 2005; del Valle and Aguilera, 1999) made mostly in Europe and the United States. Also, there are processes on a smaller scale such as extraction of essential oils, lipids, oleoresins, among others, which were reviewed and discussed by del Valle and Aguilera (1999) for its potential application in industries of food, pharmaceutical, and perfume in Latin America.

Despite of the above, many companies still think that SCFE processes are too expensive because their high investment costs compared to the processes at low pressure, restricted only to high added-value products (Perrut, 2000). This is far from reality when large volumes of material are treated, such as cases of both coffee beans and hop cones processing, manufacture of paints, soil remediation, and waste treatment (Perrut, 2000; Rosa and Meireles, 2005). Also, in these processes there are economies of scale, where capital and operation cost per ton of product decreases with increasing the plant capacity (King *et al.*, 1993). In addition, cost of equipments for industrial implementation of the SCFE has decreased in the last years, making this technology more attractive and competitive (Brunner, 2005; Rosa and Meireles, 2005). Even more, in the food industry the processing by SCFE could be the only way to meet the product specifications, which may have competitive advantages over other technologies (Brunner, 2005). In fact, a number of extraction units have been built in Asia for the extraction of phytochemicals and natural product's nutraceuticals in the last decade (Rosa and Meireles, 2005) and in South America there are several investigations in the field of SCFE, although there are no industrial applications yet (del Valle *et al.*, 2005).

Therefore, it is curious that there is little information in literature about scaling and SCFE process optimization (del Valle *et al.*, 2005). Most studies suggest mathematical expressions to estimate preliminary both capital (investment) and

operating (production) costs based on information previously known for similar processes, or so-called estimates of Level 1 (errors ≤ 50%; Harrison *et al.*, 2003) and almost non-existent cost estimates of Level 2 (where the estimation is based on the size of the principal process equipment; errors ≤ 30%) or higher.

Indeed, I would like to bring to state of the art a reliable and systematic procedure for the design and economic optimization of SCFE processes. To achieve this purpose is essential to develop a simulation tool that can monitor the progress of the residual solute contents in a packed bed of solid substrate, as it passes through a SuperCritical CO_2 (SC CO_2) flow with dissolved solute, and that it be representative of an extraction vessel in an industrial process. This will allow to estimate the productivity of the extraction vessel depending on various equipment and process parameters. With this information I will be able to dimension all components of the plant and to estimate the investment and operating costs. The last step will be the economic optimization of the process.

The results will help to evaluate the competitiveness of a SCFE process compared to traditional extraction processes for obtaining both commodities and high added-value products.

1.1 Supercritical fluid extraction of solid substrates with CO_2

The SuperCritical Fluids (SCF) are substances that are above their critical pressure and temperature, and whose main characteristic is that its density (related to power solvent, *i.e.*, capacity of a substance to dissolve another) can change into a wide range (Brunner , 2005). Its transport properties are comparatively better than those of conventional organic solvents, that is, exhibit a high diffusivity and low viscosity (del Valle and Aguilera, 1999). Finally, the SCF, which are gases under normal conditions, can be easily removed from the extracts and solid matrices by mere expansion to pressure environment (Brunner, 2005), so that products treated with SCF are virtually free of waste solvent (del Valle and Aguilera, 1999).

Among the SCFs, the carbon dioxide (CO_2) is the most advantageous and used for food processing (Brunner, 2005) and other extraction processes. CO_2 is not corrosive in the presence of water, is not flammable, non-toxic, and can be obtained from renewable resources in large quantities, with high purity, and low cost. In addition, it is recoverable at low cost and does not cause harm to the solutes (del Valle and Aguilera, 1999). Another advantage of using CO_2 (P_c = 7.38 MPa, T_c = 31 ° C) is that it works at temperatures close to the environment, which prevents damage to heat-labile compounds.

A typical solid extraction system with SC CO_2 at laboratory or pilot plant scale (20-100 dm^3) or larger, is composed of one or more extraction vessels, a series of flash tanks (for splitting the extract), a compressor or pump (solvent recirculation stage), a source of CO_2, and auxiliary equipment such as heat exchangers (Brunner, 2005). The main advantage of a SCF Extaction (SCFE) process at pilot plant is its CO_2 recovery capabalities, where the solvent is recycled to the system (Brunner, 2005). The SCFE process operation in a pilot plant consists of the following steps: (i) pretreated substrate is loaded into the extraction vessel. The substrate can be milled (average particle size $0.25 \leq d_p \leq 2.0$ mm, Reverchon and De Marco, 2006), prepressed (oilseeds), laminated, or pelletized, depending on the application; (ii) the extraction vessel is pressurized with CO_2; (iii) once the desired extraction is reached pressure, the CO_2 circulates through the entire bed to a predetermined rate flow; (iv) the rich-solute CO_2 flows through an expansion valve, the solute precipitates and it is recovered in a separator; finally, (v) the CO_2 is condensed , stored in a buffer tank, and recirculated to the cycle.

At industrial scale, it is desirable to have an extraction process with multiple extraction vessels, which would emulate a countercurrent contact during the extraction, where CO_2 is contacted with the substrate more exhausted first, and then with the more fresh substrate, in order to obtain a virtually continuous extract productio. The extract can be split according to the compound solubilities in CO_2, for different separation pressures. Therefore, such plants are formed by at least two extraction vessels, where one or more are in service, and the last one is at a reconditioning stage (depressurization,

unloading of the exhausted substrate, loading of the fresh substrate, and re-pressurization). This operation mode is convenient when the outlet solute concentration in the SCF of any of the extraction vessels does not reached the saturation, resulting in savings of solvent and energy.

A good alternative to study the large-scale or industrial process is by simulation process. This allows to determine the effect of relevant paremeters on the extraction such as particle size (d_p), superficial velocity (U) or mass flow rate (Q) of CO_2, long-to-diameter ratio (L/D) of extraction vessels, extraction pressure (P, between 30 to 70 MPa for oilseed extraction), among others, so it gives me the opportunity to systematically evaluate the costs the process.

1.2 Scaling-up of the supercritical CO_2 extraction process

To carry out a study to predict the behavior of a industrial-level SCFE process one should understand the mechanisms involved influencing the extraction rate. This rate can be controlled by solubility or diffusion. When the extraction rate is controlled by solubility (*e.g.*, in the early stages in the oil extraction) the rate of solvent-to-substrate ratio generally remains constant. When the extraction rate is controlled by diffusion (*e.g.*, in the final stages of essential oils extraction from herbs and spices), the contact time between the solvent and the substrate increases, and the flow solvent-to-charged substrate ratio remains constant. However, the reliability of any scale procedure depends critically on the kinetic extraction data quality obtained in the laboratory or pilot plant, which depend on the experimental setup (del Valle *et al.*, 2005). Lack *et al*. (2001) have listed the following parameters to design a SCFE process: raw material (pretreatment) and final product specifications; size and location of the plant; thermodynamic conditions for extraction and separation; mass transfer mechanisms, determined by diffusion (which depends on both particle size and distribution of compounds that are extracted in solid matrix) and process fluid-dynamics (influenced by both size and shape of particles, and the particle size distribution); consumption and energy optimization

considerations (pumps and/or compressors); specific problems in the separation step; and selection and design of the components of the plant.

Once the plant capacity is set, and extraction curves obtained in laboratory scale and/or pilot plant are analyzed, both optimal time for processing and solvent flow are determined, which allows setting the extraction vessel volume. An exhaustive extraction of the substrate is not always profitable. In general, the process is considered complete when it has recovered 90% of the extract, given the asymptotic form of the extraction curves. Longer processing times could increase operation costs of the plant but with negligible increases on production (del Valle *et al.*, 2005).

There are few studies on of scaling-up of SCFE processes in the literature. An key one was the work of Eggers and Sievers (1989) who studied a change of scale (1:10 in volume) for the extraction of Oenothera Bennis L. seeds (40 °C, 40 MPa bar). They used two criteria for scale-up, considering an external control on the mass transfer rate: solvent flow rate-to-loaded substrate ratio constant and residence time constant. del Valle *et al.* (2004) suggested caution applying simple procedures for scaling-up such as those syudied by Eggers and Sievers (1989) due to the complex relationship between the extraction rate and processing conditions, which does not depend only on a external mass transfer coefficient. Particularly, del Valle *et al.* (2004) showed that there are differences in the mass transfer phenomenon when is changed from a laboratory-scale to pilot plant. These differences could be explained by heterogenities of the flow, axial dispersion, or entrainment of solute droplets in the recycled CO_2 (del Valle *et al.*, 2004). Clavier *et al.* (1996) presented a procedure to extrapolate (scale-up) a SCFE process from pilot plant to industrial scale, whose objective was to determine operational conditions, an optimal configuration of the plant and its dimension, the number of extraction vessels, the capacity of the pump, among other. Those authors proposed that depending on the complexity or nature of the extraction process, what scaling-up criteria should be applied. For simple extractions, keeping U/M_o (being M_o the initial mass of substrate loaded within the extraction vessel) and M_{CO2}/M_o (being M_{CO2} the mass of CO2 used in the extraction process) ratios constant is adequated. However, for complex

extractions where both diffusion and solubility are important, or the extract is a complex mixture, the use of numerical software would help optimizing SCFE plant configuration and process itself. As example, Clavier e*t al.* (1996) have applied their procedure to the oilseed extraction with SC CO_2. Mezzomo *et al.* (2009) scaled-up the SCFE of peach almond oil with SC CO_2 at 40 ºC , and 15 and 25 MPa, using four criteria: keeping constant solvent mass-to-substrate mass; CO_2 flow rate-to-substrate mass; keeping constant both solvent mass-to-substrate mass and CO_2 flow rate-to-substrate mass; and keeping constant solvent mass-to-substrate mass and Reynolds number; being the second and the third cases the better ones. They concluded that SCFE of peach almond was controlled by diffusion, and that the extraction curves coincided for small and large scales. Prado *et al.* (2011) have applied successfully the scaling-up (extraction vessel ratio equal to 1:15) of the extraction of both clove and sugarcane residue keeping M_{CO2}/M_o constant. The shape of the extraction curves and yield in both raw materials were slightly higher in pilot plant than in laboratory scale, according with manufacturer information but opposite to literature information. Also, they applied a combined criterion to scale-up keeping both M_{CO2}/M_o and Q_{CO2}/M_o constant, but changing Q_{CO2}/M_o they obtained the same results, concluding that their simple criterion was good enough. Prado *et al.* (2012) also applied M_{CO2}/M_o constant as criterion to scale-up (1:15) the extraction of grape seeds with SC CO_2 at 40 ºC and 35 MPa with good results, where extraction curves at different scales practically overlapped. Chapter 4 includes more detail about scaling-up of SCFE processes of the works mentioned in this section.

1.3 Costs in a supercritical CO_2 extraction process

Costs in a SCFE process include capital (investment) and operational cost. Capital costs of a SCFE plant are related to the purchase of equipment for feed pre-treatment, SCFE plant itself, utilities (cooling and heating systems, electric power, etc.) and other minor units. Generally, the SCFE plant represents 70-85% of total investment (del Valle *et al.*, 2005). On the other hand, operation costs are dominated mainly by the overall consumption of energy in the process, given by the pressurization of extraction

vessels, and heating and cooling of the CO_2 current solvent. Also they include raw materials cost, labor, electricity, water (for processes and consumption), steam (if necessary), replacement of solvent (CO_2), etc. (King *et al.*, 1993; Lack and Seidlitz, 2001). An important aspect is the recovery of CO_2 in the process, especially as the capacity of the plant is higher. The solvent recycling and their subsequent employment, in a proper recycling system, should allow reduce CO_2 losses to less than 2% of all that is used in extraction (del Valle *et al.*, 2005).

There are some works in literature that studied the cost involved in a supercritical CO_2 process at industrial scale. Passey (1994) studied the feasibility of a commercial SCFE plant to manufacture low-fat peanut, concluding that a plant capacity of 16000 L, which produces 1200 ton/year (2% of the market), with a capital cost of USD 6.1 million, had a net present value (NPV, 20 years) of USD 3-7 million (depending on the location of the plant) and a return-on-equity (ROE) of 42-59%. Novak and Robey (1989) studied the design and the economics in a SCFE process of flavor extracts from spices and herbs at 80 ºC and 30 MPa (as maximum extraction conditions), considering a base case and a high capacity case. In the base case, they proposed a multiproduct 2×973L SCFE plant, processing 770 ton/year of an spice, for a capital cost of USD 2.8 million, resulting in a production cost of 1.1 USD/kg of substrate. In the high capacity case the feed rate increased to 3060 ton/year of spice, resulting in an decreasing of the production cost to 0.5 USD/kg of substrate. Körner (1993) presented capital and operational cost for a SCFE plant for spices extraction with CO_2 at 80 ºC and 40 MPa for three different capacities (450, 900, and 1800 ton/year of spice). The combination for capital and operational costs were the following: USD 3.1 millon and 4.868 USD/kg of spice; USD 3.9 million and 4.153 USD/kg of spice; and, USD 4.5 million and 3.679 USD/kg of spice, respectively (original values in Deutsche Marks, Oanda.com, 2011). Clavier *et al.* (1996) estimated costs for the oilseed extraction with SC CO_2 at 40 ºC and 25 MPa. The capital cost for a 2×209L SCFE plant and mass flow rate of 2160 kg/h was estimated in USD 1.6 million, with a production cost equal to 5.089 USD/kg of seeds for 7 ton of extract per year or 4.479 USD/kg of seeds for 10.7 ton of extract per year (original

values in French Francs, Oanda.com, 2011). For its part, Bravi *et al.* (2002) studied the optimization of a SCFE plant for extracting sunflower oil with SC CO_2 to 28 MPa and 40 °C. They reported a production cost of 0.633 USD/kg of oil (value updated; Oanda.com, 2011) and concluded that the optimal number of extraction vessels were four, to treat 4380 kg/h of seeds, with a total CO_2 flow of 60000 kg/h, extraction time of 10 minutes, and separation pressure of 16.7 MPa. Prado *et al.* (2010) reported a cost of 17.2 USD/kg of oil for the extraction of palm tree using SC CO_2 at 40-55 ºC and 20-30 MPa. Fiori (2010) reported 7.82 USD/kg of oil (value updated, Oanda.com, 2011) for the extraction of grape seed with SC CO_2 at 60 ºC and 55 MPa compared with for the grape seed extraction with SC CO_2 (Prado *et al.*, 2012). Mezzomo *et al.* (2011) reported a production cost of 4.64 USD/kg of oil for peach kernel extraction with SC CO_2 at 40 ºC and 20 MPa. Prado *et al.* (2012) estimated the production cost for the SCFE of grape seeds at 40 ºC and 35 MPa, determining a value 11.9 USD/kg (updated value, Oanda.com, 2011). Comparing the works of Fiori (2010) and Prado *et al.* (2012), it might be concluded that pressure has a positive effect on the production cost. Chapter 4 includes more detail about economics in SCFE processes.

1.4 Hypothesis

The simulation of an extraction plant of vegetable substrates using supercritical CO_2 as a solvent allows:

"Optimize both operational (number of extraction vessels, extraction and separation pressure, among others) and economic (capital and operation costs) parameters of the process", and

"The above will allow to evaluate systematically the costs involved in a supercritical CO_2 extraction process of oilseeds".

Indeed, it could evalquate the economic competitiveness of an extraction process with supercritical CO_2 as the solvent comparing with traditional extraction processes for

obtaining commodities (*e.g.* edible oils) and/or high added-value products (*e.g.* carotenoids).

1.5 Objectives

The main objective of this thesis is to develop a simulation tool to study the costs involved in an industrial extraction plant of vegetable substrates using supercritical CO_2 (SC CO_2) as the solvent in function of extraction time and relevants parameters for the process.

The specific objectives of this thesis are the following:

1. To simulate a supercritical CO_2 extraction process of oilseeds at industrial scale.
2. To study the effect on the extraction process of the following relevant parameters: particle size (d_p); superficial velocity (U) or mass flow rate (Q) of the CO_2; number of extraction vessels (n); length-to-diameter ratio (L/D) of the extraction vessels; and extraction pressure (P_{ext}). Indeed, to determine the optimal ones using the simulation tool of (1).
3. To determine both operational and capital costs of a SCFE process to evaluate the effect of the parameters listed in (2), and compare those costs with estimates proposed in the literature.

2. SIMULATION OF A SUPERCRITICAL CARBON DIOXIDE EXTRACTION PLANT WITH THREE EXTRACTION VESSELS

Abstract

Although SuperCritical Fluid Extraction (SCFE) has been successfully applied commercially the last three decades, there is no systematic procedure or computational tool in literature to scale-up and optimize it. This work proposes an algorithm to simulate dynamics in a multi-vessel (≥ three) high-pressure SCFE plant where extraction vessels operate in batches, and is thus forced to use simulated-countercurrent flow configuration to improve efficiency. The algorithm is applied to a three-vessel SCFE plant using a shrinking-core model to describe inner mass transfer in the substrate. As example, the extraction of oil from prepressed seeds using supercritical CO_2 at 40 ºC and 30 MPa is simulated. After three cycles the process reaches a pseudo-steady-state condition that simplifies the estimation of plant productivity. Use of a three- instead of two-vessel SCFE plant increases oil concentration in the stream exiting the plant and decreases CO_2 usage at the expense of increasing extraction time.

Keywords: coupled partial differential equations; industrial scale; mathematical modeling; packed bed; simulation; supercritical fluid extraction.

2.1 Introduction

There are many successful examples of commercial application of SuperCritical Fluid Extraction (SCFE) over the last three decades, including the decaffeination of green or roasted coffee beans, the production of hop extracts, the extraction of herb and spice flavors, and the extraction of oilseed lipids (Brunner, 2005). These applications use CO_2 as the solvent, mainly because CO_2 is non-flammable, non-corrosive in the presence of water, and non-toxic; can be obtained from renewable resources in large quantities, with high purity, and at low cost; and is easily recoverable without harming the substrate nor the extract (Brunner, 2005). Recommended SCFE conditions include a

near-critical temperature (T_c = 304 K for CO_2) and a pressure 5-to-10 times above the critical (P_c = 7.4 MPa for CO_2) (Brunner, 2005) so that SC CO_2 extraction has the additional advantage of being carried out at a near-environmental temperature, thus preventing thermal damage to labile compounds. However, SC CO_2 extraction has the disadvantage of being a high-pressure process, thus limiting operation with solid substrates (the case of all commercial examples above) to a batchwise mode (Brunner, 2005).

Industrial SCFE plants have two or more extraction vessels (i) to avoid dead times in the process, and (ii) to reduce solvent usage and energy requirements for solvent recycling. Indeed, in these SCFE plants while two or more extraction vessels are simultaneously in service, the remaining one is being reconditioned (a stage considering four steps: de-pressurization, unloading of exhausted substrate, loading of fresh substrate, and re-pressurization). This type of operation enables a virtually continuous extraction, even though SCFE of solid substrates is an inherently batch process, and is most desirable when solute concentration in the SC CO_2 stream exiting the first extraction vessel does not get saturated with solute and advantage in taken of (an) additional extraction vessel(s) to save solvent and energy in multi-vessel plants having three or more. When an industrial SCFE plant has two vessels, cumulative extraction curves (solute yield versus extraction time) virtually coincide with those in pilot plant units having solvent recycling capabilities and a single extraction vessel, because extraction vessels work one at a time with recycled SC CO_2. This is not the case in a multi-vessel (three, Fig. 1, or more vessels) SCFE plant, where the contact between the solid substrate and SC CO_2 during extraction emulates countercurrent contact. In a multi-vessel SCFE plant, SC CO_2 is contacted first with the more exhausted substrate and then successively with progressively fresher substrate.

Proposed mass transfer models for SCFE typically simulate SCFE plants with only one or two extraction vessels, and to the best of our knowledge, there are no computational tools to simulate extraction dynamics in SCFE plants having three or more extraction vessels where two or more operate simultaneously. Many of these mass

transfer models apply shrinking-core (Goto *et al.*, 1996), or broken-and-intact-cells (Sovova, 2005) hypothesis to a single extraction vessel. Applications of the shrinking-core model include the SCFE extraction of oleoresins from ginger (Roy *et al.*, 1996) and nutmeg (Machmudah *et al.*, 2006), and of lipids from grape seeds (Germain *et al.*, 2005) and sunflower seeds (Salgin *et al.*, 2006). On the other hand, applications of the broken-and-intact-cells model include the SCFE extraction of lipids from fennel and other seeds (Reverchon *et al.*, 1999; Reverchon and Marrone, 2001) and apricot kernels (Özkal *et al.*, 2005), and of oleoresins from nutmeg (Machmudah *et al.*, 2006).

Despite the numerous commercial applications of SCFE, there is limited literature on SCFE process scale-up and design. Reports include simple criteria for scale-up (Eggers and Sievers, 1989) and guides for cost evaluation (Passey, 1994; Perrut, 2000; Rosa and Meireles, 2005) but in our opinion these procedures are not systematic or reliable enough for scaling-up and designing purposes. We believe there is a need for more complex and predictive tools to simulate SCFE plants for solid substrates, which are paramount to economically optimize industrial SCFE processes.

The objective of this work was to model and numerically simulate mass transfer phenomena in an industrial SCFE plant having multiple extraction vessels. For that we developed an algorithm to simulate the evolution in dissolved solute concentration in the SC CO_2 exiting the last of several packed bed extraction vessels in an industrial SCFE plant, where the mass transfer from the solid substrate to the SC CO_2 stream occurs according to a shrinking-core mechanism. We applied and tested our model to the extraction of oil from prepressed seeds in a three-vessel SCFE plant using SC CO_2 at 40 ºC and 30 MPa as the solvent. Extraction conditions do not need to be modified, and the SCFE plant does not require more than three extraction vessels of the selected example as a proof-of-concept (oil extraction in preceding vessels in the solvent cycle affects initial stages of an SCFE process for a solid substrate by imposing variable inlet conditions). It is not the purpose of this manuscript to use our computational tool to economically optimize the design of SCFE processes for the extraction of solid substrates. It is however an important step in our long-term objective which is to

contribute to the state of the art with a systematic and reliable designing procedure for industrial SCFE plants.

2.2 Model development for a multi-vessel SCFE plant

This section explains the mass transfer problem in an industrial SCFE plant having multiple extraction vessels and describes the model developed to mathematically describe it. The mass transfer problem in an two-vessel SCFE plant is already solved, but there is a need for an algorithm to simulate a SCFE plant having three or more extraction vessels that interact through the SC CO_2 stream connecting them (*i.e.*, when the entering SC CO_2 stream has a time-dependent solute concentration). This section includes a description of the operation in a three-vessel SCFE plan, the mathematical model, the algorithm of numerical solution and its implementation, and the conditions for an illustrative example.

2.2.1 The problem of SCFE plants with three extraction vessels

Fig. 2-1 compares the three configurations of the solvent cycle in a three-vessel SCFE plant. In Fig. 2-1A extraction vessel 1 contains partially extracted substrate, vessel 2 contains fresher substrate, and vessel 3 is being reconditioned; in Fig. 2-1B vessel 1 with exhausted substrate is taken out the solvent cycle, vessel 2 with partially extracted substrate is moved forward in the solvent cycle, and vessel 3 with fresh substrate is taken in at the end into the solvent cycle; and, finally, in Fig. 2-1C exhausted vessel 2 is taken out of, partially exhausted vessel 3 is moved forward along, and fresh vessel 1 is moved into the solvent cycle. In all cases, the SC CO_2 moves from a vessel with more nearly exhausted substrate, to a vessel with fresher substrate. In general in an n-vessel SCFE plant, $(n - 1)$ extraction vessels are connected using a simulated countercurrent contact whereas reconditioning steps are carried out in the last extraction vessel. Available mass transfer models for one vessel laboratory or pilot plant SCFE units do not take into account the interaction between two consecutive extraction vessels in industrial SCFE plants having three or more, where the exiting stream of one vessel

corresponds to the entering stream of the next one in the solvent cycle. This problem has no trivial numerical solution and requires special treatment of the border conditions to simulate the mass transfer in an industrial SCFE plant.

In a two-vessel SCFE plant the process is similar to the that in a one-vessel SCFE plant, because the second extraction vessel enters the solvent cycle only when the first one leaves the solvent cycle so that the solid substrate at the entrance of the extraction vessel is also always in contact with solute-lean SC CO_2. Solute concentration in the SC CO_2 stream entering an extraction vessel in an industrial SCFE plant having three or more extraction vessels changes with time because CO_2 proceeds from one vessel to the next, and removes solute from substrate that contains progressively more solute (simulated countercurrent contact). Furthermore, inlet solute concentration in the SC CO_2 also experiences step changes (decreases) when the sequence of extraction vessels in the solvent cycle is altered to take out the one with exhausted substrate and take in the one with fresh substrate.

This work presents the simulation of the mass transfer dynamics of a single extraction vessel in a three-vessel SCFE plant during a complete extraction cycle, up to reaching a pseudo steady-state condition identified by comparing the mass transfer behavior in successive cycles. The cycle is defined as the time required for completing extraction of substrate in one extraction vessel, which includes extraction itself and the reconditioning steps. This is as problem that has not been addressed in literature on extraction, possibly because in conventional solid liquid extraction (at standard pressure) it is possible to feed fresh substrate to the extraction apparatus, and remove the exhausted substrate from it without difficulties, unlike in extractions of solids at high pressure (SCFEs). Thus, extractions can be carried out at standard pressure in a true countercurrent mode (true steady state conditions can be established). To our knowledge few applications in chemical engineering bear resemblance to ours, *e.g.*, adsorptive separations using simulated moving beds (Dünnebier *et al.*, 2000) (some using a SC mixture as the mobile phase, Brunner and Johannsen, 2006). However, simulated

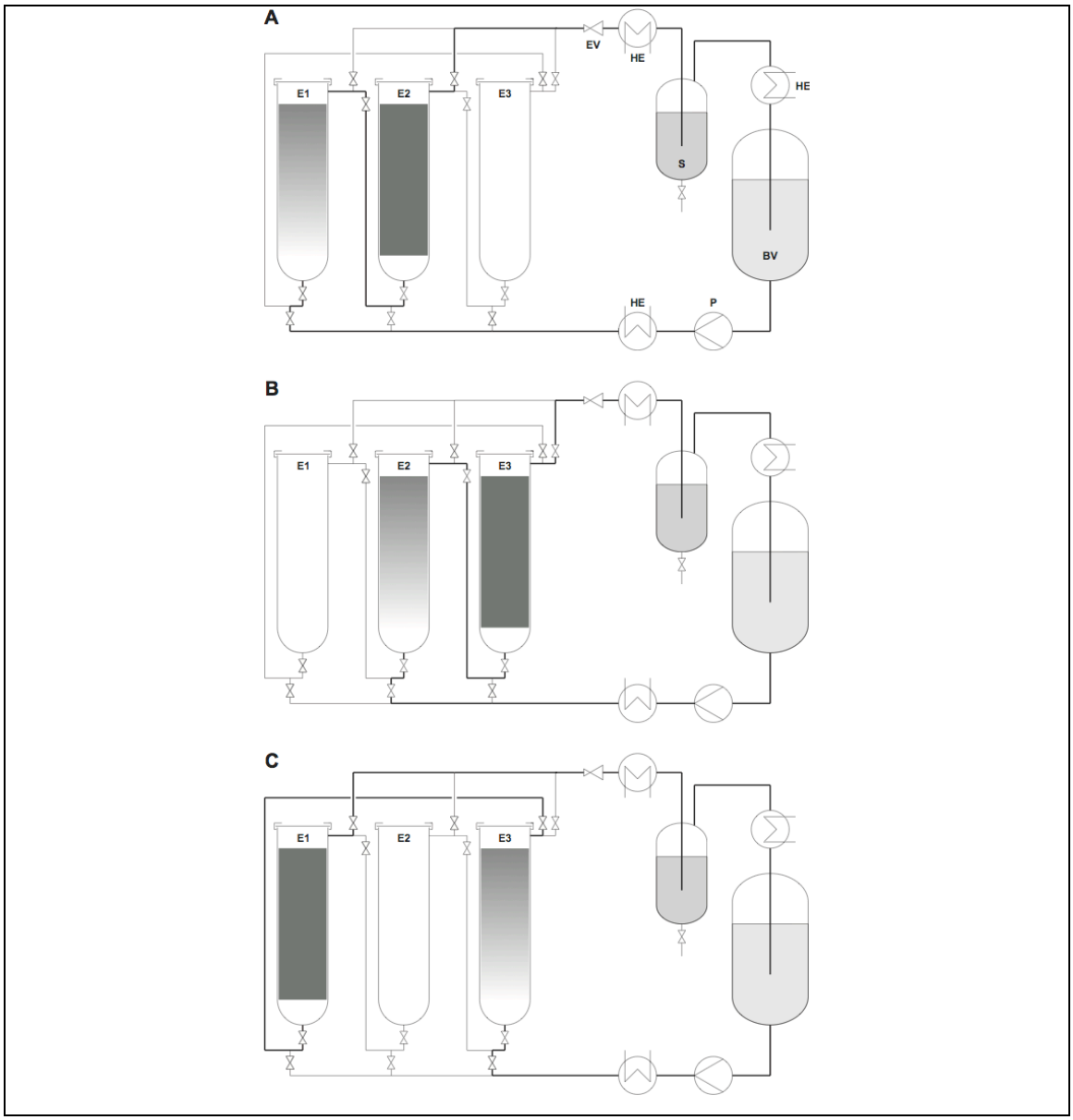

Figure 2-1: Schematic representation of a three-vessel SCFE plant for (A) extraction vessel 3 being reconditioned; (B) extraction vessel 1 being reconditioned; and, (C) extraction vessel 2 being reconditioned. Thicker lines indicate the corresponding solvent cycles. The components of the three- vessel SCFE plant are the following: (E_i) extraction vessels (with i = 1, 2, 3); (S) separator; (BV) buffer vessel for CO_2; (EV) expansion valve; (HE) heat exchanger; and, (P) pump.

moving beds are so different from our application that a mathematical solution of the problem is required, as attempted in our work.

2.2.2 Mass transfer model

We used the quasi-stationary state version of the shrinking-core model of Goto *et al.* (1996) to simulate the SCFE process because of its predictive capabilities for lipid extraction from prepressed oilseeds using SC CO_2 as the solvent (Germain *et al.*, 2005; del Valle *et al.*, 2006). In particular, the shrinking-core model describes the physical situation of a boundary between a solute-rich center (core) and an outside region where a dissolved solute gradient develops, and located in a receding radial position ($r = r_c$) in a porous particle (*i.e.*, the core shrinks as extraction proceeds). The model assumes isothermal conditions, a spherically-shaped porous matrix with evenly distributed solute initially, irreversible desorption of the solute, and constant physical properties of the SC CO_2 stream during extraction. These conditions are appropriated for the SC CO_2 extraction of prepressed oilseeds (del Valle *et al.*, 2006). Although prepressed and pelletized substrates are cylindrically shaped, Ma and Evans (1968) showed that dimensionless solutions for the extraction of various bodies of regular geometry in a perfectly agitated medium virtually superimposed when using as the characteristic dimension of the particle three times the ratio between its total volume and external surface (R, in the case of a sphere). In the typical case of a cylinder with an aspect (height-to-diameter) ratio of one, this characteristic dimension coincides with the cylinder radius. del Valle *et al.* (2006) adopted this assumption and showed that shear efforts during pre-pressing obliterated cells walls in parenchymatous tissue of oilseeds thus releasing oils to the interconnected pore network that resulted from applying this pretreatment.

The equations of the shrinking-core model represent the differential mass balance for the solute in a packed bed describing the external mass transfer in the SC CO_2 phase, Eq. (2.1), inner mass transfer by diffusion in porous substrate particles, Eq. (2.2),

shrinking of the solute-rich core within solid particles, Eq. (2.3), and calculation of extraction yield, Eq. (2.4).

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z} = D_{\mathrm{L}}\frac{\partial^2 C}{\partial z^2} + \frac{(1-\varepsilon)}{\varepsilon}\frac{3k_{\mathrm{f}}}{R}\left(C_{\mathrm{p}}\Big|_{r=R} - C\right) \tag{2.1}$$

$$\frac{D_{\mathrm{e}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{\mathrm{p}}}{\partial r}\right) = 0 \tag{2.2}$$

$$\frac{\partial r_{\mathrm{c}}}{\partial t} = \frac{R^2 k_{\mathrm{f}}}{r_{\mathrm{c}}^2 C_{\mathrm{o}}}\left(C - C_{\mathrm{p}}\Big|_{r=R}\right) \tag{2.3}$$

$$\frac{\partial E}{\partial t} = \frac{F_{\mathrm{CO_2}}}{M}\cdot C\Big|_{z=L} \tag{2.4}$$

Initial conditions ($t = 0$) to solve these partial differential equations are that solute concentration in the SC CO_2 phase is zero along the entire extraction vessel, Eq. (2.5), that the radius of the core equals the particle radius for all particles in the vessel, Eq. (2.6), and that extraction yield is zero at the beginning of the extraction.

$$C\Big|_{t=0} = 0 \qquad 0 \le z \le H \tag{2.5}$$

$$r_{\mathrm{c}}\Big|_{t=0} = R \qquad 0 \le z \le H \tag{2.6}$$

$$E\Big|_{t=0} = 0 \tag{2.7}$$

Boundary conditions, on the other hand, include the Danckwerts boundary conditions for axial dispersion at the inlet ($z = 0$), Eq. (2.8), and outlet ($z = H$), Eq. (2.9), of the extraction vessel; the continuity equation for mass transfer from the porous space in the solid particle (diffusion) to the SC CO_2 phase (convection), at the substrate-solvent boundary ($r = R$), Eq. (2.10); and the equilibrium condition between the inner

condensed solute core and the outer pore space (SC CO_2 saturated with solute) at the shrinking-core boundary ($r = r_c$), Eq. (2.11).

$$D_L \left.\frac{\partial C}{\partial z}\right|_{z=0} = uC \qquad t \geq 0 \tag{2.8}$$

$$\left.\frac{\partial C}{\partial z}\right|_{z=H} = 0 \qquad t \geq 0 \tag{2.9}$$

$$D_e \left.\frac{\partial C_p}{\partial r}\right|_{r=R} = k_f\left(C - C_p\big|_{r=R}\right) \qquad t \geq 0 \tag{2.10}$$

$$C_p\big|_{\zeta=r} = C_{sat} \qquad t \geq 0 \tag{2.11}$$

To solve this problem numerically, we transformed the variables into dimensionless forms using the following definitions: $Y = C/C_{sat}$; $X = C_p/C_{sat}$; $\theta = t \cdot u/L$; $\zeta = z/L$; $\delta = r/R$; $\delta_c = r_c/R$; $u = U/\varepsilon$; $a_p = 3/R$; $b = C_{sat}/C_o$; $\mathrm{Bi} = k_f \cdot R/D_e$; $\mathrm{Pe} = u \cdot L/D_L$; and $\tau_e = u/\left(k_f \cdot a_p \cdot L\right)$. The model equations and initial and boundary conditions become Eqs. (2.12)-(2.22) when written in dimensionless form:

$$\frac{\partial Y}{\partial \theta} + \frac{\partial Y}{\partial \zeta} = \frac{1}{\mathrm{Pe}}\frac{\partial^2 Y}{\partial \zeta^2} + \frac{(1-\varepsilon)}{\varepsilon}\frac{1}{\tau_e}\left(X\big|_{\delta=1} - Y\right) \tag{2.12}$$

$$\frac{D_e}{\delta^2}\frac{\partial}{\partial \delta}\left(\delta^2 \frac{\partial X}{\partial \delta}\right) = 0 \tag{2.13}$$

$$\frac{\partial \delta_c}{\partial \theta} = \frac{b}{3\delta_c^2}\frac{1}{\tau_e}\left(Y - X\big|_{\delta=1}\right) \tag{2.14}$$

$$\frac{\partial S}{\partial \theta} = \frac{b \cdot \varepsilon}{(1-\varepsilon)} Y\big|_{\zeta=1} \tag{2.15}$$

$$Y\big|_{\theta=0} = 0 \qquad 0 \le \zeta \le 1 \qquad (2.16)$$

$$\delta_c\big|_{\theta=0} = 1 \qquad 0 \le \zeta \le 1 \qquad (2.17)$$

$$S\big|_{\theta=0} = 0 \qquad 0 \le \zeta \le 1 \qquad (2.18)$$

$$\left.\frac{\partial Y}{\partial \zeta}\right|_{\zeta=1} = 0 \qquad \theta \ge 0 \qquad (2.19)$$

$$\left.\frac{\partial Y}{\partial \zeta}\right|_{\zeta=0} = \mathrm{Pe}\, Y \qquad \theta \ge 0 \qquad (2.20)$$

$$\left.\frac{\partial X}{\partial \delta}\right|_{\delta=1} = \mathrm{Bi}\left(Y - X\big|_{\delta=1}\right) \qquad \theta \ge 0 \qquad (2.21)$$

$$X\big|_{\delta=\delta_c} = 1 \qquad \theta \ge 0 \qquad (2.22)$$

2.2.3 Numerical solution of the problem using MATLAB

The spatial derivatives of the model were computed using second-order central finite differences (as previously used by Germain *et al.*, 2005). We divided both the extraction vessel and the particles in 30 nodes, resulting in a system with sixty-one differential equations: (i) thirty differential equations to account for mass transfer from the particles to SC CO_2 by convection and solute conservation in the extraction vessel; (ii) thirty differential equations to account for mass transfer in the particles by diffusion; and, (iii) one differential equation to calculate cumulative extraction curves. We solved the resulting time-dependent equations using the *ode15s* solver (variable order solver based on the numerical differentiation formulas) of MATLAB R2008b in a personal computer with processor Intel Core 2 Duo @ 1.83 GHz and 1 GB of RAM.

Eq. (2.23) defines the vector with the conditions at the beginning of every stage in the extraction:

$$\mathbf{IC}_{\mathrm{i}} = \begin{bmatrix} \mathbf{I}_{\mathrm{Ai}} & \mathbf{I}_{\mathrm{Bi}} & I_{\mathrm{Ci}} \end{bmatrix}, \tag{2.23}$$

where $\mathbf{I}_{\mathrm{Ai}}$ represents dimensionless solute concentration in the SC CO_2 phase, $\mathbf{I}_{\mathrm{Bi}}$, the dimensionless radius of the solute-rich particle core; and I_{Ci}, the extraction yield (scalar), all at the end of extraction stage (i – 1). At the beginning of the process, when the first extraction vessel in the solvent cycle has fresh substrate, the elements in Eq. (2.23) take the following values: $\mathbf{I}_{\mathrm{Ai}} = \mathbf{0}$, which is a vector composed of 30 zeros, and represents the SC CO_2 phase without solute; $\mathbf{I}_{\mathrm{Bi}} = \mathbf{I}$, is a vector composed of 30 ones and represents the initial dimensionless radius of the solute-rich core of the particles, when particles are unextracted; and $I_{\mathrm{Ci}} = 0$, is an scalar and represents null yield. For the next stages, the elements in Eq. (2.23) are updated constantly according with the evolution of the oil concentration through the extraction vessels. The updating process in this work is extended up to reaching a pseudo-steady-state (when the assumed evolution in solute concentration in the stream entering the extraction vessel virtually coincides with actual, updated, one).

In turn, the inlet SC CO_2 stream of the extraction vessel varies depending on how much solute it is removed in the preceding extraction vessel. Thus, when the inlet stream of the extraction vessel comes from the buffer vessel with recycled CO_2 (solute-lean), solute concentration is constant and corresponds to solute solubility in CO_2 at separation conditions,-Eq. (2.24):

$$Y\big|_{\theta=0} = C_{\mathrm{sep}} \big/ C_{\mathrm{sat}} \tag{2.24}$$

On the other hand, when the inlet SC CO_2 stream of an extraction vessel is the SC CO_2 stream exiting another vessel, the solute concentration varies according to a history stored as indicated in Eq. (2.25):

$$\mathbf{Y}_i\big|_{\theta=0} = \mathbf{y}_{i-1}\big|_{\zeta=1}(t), \tag{2.25}$$

where vector $\mathbf{y}_{i-1}\big|_{\zeta=1}(t)$ stores the history of the SC CO_2 stream exiting ($\zeta = 1$) the extraction vessel in extraction stage ($i - 1$), and vector $\mathbf{Y}_i\big|_{\theta=0}$ indicates the initial solute concentration at the beginning of extraction stage i for any extraction vessel. All inlet streams represented by Eq. (2.24) or Eq. (2.25) are fed to the next extraction stage through a "zero node", which is physically located at the entrance of the extraction vessel. This is required, because of the use of central-type finite differences in which any changes in node condition are defined using the information from the preceding and following nodes. Depending on the case, in order to initialize our algorithm, we assigned the elements of $\mathbf{Y}_i\big|_{\theta=0}$ (Eq. (2.24)) or $Y\big|_{\theta=0}$ (Eq. (2.25)) to the zero node at the entrance of the extraction vessel.

2.2.4 Implementation of the algorithm

Firstly, we determined the state of the substrate at the beginning of the extraction, which could be fresh or partially extracted. For fresh substrate (*e.g.*, first stage $i = 1$), the initial state in the extraction vessel is given by Eq. (2.23), with $\mathbf{I}_{Ai} = \mathbf{0}$, $\mathbf{I}_{Bi} = \mathbf{I}$, and $\mathbf{I}_{Ci} = 0$, and extraction is simulated as being carried out by a solute-rich SC CO_2 stream having a solute concentration given by Eq. (2.25). Secondly, to simulate the whole extraction process, we updated the values in vector $\mathbf{Y}_i\big|_{\theta=0}$, Eq. (2.25), and matrix $\mathbf{IC}_i$, Eq. (2.23), every 60 seconds. For partially extracted substrate after the switch time (*cf.* Fig. 2), we applied Eq. (2.23) updated at this point of the extraction, and simulated extraction as being carried out by recycled SC CO_2 using Eq. (2.24). Finally, we stored the outputs of the algorithm in matrix $\mathbf{H}_i(t)$, Eq. (2.26):

$$\mathbf{H}_i(t) = \left[\begin{array}{ccc} \mathbf{t}_i & \mathbf{y}_i\big|_{\zeta=1}(t) & \mathbf{S}_i(t) \end{array}\right], \tag{2.26}$$

where $\mathbf{H}_i(t)$ is a matrix that contains the outputs of the simulation for an extraction unit at any stage *i*. $\mathbf{H}_i(t)$ has three column vectors, where we recorded the extraction time ($\mathbf{t}_i$, in seconds), the concentration of the SC CO_2 stream exiting the extraction vessel ($\mathbf{y}_i|_{\zeta=1}(t)$, dimensionless), and the extraction yield ($\mathbf{S}_i(t)$, dimensionless) as a function of time. We used vector $\mathbf{y}_i|_{\zeta=1}(t)$ as an input for the next extraction vessel.

2.2.5 Operational conditions of the oil extraction from prepressed rapeseeds

For a three-vessel SCFE plant, the total extraction volume of the plant was 6 m^3, and each vessel (V_E = 2 m^3) had an inner diameter of 0.8 m and a height of 4 m. The extraction conditions in the plant were 40 ºC and 30 MPa, whereas the separation conditions were arbitrarily set at 60 ºC and 8 MPa. The physical properties (ρ and μ) of CO_2 were estimated using NIST Database (Lemmon *et al.*, 2010) for pure CO_2. Extraction was extended to remove 90% of the oil in the substrate, using a SC CO_2 mass flow rate of 0.915 kg/s (3300 kg/h). Particle size (d_p), and porosity (ε_b) and bulk density (ρ_b) of the bed were assumed (typical values for packed beds of vegetable substrates). Finally, the assumed initial oil content (C_o) in prepressed oilseeds was 20% (w/w).

The model parameters were calculated or estimated using correlations or mathematical expressions available in the literature. Table 2-1 summarizes the values of model parameters. We estimated oil solubility in SC CO_2 (C_{sat} and C_{sep}) using the correlation of del Valle, *et al.* (2012a). In addition, we estimated the effective diffusivity ($D_e = D_{12} \cdot F$) as the product of value of the microstructural correction factor (F) the reported by del Valle *et al.* (2006) and the diffusivity of oil in CO_2 (D_{12}) estimated using the correlation of Funazukuri *et al.* (2009). Finally, we estimated the external mass transfer coefficient (k_f) using the correlation of King and Catchpole (1993), and the axial dispersion coefficient (D_L) using the correlation of Catchpole *et al.* (1996).

Table 2-1: Model parameters calculated at extraction conditions (P_{ext} = 30 MPa; T_{ext} = 40 ºC), and separation conditions (P_{sep} = 8 MPa; T_{sep} = 60 ºC)

Parameter	As function of	Value		Unit
V	-	6	(assumed)	m^3
V_E	-	2	(assumed)	m^3
L/D_{ext}	-	5	(assumed)	-
D_{ext}	$f(V_E, L/D_{ext})$	0.8	(calculated)	m
L	$f(V_E, D_{ext})$	4	(calculated)	m
F_{CO2}	-	0.915	(assumed)	$kg \cdot s^{-1}$
d_p	-	0.005	(assumed)	m
ε_b	-	0.6	(assumed)	-
ρ_b	-	500	(assumed)	$kg \cdot m^{-3}$
C_o	-	0.2	(assumed)	kg oil·kg^{-1} substrate
ρ	$f(P_{ext}, T_{ext})$	909.9	(calculated)	$kg \cdot m^{-3}$
ρ_{sep}	$f(P_{sep}, T_{sep})$	191.6	(calculated)	$kg \cdot m^{-3}$
μ	$f(P_{ext}, T_{ext})$	9.4×10^{-5}	(calculated)	Pa·s
U	$f(\rho, F_{CO2}, D_{ext})$	0.002	(calculated)	$m \cdot s^{-1}$
u	$f(U, \varepsilon)$	0.003	(calculated)	$m \cdot s^{-1}$
C_{sat}	$f(T_{ext}, \rho)$	7.9×10^{-3}	(calculated)	kg oil·kg^{-1} CO_2
C_{sep}	$f(T_{sep}, \rho_{sep})$	1.6×10^{-4}	(calculated)	kg oil·kg^{-1} CO_2
D_{12}	$f(T_{ext}, \rho)$	3.0×10^{-9}	(calculated)	$m^2 \cdot s^{-1}$
F	-	0.172	(assumed)	-
D_e	$f(F, D_{12})$	5.2×10^{-10}	(calculated)	$m^2 \cdot s^{-1}$
Re	$f(d_p, \rho, \mu, U)$	97	(calculated)	-
D_L	$f(Re, L, u)$	1.9×10^{-4}	(calculated)	$m^2 \cdot s^{-1}$
Sc	$f(\rho, \mu, D_{12})$	34	(calculated)	-
k_f	$f(Re, Sc)$	3.3×10^{-5}	(calculated)	$m \cdot s^{-1}$

2.3 Results and Discussion

This section first explains the difference between the oil extracted in a vessel, expressed as the product of the mass flow rate of SC CO_2 and the difference in concentration of oil between the streams entering and exiting the vessel, and the oil extracted in the two vessels in the solvent cycle, expressed as the product of the mass flow rate of SC CO_2 and the concentration of oil in the stream exiting the second vessel in the solvent cycle. This explanation is necessary to clearly understand the advantage of having three or more vessels in an industrial SCFE plant. A discussion follows about the number of iterations required to reach the pseudo-steady-state condition characterizing the operation of a typical extraction vessel in a multi-vessel plant. Finally the pseudo-steady-state conditions and productivities of a two- and three-vessel SCFE plants are compared.

Fig. 2-2 compares the time dependency between the actual, pseudo-steady-state concentration of oil in the SC CO_2 stream exiting an extraction vessel, and the difference in concentration between that stream and the SC CO_2 stream entering the extraction vessel. This comparison is important because the difference between inlet and outlet concentration, which we will refer to as the concentration of "extracted" oil, accounts solely for the oil extracted in the vessel. Fig. 2-2 defines a switch time when the extraction vessel remains in the same position (first or second) in the solvent cycle, and the extraction time (twice the switch time) when the extraction vessel remains in the solvent cycle. For the purpose of discussion, the cycle time (t_c) includes the reconditioning of the extraction vessel and corresponds to the addition of the switch time and the extraction time (three times the switch time).

The number of batches in one year that each extraction vessel in a multi-vessel SCFE plant can be estimated roughly as the total production time divided by the cycle time. Thus, a three-vessel SCFE plant operating continuously (three 8 h-shifts per day) 300 days per year, allows a grand total of ca. $3\times300\times24 / t_c$ batches per year.

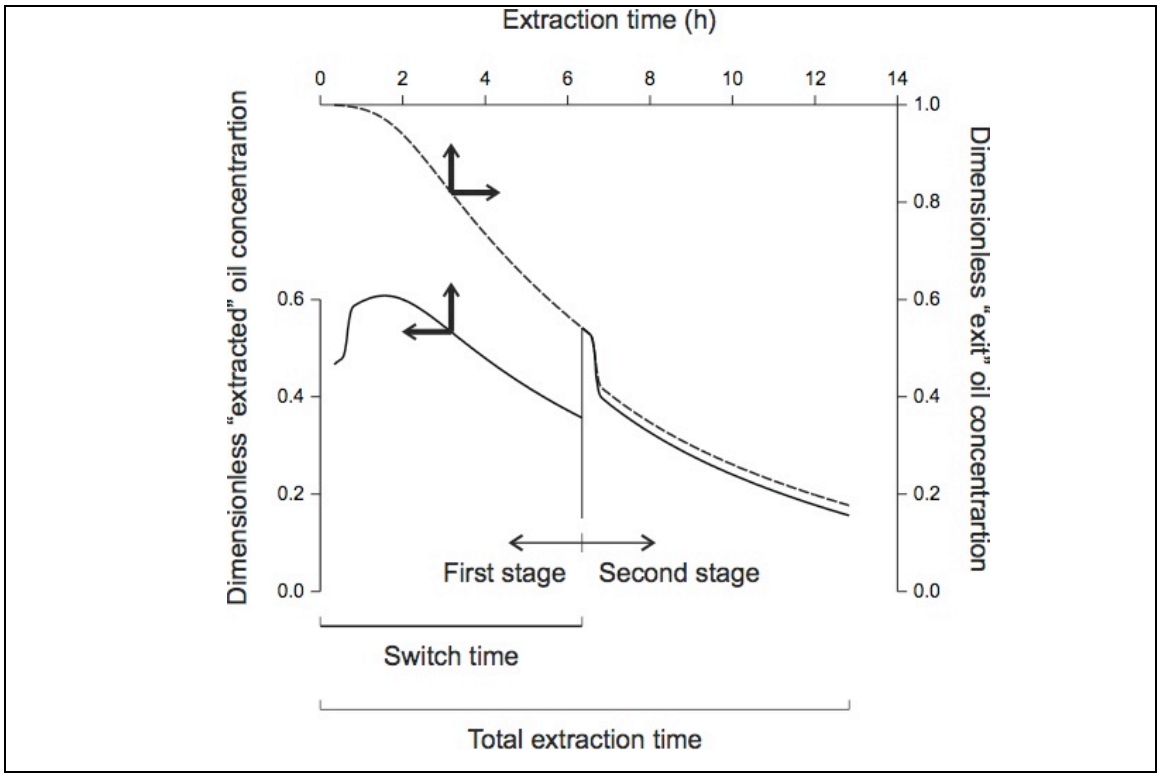

Figure 2-2: Comparison between the actual, pseudo-steady-state concentration of oil in the SC CO_2 stream exiting an extraction vessel (dashed line), and the "extracted" oil stream (solid line, defined as the difference in concentration between the stream represented by dashed line and the SC CO_2 stream entering the extraction vessel). The line in the middle of the graph defines the switch time (t = 6.35 h) as that time when the extraction vessel remains in the same position in the solvent cycle. Total extraction time (twice the switch time) defines the whole period when the extraction vessel remains in the solvent cycle.

This is important in defining the productivity of the SCFE plant. In Fig. 2-2, concentrations are expressed in dimensionless form ($Y = C/C_{sat}$), so that $Y = 1$ represents a SC CO_2 stream saturated with oil (C_{sat} = 7.915 g oil/kg CO_2), and $Y = 0$, a stream without oil. The outlet concentration and the "extracted" oil concentration were computed and updated every 60 seconds in the simulation. The two curves in Fig. 2-2 do not begin at $t = 0$ but at $t = 1200$ s, because this corresponds to the residence time of SC

CO_2 in the extraction vessel. The same consideration applies to Fig. 2-3 and Fig. 2-4. The concentration of "extracted" oil in the SC CO_2 stream exiting the second extraction vessel in the solvent cycle cannot begin in $Y = 1$ because part of the oil in the stream is removed from the substrate in the first extraction vessel. The discontinuity in the curve of "extracted" oil for the second stage (at 6.35 h) corresponds to a switch in the feed of the extraction vessel from an oil-containing stream from a preceding vessel (when the vessel is located second in the solvent cycle) to the oil-lean recycled SC CO_2 stream (when the vessel is located first in the solvent cycle). This switch results in an abrupt increase in extraction rate due the sudden increase in the driving force for mass transfer. This abrupt increase in extraction rate is in turn responsible for the shoulder observed in Fig. 2-2 for the first stage in the extraction process; the initially high concentration of oil in the entering stream is responsible for a low initial driving force for mass transfer in the second vessel in the solvent cycle.

Fig. 2-3 shows (A) changes in the dimensionless concentration of "extracted" oil in the SC CO_2 stream exiting an extraction vessel and (B) the cumulative oil extraction curve in the same vessel in a three-vessel SCFE plant for a first, second, and third iterations as a function of extraction time. Extraction times were 12.5 h (cycle time 18.8 h) for the first iteration, 12.9 h (cycle time 19.4 h) for the second, and 12.8 h (cycle time 19.2 h) for the third (Fig. 2-3A).

Percent changes (absolute basis) decreased from 3% between the first and second iteration, to 1% between the second and the third ones. Corresponding simulated cumulative oil extraction curves nearly overlapped suggesting that three iterations are enough to converge to a pseudo-steady-state operational condition of the SCFE plant (Fig. 2-3B). In fact, discrepancies in cumulative oil extraction between the second and third simulations were in average smaller than 0.1%. This observation simplifies the analysis of the SCFE plant because the performance of any extraction vessel in the plant is roughly equivalent to that of the extraction vessel in Fig. 2-3 after the third iteration.

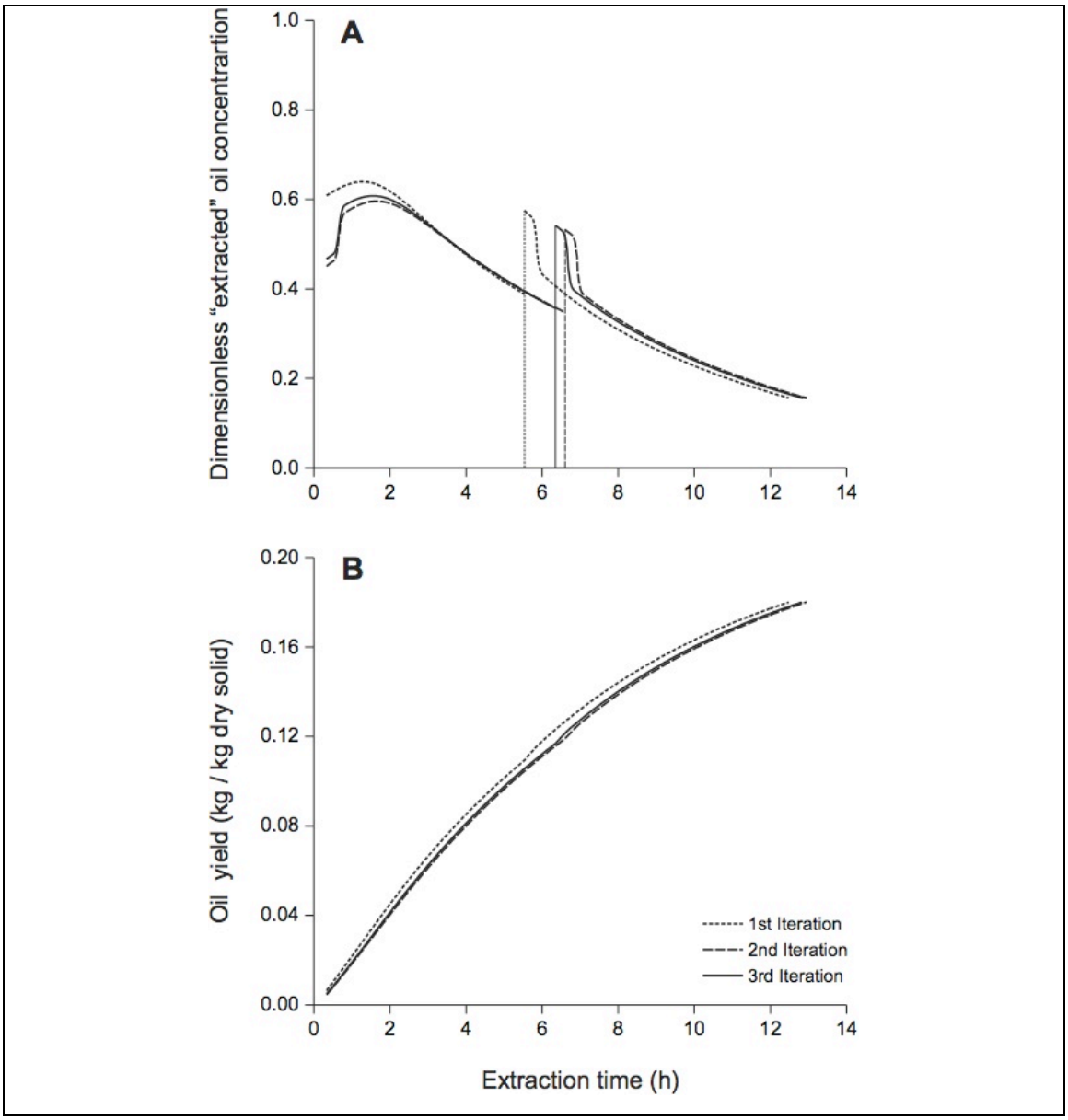

Figure 2-3: Comparison of the simulated curves for three iterations as a function of extraction time for (A) changes in the dimensionless concentration of "extracted" oil in the SC CO_2 stream exiting an extraction vessel and (B) the cumulative oil extraction curve for the same vessel in a three-vessel SCFE plant. The switch time was 5.53, 6.60, and 6.35 h, for first, second, and third iterations.

Fig. 2-4 shows the evolution of the dimensionless oil concentration profiles in an extraction vessel as a function of time (extraction history) and axial position, when the pseudo-steady-state condition is reached. This evolution shows an enrichment of the SC CO_2 stream as it moves along the packed bed, for each extraction time. However, this does not happen always, because at the beginning of first stage of the extraction process (t < 1 h) the SC CO_2 stream gets saturated with oil before reaching the exit of the extraction vessel (L ~ 2.8 m). For extraction times longer than about one hour, advantage is taken of the solvation capacity of the SC CO_2 along the entire packed bed. The last curve (L = 4 m) in Fig. 2-4 corresponding to the second stage of the extraction process represents the stream exiting the first extraction vessel in the solvent cycle and is the same curve showed (dashed line) in Fig. 2-2. In contrast, the first curve (L = 0 m) in Fig. 2-4 corresponding to the first stage of the extraction process represents the stream that comes from the extraction vessel placed before (the first) in the solvent cycle and that is fed to the next extraction vessel (placed second) in the solvent cycle.

The history (concentration profile as a function of time) of the inlet stream (in L = 0 m) during the first stage of the extraction process (that ends when reaching the switch time of 6.35 h) virtually coincides with the history of the outlet stream (in L = 4 m) during the second stage of the extraction process (that begins after reaching the switch time) as required for the operation of the SCFE plant under a pseudo-steady-state condition. Consequently Fig. 2-4 represents two things: i) the whole history of the extraction of a single batch; and, ii) the simultaneous histories of two vessels operating simultaneously in a three-vessel SCFE plant.

Fig. 2-5 compares (A) the time-dependency of the dimensionless concentration of oil in the SC CO_2 stream exiting an extraction vessel and (B) the cumulative oil extraction curve in the same vessel between a two-vessel and three-vessel SCFE plants for the third iteration. The time required to extract 90% of the oil in the substrate in the two-vessel SCFE plant (11.1 h, cycle time = 12.8 h) was smaller than in the three-vessel plant (12.8 h, cycle time = 19.2 h). Differences in oil concentration between the entering

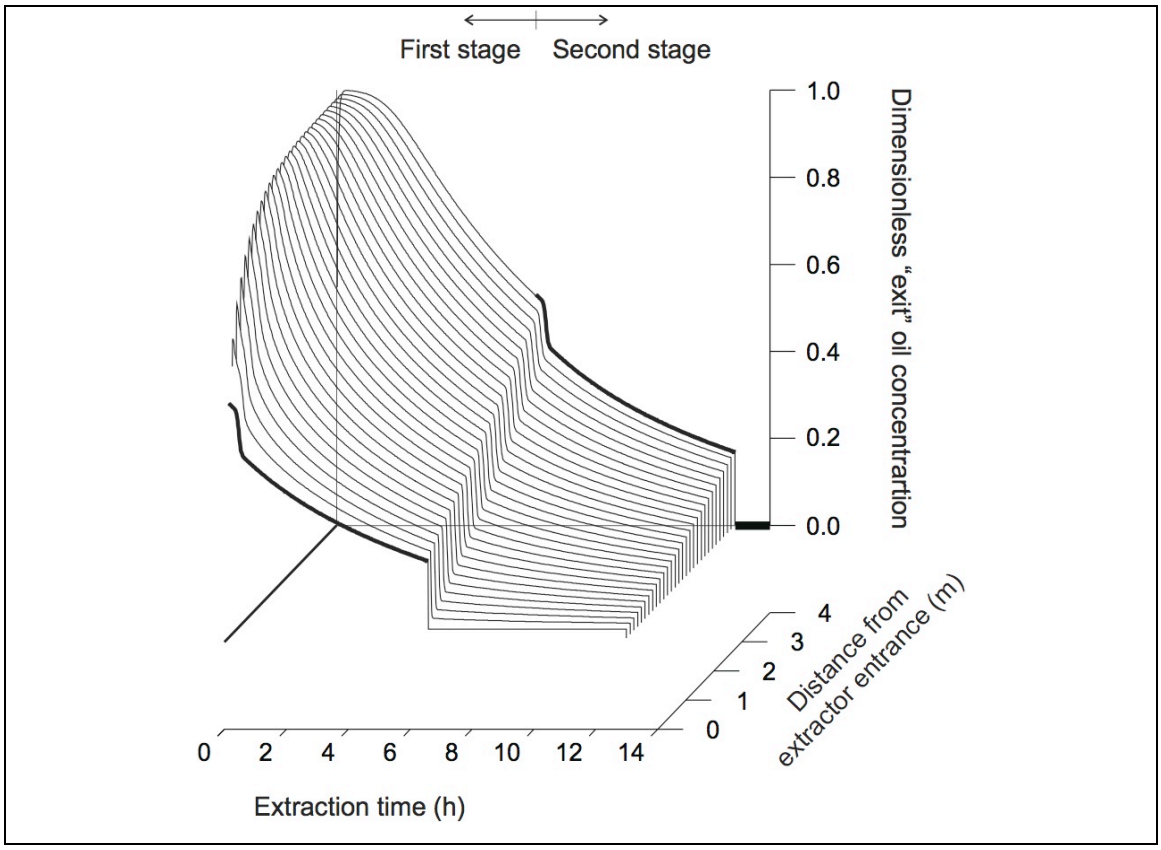

Figure 2-4: Evolution of the dimensionless concentration of oil in the SC CO_2 stream in an extraction vessel as function of time and axial position after reaching a pseudo-steady-state condition. The curve at the front represent the history of the stream entering the extraction vessel (L = 0 m) and its first part (thicker line portion, corresponding to the first stage) coincides with the history of the stream exiting the extraction vessel (L = 4 m) in the second stage of the extraction process (thicker line portion of the curve at the back) as required for the operation under pseudo-steady-state conditions.

SC CO_2 streams explain these differences between extraction times. In the two-vessel SCFE plant (dashed line in Fig. 2-5) the substrate is always extracted with recycled, oil-lean SC CO_2 (C_{sep} = 0.164 g oil/kgCO_2). On the other hand, in the three-vessel SCFE plant (solid line in Fig. 2-5) the oil concentration in the SC CO_2 stream entering the extraction vessel during the first stage has a higher concentration of oil (the oil content

of the SC CO_2 stream exiting the first extraction vessel in the solvent cycle), which decreases the driving force for mass transfer and, consequently, the extraction rate (Fig. 2-5B). However, the exiting SC CO_2 stream from the three-vessel SCFE plant carries more oil than the corresponding stream from the two-vessel SCFE plant (absolute differences up to 1.81 g oil/kg CO_2, Fig. 2.5A). Industrial multi-vessel SCFE plants take advantage of the additional capacity of the SC CO_2 stream to dissolve solute to save on solvent usage.

Indeed, under reasonable assumptions, if we compare our three-vessel SCFE plant with an SCFE plant having the three extraction vessels operating independently (not interconnected), total savings in CO_2 would be roughly 50%. Switch time for the three-vessel SCFE plant (at 6.35 h) is manifested in Fig. 2-5A with the sharp decrease in dimensionless concentration of oil in the exiting SC CO_2 stream that was explained in Fig. 2-2, but this translates in a nearly imperceptible inflexion in the cumulative oil extraction curve.

In the illustrative example, being the initial oil content in the substrate C_o = 0.2 kg oil/kg substrate, the simulation stopped when the average concentration of oil in the treated substrate decreased to 0.02 kg oil/kg substrate. Under these conditions, the three-vessel SCFE plant would have an approximate productivity of 150 ton oil/year calculated as the oil extracted in a cycle ($0.9\times\rho_b\times V_E\times C_o$) times the number of batches in a year ($21600 / t_c$).

2.4 Conclusions and Perspectives

This work addresses a new relevant problem in Chemical Engineering operations, which is the establishing the pseudo-steady-state conditions in an extraction vessel in multi-vessel (three or more) plants operating at high pressure, such any one in a SCFE plants for solid substrates. This work addresses the problem and presents the algorithm to solve it. The algorithm estimates cumulative oil extraction curves in a three-vessel SCFE plant (Fig. 2-1). The results showed that extraction in the plant reaches a pseudo-steady-state condition following three iterations in the extraction time,

with discrepancies in cumulative oil yield between the second and third iterations being smaller than 0.1%. This result allowed estimating the annual productivity of a three-vessel SCFE plant using the cumulative extraction curve of a single extraction vessel.

The program implemented in MATLAB using the proposed algorithm allows analysis changing relevant parameters affecting the productivity of the plant. Such parameters include the size of the plant (total volume of the extraction vessels), the number and aspect ratio of extraction vessels (or height-to-diameter ratio), the extraction and separation conditions (pressure and temperature), the mass flow of the SC CO_2, the bulk density and porosity of the bed, and the particle diameter. Some of these parameters affect the design and cost of main plant components (extraction and separation vessels, CO_2 storage vessel, pumps and compressors, heat exchangers, expansion valve), thus the capital cost, whereas others affect operational costs. This information together with the productivity of the SCFE plant can be the basis for making informed investment decisions based on economical analysis.

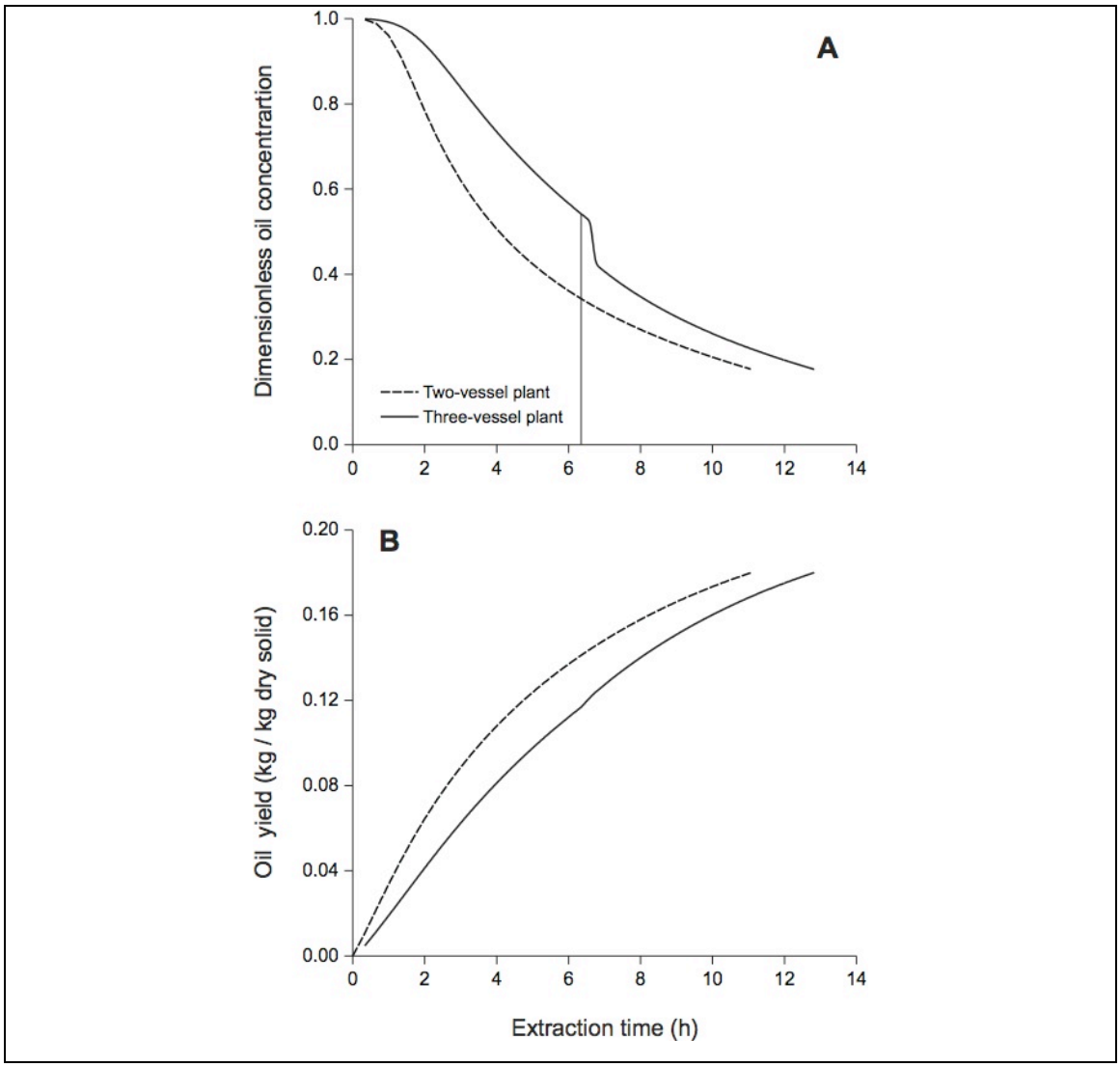

Figure 2-5: Comparison of the performance of an extraction vessel between a two-vessel and three-vessel SCFE plant for the third iteration (when the pseudo-steady operational condition is reached) for (A) the time-dependency of the dimensionless concentration of "extracted" oil in the SC CO_2 stream exiting an extraction vessel and (B) the cumulative oil extraction curve. (C) shows the inflexion point in the cumulative oil extraction curve at the switch time (t = 6.35 h) when the inlet stream of the extraction vessel switches from a time-dependent oil concentration SC CO_2 stream to an oil-lean recycled SC CO_2 stream.

3. SUPERCRITICAL CO_2 OILSEED EXTRACTION IN MULTI-VESSELPLANTS. 1. MINIMIZATION OF OPERATIONAL COST

Abstract

This work uses a fully predictive mass transfer model to simulate the supercritical CO_2 extraction of vegetable oils from prepressed oilseeds in the 1-m^3 vessel of an industrial multi-vessel plant operating at 40 °C and 30 MPa with the purpose of minimizing the operational cost. This work analyses the effect of particle diameter (0.5, 1, 2, 3, and 4 mm), superficial CO_2 velocity (2.75, 5.50, or 11.0 mm/s), and number of extraction vessel (2, 3, or 4) on optimal extraction time and minimal operational cost. Keeping other variables constants, cost diminishes as particle diameter decreases. Although the optimal superficial CO_2 velocity increases as particle diameter decreases, in the case of small (≤ 1 mm) particles, substrate fluidization may place an upper limit to the superficial velocity. Within the studied region, best superficial CO_2 velocities are 11.0 mm/s for particles smaller than 1-to-2 mm, 2.75 mm/s for particles larger than 3-to-4 mm, and 5.50 mm/s for particles in between. Keeping other variables constant, the cost of extraction of medium-to-large (≥2 mm) particles decreases as the number of extraction vessels increases, at the expense of an increase in extraction time. The lowest operational cost observed in this work was USD 4.081/kg oil for the extraction of 2-mm particles using 3.30 m^3/h of CO_2 (U = 2.75 mm/s) in a four-vessel plant.

Keywords: Extraction; industrial plant; operational cost; optimal extraction time; prepressed oilseed; supercritical CO_2; vegetable oil.

3.1 Introduction

Supercritical carbon dioxide (SC CO_2) is commercially applied for the extraction of bitter flavors from hops and the decaffeination of coffee beans (Brunner, 2005). Commercial application of SuperCritical Fluid Extraction (SCFE) appears to be also economically feasible to recover high-value compounds from other selected solid

substrates such spices, herbs, and oilseeds. In the case of new commercial SCFE applications, however, informed decisions on investment demand accurate cost estimates.

A factor that affects critically the cost of SCFE processes for solid substrates is selected extraction time (Rosa and Meireles, 2005), which in turn affects extraction yield depending on substrate pretreatment and particle size (d_p), and CO_2 temperature (T), pressure (P), and superficial velocity (U). Although process conditions (d_p, T, P, U) are usually optimized in laboratory experiments (Rosa and Meireles, 2005) the relationship between extraction yield and process time (cumulative extraction curve) depends also on scale-specific variables such as the height of the packed bed (L) and, in industrial SCFE plants, the number of extraction vessels (n). Because extraction vessels operate one at a time in industrial SCFE plants having two vessels, cumulative extraction curves in this case may coincide virtually with those in pilot plants having a single vessel and solvent recycling capabilities (Núñez *et al.*, 2011). However, in SCFE plants equipped with three or more extraction vessels (Fig. 3-1), extract concentration in the SC CO_2 stream entering a vessel changes initially with time because this feed stream carries extract from (a) vessel(s) located upstream in the solvent cycle (Núñez *et al.*, 2011). Indeed, SC CO_2 is contacted first with the more exhausted substrate (in the extraction vessel placed first in the solvent cycle) and then successively with increasingly fresher substrate to give better use of the driving force for the extraction process (the difference between extract concentration in the stationary substrate and in the flowing CO_2 stream), thus diminishing solvent usage (Núñez *et al.*, 2011). Rather than experimentally (Mezzomo *et al.*, 2011; Prado *et al.*, 2010; Prado *et al.*, 2012; Rosa and Meireles, 2005), the problem of optimizing extraction time in industrial SCFE plants can be tackled better by computer simulation using a mass transfer model of the extraction process (Clavier *et al.*, 1996), particularly for those plants equipped with three or more extraction vessels that require a time-dependent border condition. Núñez *et al.* (2011) illustrated this for the SC CO_2 extraction of oil from prepressed seeds in an industrial three-vessel SCFE plant operating at 40 ºC and 30 MPa.

Estimates of production cost for the SC CO_2 extraction of solid substrates include the investment (capital) and running costs involved in the purchase and operation, respectively, of the industrial SCFE plant. Operational costs relate to labor, pretreated substrate, energy demand of the solvent cycle and for the reconditioning of extraction vessels, and CO_2 losses with the extract and exhausted substrate. Capital cost estimates are possibly more questionable than operational cost estimates because of uncertainties in prices of industrial SCFE plants; plant manufacturers are reluctant to share these values with anyone but potential clients (Lack, 2009; Martínez, 2010; Perrut, 2011; Steinhagen, 2010). It is possible, however, to provide meaningful estimates of production costs without valid capital cost estimates for SCFE plants having idle capacity whose owners may consider offering toll-processing services to third parties. Under these circumstances, the owner of the SCFE plant should consider a break-even service price corresponding to the operational cost.

The objective of this work is to minimize the operational cost of the SC CO_2 extraction of oil from prepressed seeds as a function of process time under industrial conditions. Particularly, authors evaluated the effect of the particle size of the substrate, volumetric flow rate of CO_2 (Q_{CO_2}), and number of extraction vessels of the plant on the operational cost of a single 1-m^3 extraction vessel placed in a two-, three-, or four-vessel SCFE plant. Foregoing manuscripts will analyze the effect of additional variables such as vessel diameter (D) and shape (L/D ratio), extraction pressure, and plant size (total volume of extraction vessels), among others, on the total production cost of industrial SCFE plants.

3.2 Problem statement and solution

This section describes an industrial multi-vessel SCFE plant and the operation conditions analyzed in this work, then describes the mathematical simulations of plant operation together with the estimation of model parameters, and ends up with the procedure applied to estimate operational cost per unit mass of extracted oil.

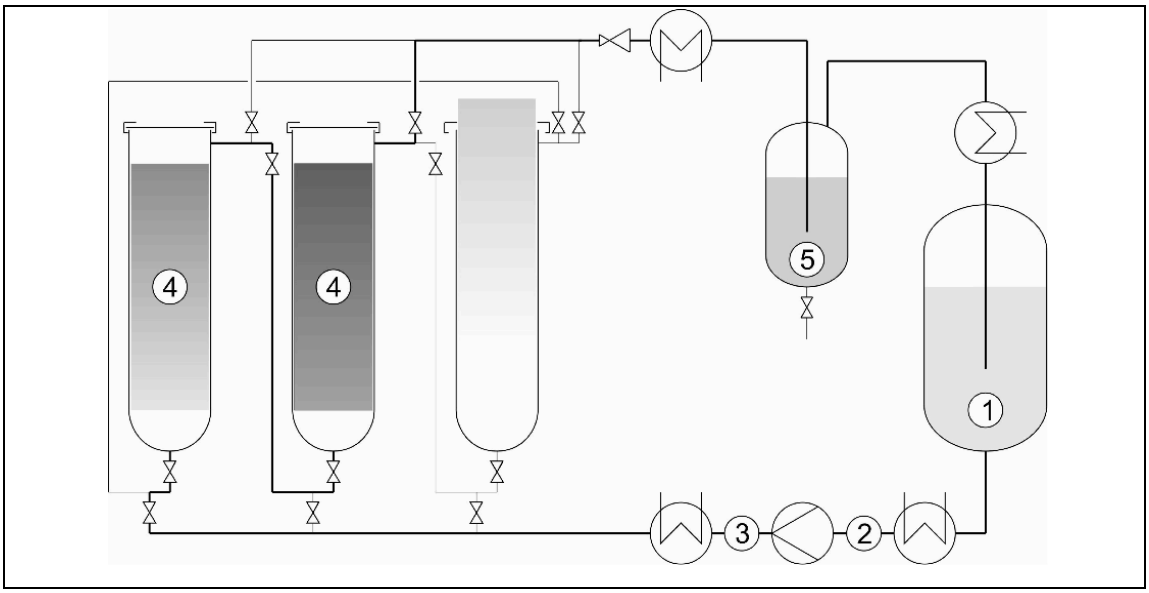

Figure 3-1: Solvent cycle in a SCFE plant with three extraction vessels operating at 40 °C and 30 MPa as extraction conditions. The figures is a schematic representation of a plant where third extraction vessel is out of the solvent cycle for the recondition steps, and SC CO_2 stream flows through first and then for second extraction vessels (stage 4) by means of a pump (process 2-3). The oil is separated from the SC CO_2 by expansion in the separator (stage 5). Finally, CO_2 is recovered in a buffer vessel to recycle it again to the extraction process. In this solvent cycle the heat exchangers are associated to the cooling energy (process 5-1), and heating (process 4-5) and heating or cooling (process 3-4).

3.2.1 The supercritical extraction plant and thermodynamic cycle of the solvent

Fig. 3-1 exemplifies industrial SCFE in the case of a three-vessel plant. The two main components of the plant are the solvent cycle and the extraction vessels. The thick line in Fig. 3-1 represents the solvent cycle circled by CO_2 clockwise starting in the buffer vessel. Beside the buffer vessel, the main components of the solvent cycle are the pump, expansion valve, separation vessel, buffer vessel, and heat exchangers that condition the CO_2 stream to required temperatures for pumping, extraction, separation,

and holding (process storage). The components of the second part of the SCFE plant include the extraction vessels and on/off valves in the lines connecting the vessels to the solvent cycle, or interconnecting them. In the example, two extraction vessels are placed to the solvent cycle (the one on the left, first, and the middle one, second), whereas the last one (on the right) is being reconditioned. Reconditioning of a vessel includes depressurization from the extraction pressure to the buffer vessel pressure, venting of CO_2 remaining in the extraction vessel to the environment, unloading of exhausted substrate, loading of fresh substrate, and repressurization up to the extraction pressure again. On/off valves allow switching the relative positions of the extraction vessels in the solvent cycle as described by Núñez *et al.* (2011). Fig. 3-1 does not include the CO_2 storage vessel that feeds make-up solvent to the buffer vessel, nor auxiliary components used in the reconditioning process to send CO_2 from the vessel with extracted substrate to the buffer vessel during depressurization, and from the buffer vessel to the vessel with fresh substrate during repressurization.

Fig. 3-2 pictures the conditions of CO_2 as it moves along the solvent cycle in a temperature-entropy (*T*-*s*) diagram where numbers signal conditions of state in positions identified in Fig. 3-1. The diagram was constructed using estimates of thermodynamic properties of CO_2 provided by NIST Database (Lemmon *et al.*, 2010). Selected conditions were 40 °C and 30 MPa for extraction, 60 °C and 8 MPa for separation, and 25 ºC and 6.4 MPa (saturated liquid) for CO_2 holding in the buffer vessel.

Authors made the following assumptions: i) sub-cooling to 15 ºC to avoid cavitation in the pump; ii) isentropic efficiency of the pump (η_i) of 90% (Sievers, 1998) and electric efficiency of the pump motor (η_e) of 85% (Boyce *et al.*, 2008); iii) isothermal conditions and negligible pressure losses of CO_2 in extraction vessels; and, iv) no effect of dissolved oil on conditions of state of the CO_2 stream. Table 3-1 reports unitary (per unit weight of CO_2) energy demands to pump, heat, cool (condense) CO_2 in the solvent cycle based on conditions of state presented in Fig. 3.2. The total cost for energy requirements was 5.94 USD/ton of CO_2.

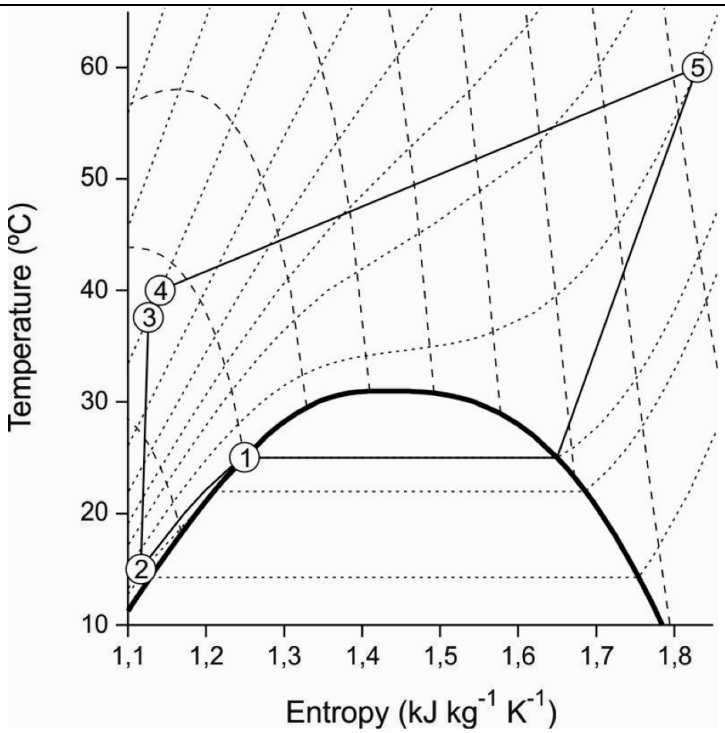

Figure 3-2: Solvent cycle (steps 1-5) of the SCFE plant (Fig. 3-1) represented in a *T*-s diagram. Dotted lines represent isobar, and dashed lines isoenthalpy. Pressure increases for bottom right to top left (5, 6, 6.4343, 8, 10, 12, 15, 20, 30, 50, and 70 MPa). Enthalpy increase from bottom left to up and right (225, 250, 275, 300, 325, 350, 375, 400, and 425 kJ/kg). Thick lines separate the two phase region from the liquid (left) and gas (right). Conditions of state in positions identified in Fig. 1: buffer vessel, 1; pump inlet, 2; pump exit, 3 (not isentropic one); extraction vessels in solvent cycle (extraction conditions at 40 ºC and 30 MPa), 4; and separation vessel (separation conditions at 60 ºC and 8 MPa), 5.

Table 3-1: Energy requirements in the solvent cycle for extraction conditions at 40 ºC and 30 MPa, and separation conditions at 60 ºC and 8 MPa.

Item	Energy requirement (kJ/kg)
Heating	192.7
Cooling	222.1
Electric	34.6

3.2.2 Extraction conditions and process simulation

Being selected substrate and extraction and separation conditions coincidental, values of physical properties [density (ρ), viscosity (μ), diffusivity (D_{12}) and saturation concentration (C_{sat}) of oil in CO_2, and effective diffusivity of oil in the substrate (D_e) at extraction conditions, and saturation concentration of oil in CO_2 at separation conditions (C_{sep}) reported in Table 3-2 were taken from Núñez *et al.* (2011). The physical properties (ρ and μ) of CO_2 were estimated using NIST Database (Lemmon *et al.*, 2010) for pure CO_2. For the purpose of the manuscript, authors assumed that prepressed oilseeds contained 20% oil (C_o = 0.20 kg oil per kg substrate), and packed in a bed with 36% interparticle void volume (ε_b = 0.36) and bulk density ρ_b = 500 kg/m^3. Authors also assumed that extraction was carried out in a 1-m^3 vessel with a shape characterized by an aspect ratio of 4.5 (D = 65.6 cm, L = 2.96 m).

SC CO_2 extraction of prepressed oilseed was simulated using the algorithm of Núñez *et al.* (2011) using a predictive model for the inner mass transfer in the substrate based on the shrinking-core hypothesis. The original algorithm was programmed in MATLAB to describe dynamics in a three-vessel SCFE plant. For the purposes of this manuscript, the algorithm was modified slightly to simulate also the pseudo-steady-state operation in two- and four-vessel SCFE plants. Besides the number of vessel in the plant, two additional parameters that affect extraction rate were modified in this work,

Table 3-2: Physical properties of the CO_2 at extraction conditions (40 ºC and 30 MPa), oil solubility in CO_2 at extraction and separation (60 ºC and 8 MPa) conditions, and effective diffusivity of oil in the substrate

Parameter	Value	Unit
ρ	909.9	$kg \cdot m^{-3}$
μ	9.4×10^{-5}	Pa·s
C_{sat}	7.915×10^{-3}	kg oil·kg^{-1} CO_2
C_{sep}	0.164×10^{-3}	kg oil·kg^{-1} CO_2
D_{12}	3.0×10^{-9}	$m^2 \cdot s^{-1}$
F	0.172	-
D_e ($=F \times D_{12}$)	5.2×10^{-10}	$m^2 \cdot s^{-1}$

the diameter of prepressed oilseed particles ($0.5 \leq d_p \leq 4$ mm), and the volumetric flow rate of CO_2 ($3.30 \leq Q_{CO2} \leq 13.2$ m^3/h). The volumetric flow rate of the solvent and cross section of the extraction vessel (0.332 m^2) determine the superficial velocity of CO_2 in the packed bed ($2.76 \leq U \leq 11.0$ mm/s). The incipient fluidization velocity (U_{mf}) of the particles was estimated using the procedure of Yang et al. (1985) for each combination of d_p and Q_{CO2}, and for those conditions where U_{mf} was below U no simulations were carried to optimize operation time (conditions that permitted fluidization of particle in the packed bed were disregarded). Values of physical properties in Table 3-2, d_p, and U defined values of additional mass transfer parameters, such as the axial dispersion coefficient (D_L) that was estimated using the correlation of del Valle *et al.* (2011), and the film mass transfer coefficient (k_f) that was estimated using the correlation of King and Catchpole (1993).

Outputs of the simulation program included the yield and residual concentration of oil in CO_2 in the vessel as a function of extraction time. Oil yield was estimated as the product of "extracted oil concentration" (Núñez *et al.*, 2011) and mass flow rate of CO_2 in the stream exiting the extraction vessel integrated over extraction time. Residual oil

concentration was estimated as the average concentration of oil in the SC CO_2 within the extraction vessel at any particular time. These values were estimated continuously during the simulation of a two-vessel SCFE plant. On the other hand, for each extraction time simulations went through three whole cycles to reach a pseudo-stationary-state in three- or four-vessel SCFE plants (Núñez *et al.*, 2011). Each cycle included two changes in the extraction vessel sequence (switches) in the three-vessel SCFE plant, or three switches in the four-vessel plant.

3.2.3 Estimation of operational cost

To estimate operational costs, these were divided first in two categories: (i) the ones depending on the solvent cycle corresponding to the cost of energy to pump, heat, cool, or condense CO_2 and that are proportional to volumetric flow rate of CO_2 and extraction time; and, (ii) the ones associated with the operation of extraction vessels such as the costs of prepressed oilseeds (0.5 USD/kg, Lack and Seidlitz, 2010), CO_2 make-up (0.4 USD/kg, Lack and Seidlitz, 2001), and energy to depressurize and re-pressurize the vessel. The cost of the solvent cycle can be estimated as the weighted average of the energy requirements in Table 3-1 and the costs of heat (6 USD/GJ, SuperPro Designer 7.5 evaluation version), cooling water (19 USD/GJ, SuperPro Designer 7.5 evaluation version), and electricity (17 USD/GJ, Rosa and Meireles, 2005).

The amount of CO_2 lost with the substrate was estimated assuming that part of it up to a final pressure of 6.4 MPa was recovered in the solvent cycle, and the remainder vented to the atmosphere. Considering the density of CO_2 at 40 °C and 6.4 MPa (166.7 kg/m^3, Lemmon *et al.*, 2010) and the extra space in the extraction vessel resulting from the removal of oil (ε_t = 0.60 at most), authors estimated that 100 kg CO_2 could be vented from a 1-m^3 vessel. Although CO_2 lost with the recovered oil in the separator should be considered as an item in the first category (dependent on the solvent cycle), authors decided to include it in the second one because it can be estimated directly based on the output of the simulation program. Indeed, when assuming complete recovery of CO_2-saturated oil an estimate of 0.1 kg CO_2 lost per kg of extracted oil can be estimated

based on the solubility of a typical vegetable oil in SC CO_2 at 60 °C and 8 MPa (Klein and Schulz, 1989).

Appendix A summarizes calculations of energy requirement for depressurization (heat supplied to the extraction vessel to minimize safety concerns associated with dry ice formation in extraction vessel and venting lines) and repressurization (CO_2 precooling, compression, and cooling to extraction conditions) of the extraction vessel. Considering these requirements and aforementioned prices of heat, cooling water, and electricity, authors estimated cost of USD 0.221 for decompression, and USD 0.669 for recompression of a 1-m^3 extraction vessel.

There are more cost items in addition to the operational costs of the solvent cycle and those associated with the operation of the extraction vessel. These additional items include manpower (three operators per 8-h shift for continuous operation, at a cost of 7.0 USD/h-man, Lack and Seidlitz, 2001), and auxiliaries and other minor costs (administration, maintenance, and energy requirement of closure systems of extraction vessels, among others), which were assumed to account for 5% of the operational costs.

The operational cost was expressed per unit of extracted oil. Besides the oil accounted by extraction yield, there is some additional oil that may be considered in computations. Indeed, part of the oil dissolved in the CO_2 remaining in the extraction vessel at the end of the extraction process can be recovered in the solvent cycle, whereas the remaining part condenses back in the substrate as a result of the reduction in the solvation capacity of SC CO_2 during depressurization. The amount of complimentary oil recovered was computed as informed in Appendix B.

When computing the operational cost of a batch, authors considered that they also depend on the number of extraction vessels of the SCFE plant. Indeed, at any time in two out of the three periods limited by switches in the solvent cycle that define a whole extraction cycle (including the reconditioning of the extraction vessel), a single extraction vessel in a three-vessel SCFE plant shares solvent cycle costs with another vessel, and shares manpower costs with the two other vessels permanently (in three out

of these three periods). On the other hand, the extraction vessel in a four-vessel SCFE plant shares solvent cycle costs with another two vessels in three out of the four periods limited by switches in the solvent cycle, and shares manpower costs with all vessels, so that for each whole extraction cycle (including the reconditioning of the extraction vessel) a vessel can be imputed the whole cost of the solvent cycle, manpower, auxiliaries, and other minor costs for the duration of a single in-between-switches period. Readers can surmise the validity of Eq. (3.1) for the operational cost of an industrial *n*-vessel SCFE plant expressed per unit weight of recovered oil:

$$C_{\text{operational}} = \frac{290.703 + t_{\text{extraction}} \cdot \{21.007 \cdot Q + 0.04 \cdot Y\}}{500 \cdot Y + 4.321 \cdot M_{\text{final oil average}}} \tag{3.1}$$

3.3 Results

The optimal extraction time and minimal operational cost diminish as particle size decreases. This is illustrated in Fig. 3-3 for the extraction of vegetable oil from prepressed oilseed particles of 0.5 to 4 mm diameter in an industrial two-vessel SCFE plant that uses 3.30 m^3/h of SC CO_2 at 40 ºC and 30 MPa (U = 2.75 mm/s) as the solvent. Curves for 0.5-mm and 1-mm particles virtually overlap. Furthermore, the shape of these two curves differ from the others in that the operational cost increases more sharply when extraction time increases above the optimal, so that the cost depends markedly on extraction time unlike when using larger particles ($d_p \geq 2$ mm). Another difference between ≤ 1 mm (small) and ≥ 2 mm (medium-to-large) particles is that the optimal extraction time virtually coincides with complete extraction of the substrate in the former case.

Fig. 3-4 explains the difference in the dependence of the operational cost on extraction time between small ($d_p \leq 1$ mm) and medium-to-large ($d_p \geq 2$ mm) particles. Indeed the dimensionless concentration profile of the oil (oil concentration in the stream leaving the extraction vessel expressed as C/C_{sat} *versus* extraction time) to a practical extent corresponds to a step change for small particles, which is in turn associated to the

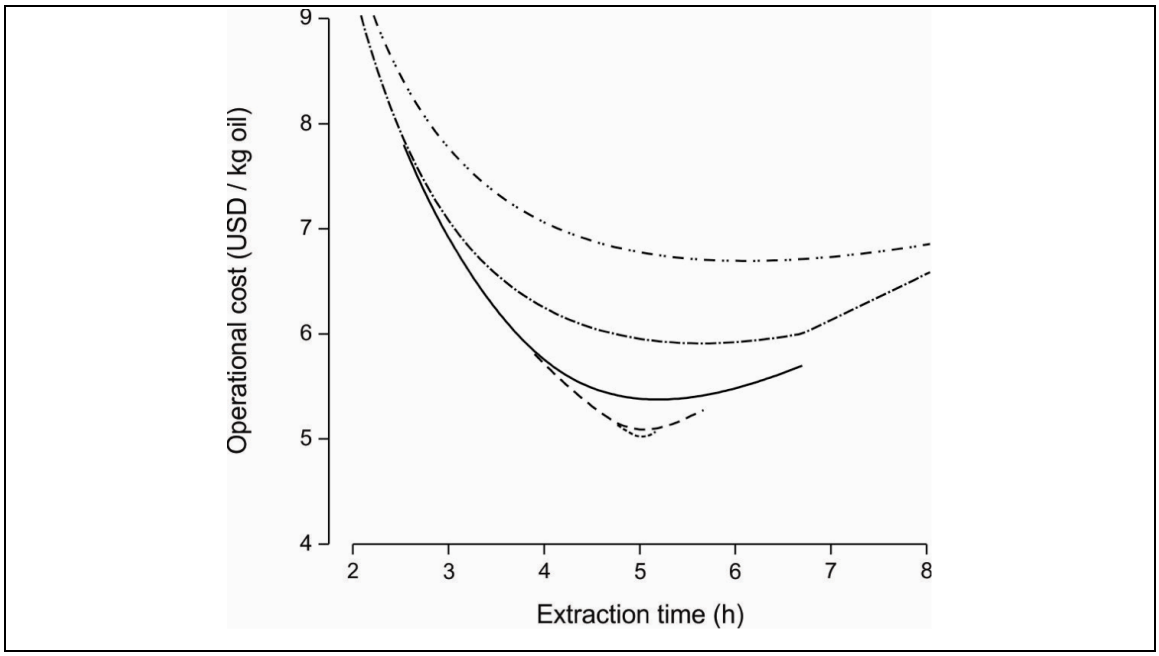

Figure 3-3: Effect of particle size on changes in operational cost for a two-vessel SCFE plant using Q_{CO2} = 55 L/min (U = 2.8 mm/s) as a function of extraction time. Particle diameters are (·····) 0.5 mm, (– – –) 1 mm, (——) 2 mm, (–·–·–) 3 mm, and (– ·· –) 4 mm.

displacement of a wave of oil-saturated CO_2 along the extraction vessel. This step change in oil concentration in SC CO_2 in an intermediate position of the extraction vessel is due to the fast extraction of small particles that allows saturation of the SC CO_2 stream with the oil in a thin section of the vessel. As a result of saturation no further removal of oil is possible upstream from this moving wave. Downstream from the moving wave, particles are rapidly depleted. Reverchon and Marrone (1997) modeled mass transfer during SCFE of clove bud essential oil at 50 ºC and 9 MPa neglecting mass transfer resistance and using a linear equilibrium relationship, and informed waves of extract-saturated SC CO_2 stream. That is not the case for medium-to-large particles for which restrictions to mass transfer within particles precludes saturation of SC CO_2 with oil in a thin section of the extraction vessel. This causes a smooth decline in oil

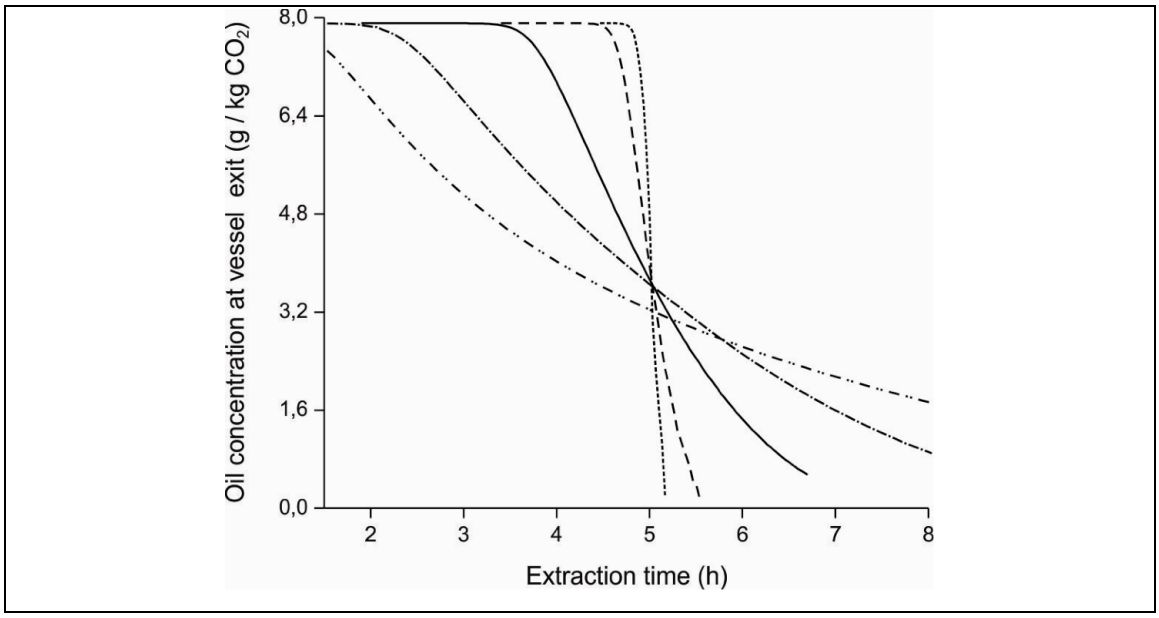

Figure 3-4: Dimensionless oil concentration (C/C_{sat}) at the exit of an extraction vessel placed in a two-vessel plant in function of extraction time for $0.5 \leq d_p \leq 4$ mm, using Q_{CO2} = 55 L/min (U = 2.8 mm/s). In all cases the extraction was simulated at least to the exhaustion of the substrate. Particle diameters are (·····) 0.5 mm, (– – –) 1 mm, (——) 2 mm, (–·–·–) 3 mm, and (– ·· –) 4 mm.

concentration in the SC CO_2 stream leaving the vessel (Fig. 3-4). Trends for the dependence of optimal extraction time in industrial two-vessel SCFE plants as a function of the diameter of prepressed oilseed particles were similar to those observed in Fig. 3-3 when increasing the superficial velocity of CO_2. However, the optimal time decreases when increasing Q_{CO2} because of the increase in extraction rate (the external resistance in the fluid film surrounding the particles decreases) and the increase in solvent-to-substrate ratio, *SSR* (kg kg^{-1} CO_2/substrate), Eq. (3.2) (unreported results):

$$SSR = \frac{Q_{CO_2}\, t}{M} \tag{3.2}$$

Fig. 3-5 summarizes minimal operational costs as a function of d_p and U for the 1-m^3 extraction vessel in the industrial two-vessel SCFE plant. Authors did not simulate

the extraction of 1-mm particles using 13.2 m^3/h of CO_2 (U = 11.0 mm/s) or of 0.5-mm particles using 6.60 m^3/h (U = 5.52 mm/s) or 13.2 m^3/h of CO_2 because under these conditions U is above the particles' U_{mf} (U_{mf} = 6.73 mm/s for 1-mm particles and U_{mf} = 2.93 for 0.5-mm particles). In all cases minimal cost decreases as d_p decreases but, because cost depends more pronouncedly on d_p as U increases, the optimal superficial velocity of CO_2 depends on particle size: as d_p increases, optimal U decreases. Under studied conditions, operational cost is the highest when U = 11.0 mm/s for particles larger than 2 mm. The increase in Q_{CO2} (or U) increases extraction rate and decreases extraction time with a resulting decrease in the operational cost of the extraction vessel, but at the expense of an increase in the energy consumption and cost of the solvent cycle per unit time.

When simulating an industrial two-vessel SCFE plant, the operational cost can be estimated step-by-step during the simulation. This is not possible for plants having three or more vessels, in which case a switch time must be selected first, and then several iterations of the simulation program are run to converge to the pseudo-state-condition of the plant (Núñez *et al.*, 2011). Thus, estimating the operational cost requires separate simulations for each extraction time. To save on computational time, an algorithm was developed based on observations of the dependence of operational cost on extraction time for the industrial two-vessel SCFE plant. Apparently, the operational cost is a continuous, smooth function exhibiting a minimal (Fig. 3-3). Because of that, the minimal is always located within an interval where an intermediate (middle) time has lower operational cost than the two extremes. When that condition was identified, the two intervals (from the lower to the middle extraction time, and from the middle to the upper extraction time) were halved, new simulations were carried out for these intermediate times, and a new interval containing the minimal was identified.

This procedure can be repeated with the end result of a reduction in half of the interval containing the minimal after each step. Because extraction times were spaced 80 min initially, the procedure had to be repeated four times (two additional simulations in each step) to identify the 10-min interval where the optimal extraction time was located.

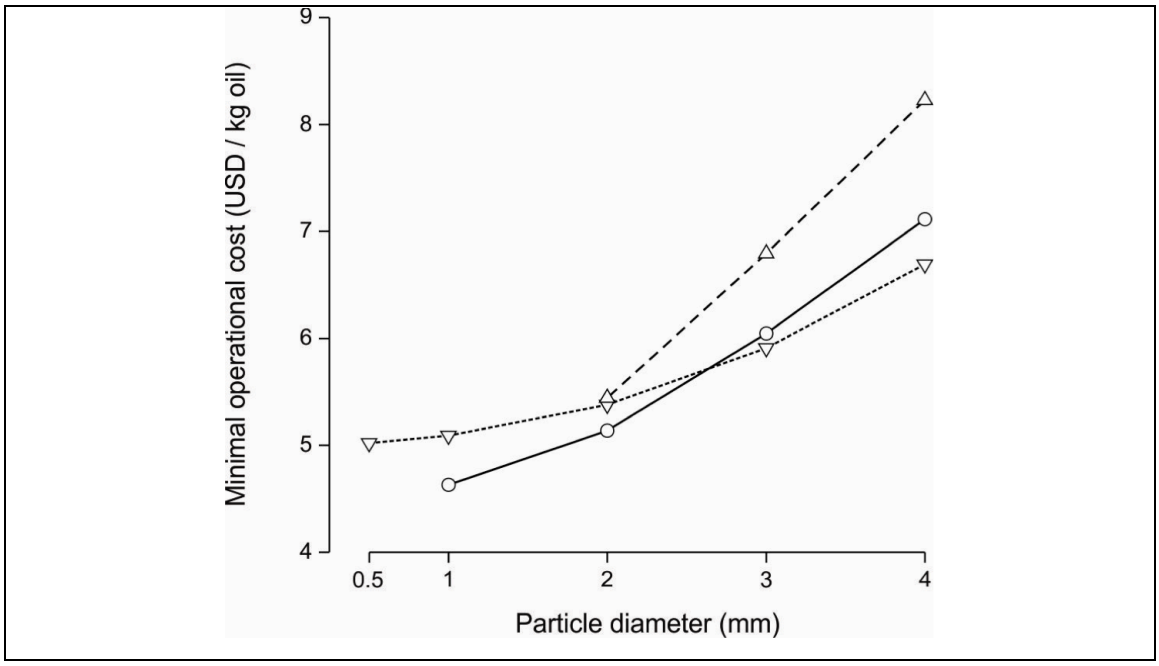

Figure 3-5: Summary of the minimum operational cost in function of d_p and U for a two-vessel SCFE plant. Superficial CO_2 velocities are (···▽···) 2.71 mm/s, (—○—) 5.52 mm/s, and (– △ –) 10.83 mm/s.

As an initial guess, optimal extraction times for the industrial two-vessel SCFE plants were considered, because the optimal extraction time increases when the number of extraction vessels of the plant increase. If the operational cost for the second simulation was higher than the first simulation, a third simulation was run for an extraction time below the initial value, and subsequent simulations were run reducing the extraction time 40 min up to identifying an 80 min interval where the optimal was located. Otherwise, the true function of the operational cost *versus* extraction time was explored by increasing extraction time 40 min in each simulation up to locating the 80-min interval containing the optimal. This, together with the mathematical expression for the effect of extraction time on operational cost, Eq. (3.3), allowed an accurate description of the true function of the operational cost *versus* extraction time.

$$C = a + b \cdot t + \frac{c}{t^d} \tag{3.3}$$

where t is the extraction time and a, b, c, and d are fit parameters for each case studied.

The same as for the industrial two-vessel SCFE plant, optimal extraction times diminish as particle diameter decreases and as superficial CO_2 velocity increases in three- and four-vessel plants. This is illustrated in Fig. 3-6A for the SC CO_2 extraction of medium-to-large ($d_p \geq 2$ mm) oilseed particles in three-vessel plants. The operational cost also decreases as the particle diameter decreases for all superficial CO_2 velocities (data for 3- and 4-mm particles not shown). On the other hand, there is no consistent trend for changes in operational cost as a function of superficial solvent velocity. Similar trends were observed for industrial four-vessel SCFE plants (Fig. 3-6B).

Fig. 3-7 summarizes results for the minimal operational cost for medium-to-large oilseed particles as a function of superficial CO_2 velocity in the three- and four-vessel plants. The same as for the two-vessel plants, optimal superficial CO_2 velocity depends on particle diameter; it decreases as the particle diameter increases. It is surmised that U = 5.52 mm/s is better than U = 2.76 mm/s for particles smaller than 3-to-4 mm, and that U = 2.76 mm/s is better than U = 5.52 mm/s for larger particles.

Optimal extraction time decreases as the number of extraction vessel of the industrial SCFE plant decrease, but at the expense of an increase in operational cost (Fig. 3-8). The trend shown in Fig. 8 for d_p = 2 mm and Q_{CO2} = 6.60 m^3/h is a general one that applied for all combinations of d_p and Q_{CO2}. This is explained by the cumulative extraction curves (Fig. 3-9A) and the profiles of oil concentration *versus* time in the CO_2 stream leaving the extraction vessels and entering the separator (Fig. 3-9B). Extraction rate decreases as the number of vessels of the industrial SCFE plant increase because of the decreasing driving force for extraction (the differences in oil concentration between the SC CO_2 stream entering the vessel and the substrate) in the vessels upstream in the solvent cycle. However the concentration of oil in the SC CO_2 stream leaving the extraction vessel placed last in the solvent cycle increases as the number of extraction vessels increase (Fig. 3-9B) because of improved usage of the solvent when the contact between SC CO_2 and the substrate approaches a countercurrent pattern (Núñez *et al.*, 2011).

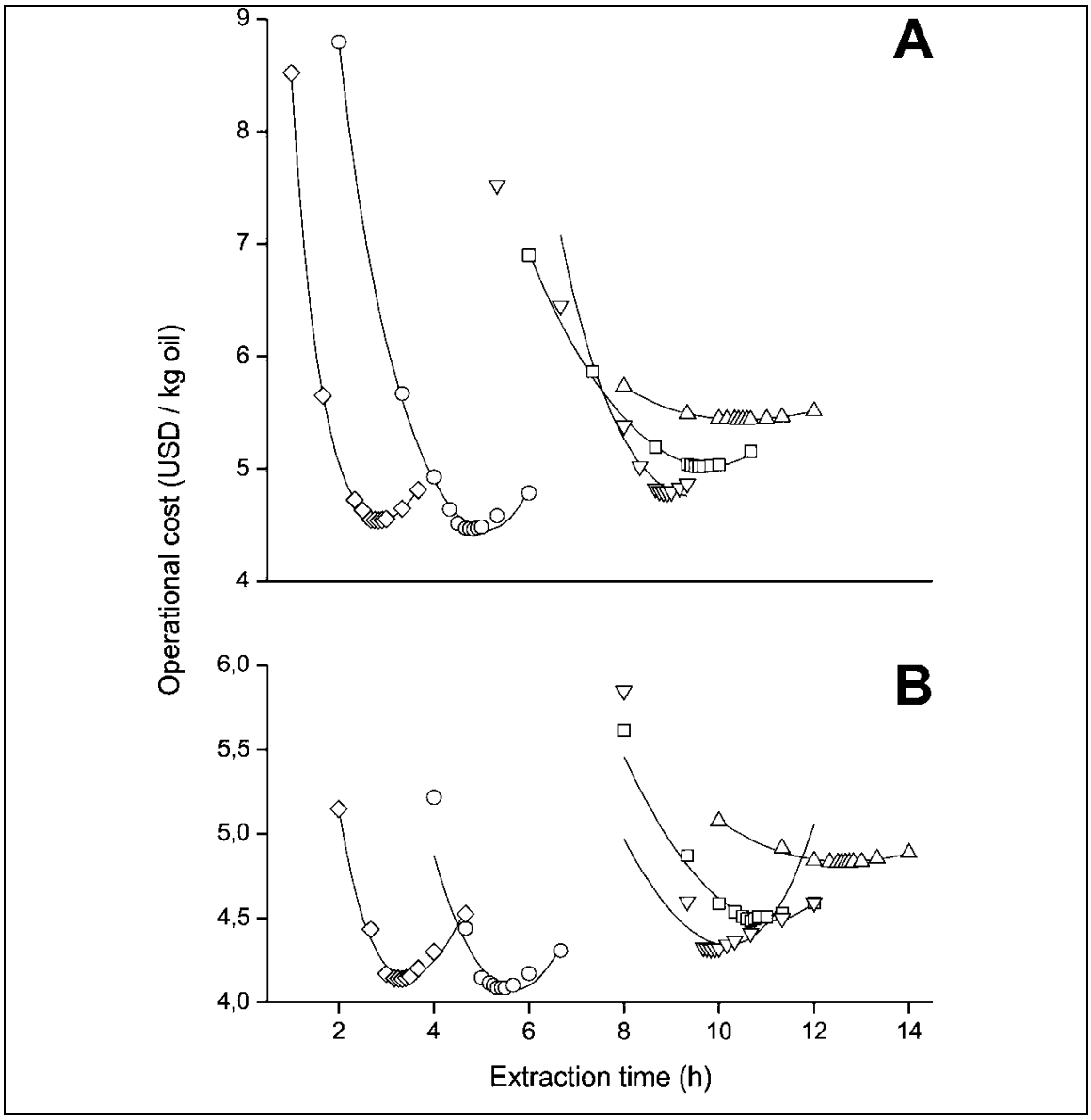

Figure 3-6: Combined effect of d_p and U on operational cost for industrial **(A)** three-vessel or **(B)** four-vessel SCFE plants as a function of extraction time. The combinations of particle diameter (d_p, mm) and superficial CO_2 velocity (U, mm/s) are (△) 4 mm and 2.71 mm/s, (□) 3 mm and 2.71 mm/s, (▽) 2 mm and 2.71 mm/s, (○) 2 mm and 5.52 mm/s, and (◇) 2 mm and 10.83 mm/s.

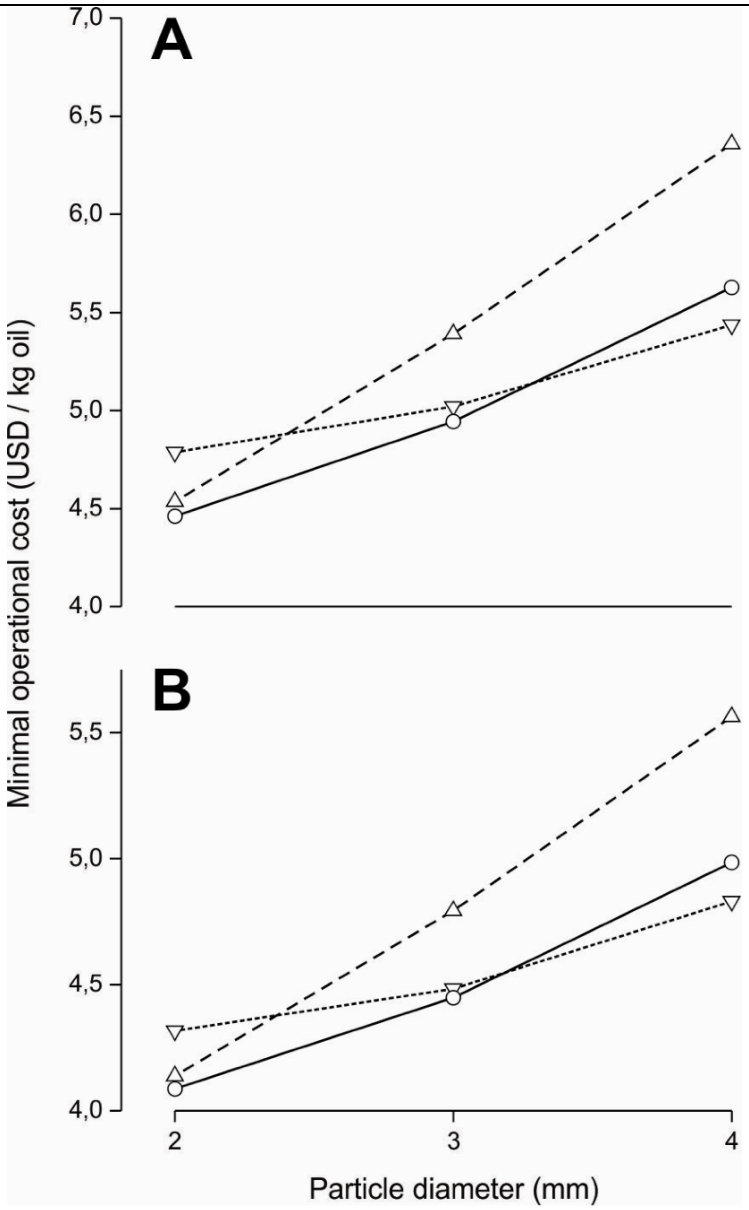

Figure 3-7: Summary of the minimum operational cost in function of d_p and U for a SCFE plant with (A) n = 3, and (B) n = 4 extraction vessels. Superficial CO_2 velocities are (···▽···) 2.71 mm/s, (—○—) 5.52 mm/s, and (– △ –) 10.83 mm/s.

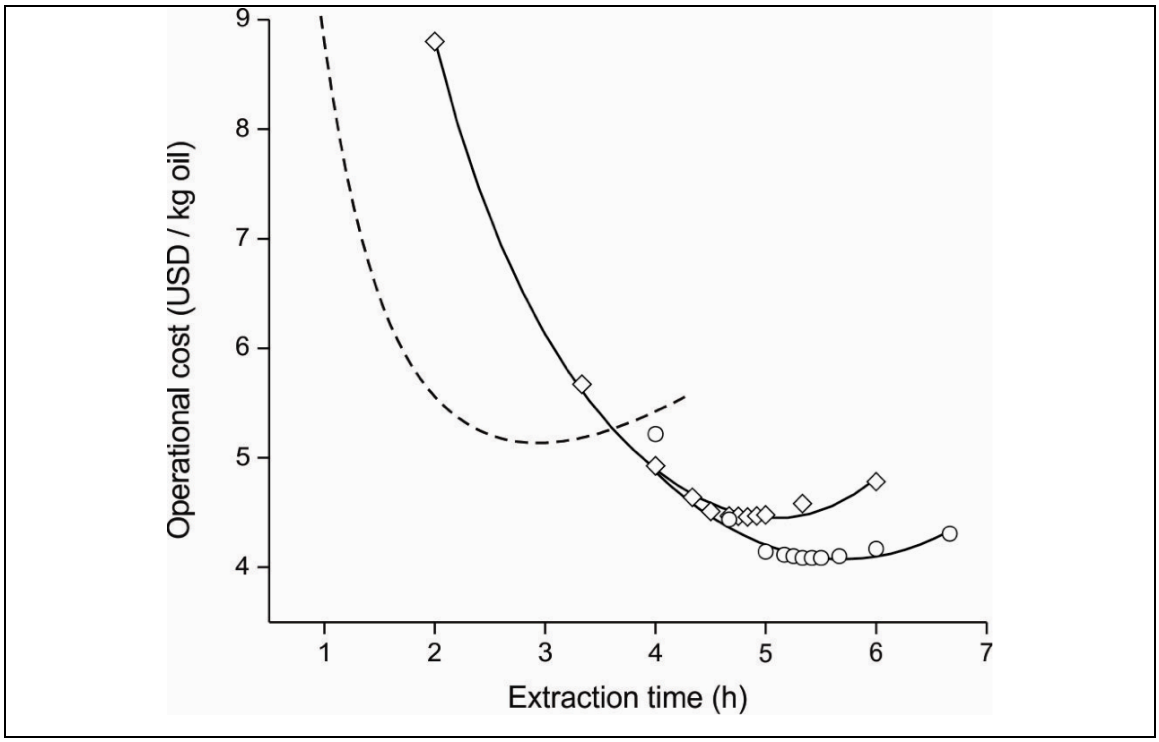

Figure 3-8: Effect of extraction vessel number on operational cost in function of extraction time for a SCFE processing particles of 2 mm and using 110 L/min of CO_2. The number of vessels of the industrial SC CO_2 extraction plant are (- - -) two, (◇) three, or (○) four.

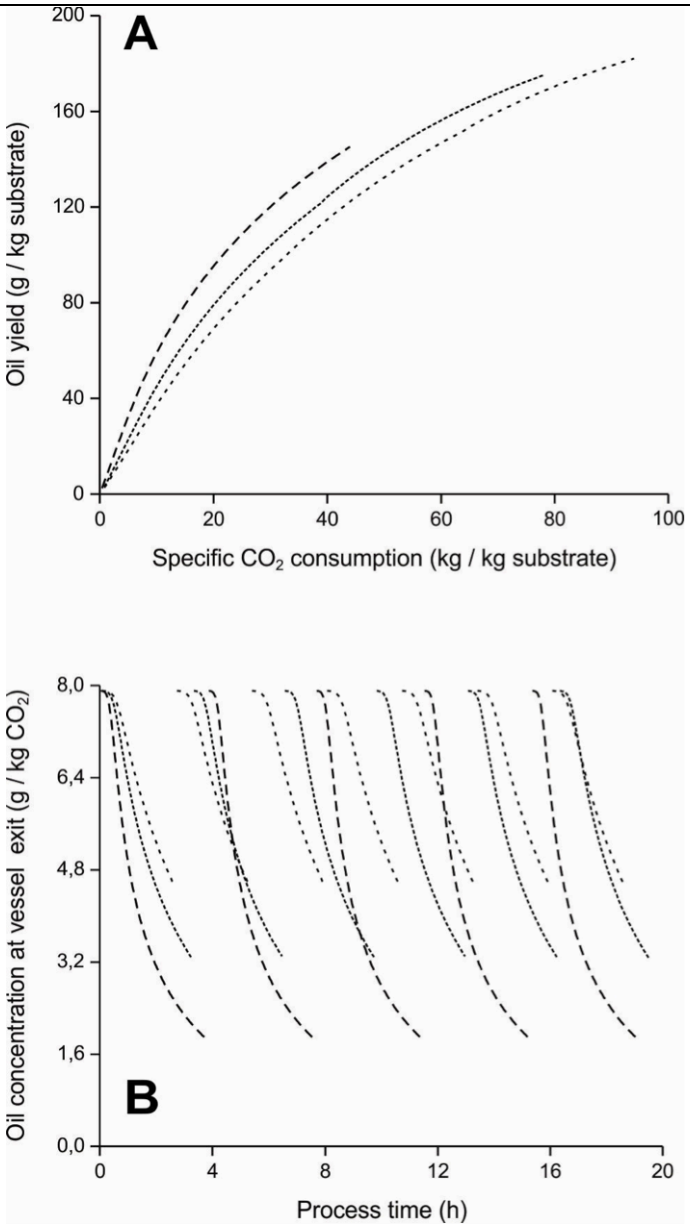

Figure 3-9: Effect of number of extraction vessels in (A) the extraction yield curves for extraction of particles of 4 mm using 110 L/min of CO_2 and (B) the dimensionless oil concentration of the CO_2 stream exiting an extraction vessel. In both cases show consider the optimum operational cost point. The number of vessels of the industrial SC CO_2 extraction plant are (– – –) two, (·····) three, or (- - - - ·) four.

3.4 Discussion

This work illustrates the dependency of cumulative extraction curves on plant configuration for industrial multi-vessel SCFE plants, which precludes using curves experimentally obtained in one-vessel laboratory or pilot plant units to estimate the dependence on extraction time of extract yield, at least for the more convenient plants having three or more vessels. Indeed the reduction in extraction rate in the latter plants (Fig. 3-9A) is compensated by an improved usage of the driving force for extraction between the SC CO_2 stream circling the solvent cycle and the stationary substrate in the extraction vessels, with the end result of carryover of more extract to the separator (Fig. 3-9B).

Although extraction rate increases as particle diameter increases, it is apparent that there is no advantage in using industrial SCFE plants having more than two extraction vessels when processing small ($\leq$ 1 mm) particles because under those conditions (limited inner resistances to mass transfer) a sharp transition develops along the extraction vessel (Fig. 3-4). Away from this transition zone no extraction is possible because either the substrate is exhausted (downstream) or the SC CO_2 stream is saturated with oil (upstream). This causes that during the first part of the extraction process (when the aforementioned wave is still moving along the vessel placed first in the solvent cycle) there is no removal of oil in the extraction vessel placed second in the solvent cycle of an industrial three-vessel SCFE plant. The operation of a four-vessel plant is even less convenient. For this reason, analysis of three- or four-vessel SCFE plant was limited to medium-to-large ($\geq$2 mm) particles.

Despite results in Fig. 3-4, use of small ($\leq$ 1 mm) particles may be inconvenient when operating industrial two-vessel SCFE plants for several reasons. Particles fluidize at progressively smaller superficial velocities as their size decreases, and these small particles may block the screens of product baskets that prevent entrainment of particulates in the solvent cycle. Consequently, it is not possible taking full advantage of improved economics when using high superficial CO_2 velocities. This is especially

relevant considering that the positive effect on operational cost of the reduction in particle size becomes progressively smaller as the superficial velocity of CO_2 decreases.

Besides the eventual limitation brought about by fluidization of particles, another effect of particle diameter on operational cost that authors disregarded is related to the packing characteristics of oilseed particles. There are reasons to believe that small particles are more prone to experience undesirable agglomeration problems (del Valle *et al.*, 2012b; del Valle *et al.*, 2008). Agglomeration depends also on substrate moisture and has been observed in oilseeds (Eggers *et al.*, 2000). It negatively impacts SC CO_2 extraction by causing solvent channeling in the packed bed. Small particles have larger specific surface than larger ones with the end result of an increase in contact points in the packed bed where particles can stick together and prevent passage of CO_2 (del Valle *et al.*, 2012b; del Valle *et al.*, 2008). This is more problematic for deformable particles exposed to axial compression. It can be possible to increase bulk density of the substrate in the packed bed, another parameter that affects extraction cost (Lack and Seidlitz, 2001), not taken into account in this manuscript, by applying axial compression in attempts.

Optimal flow rate of CO_2 depends on particle diameter and number of extraction vessels (Fig. 3-5 and Fig. 3-6). It increases as particle diameter decreases, and is limited to 6.6 m^3/h for practical purposes; values as large as 13.2 m^3/h are best only for small ($\leq$1 mm) particles. Among tested values, the superficial velocity recommended in this article is 2.75 mm/s for particles slightly less than 3-mm diameter being extracted in industrial two-vessel SCFE plants or particles of 3-to-4 mm in industrial three- or four-vessel SCFE plants. The recommended superficial velocity increases to 5.50 mm/s for smaller particles. As the superficial velocity of CO_2 increases the film coefficient k_f increases so that there is less resistance to oil transfer from the particle surface to the bulk of the SC CO_2 phase. This manuscript shows that this is the case for 2-mm-particles when the superficial velocity is in the upper limit recommended in literature (1-to-5 mm/s for the SC CO_2 extraction of oilseeds, Eggers, 1996). Increasing superficial CO_2

velocity is of limited advantage, however, when mass transfer is limited by inner resistances within the prepressed oilseed, as in the case of large particles.

There is some information in literature on economics of SC CO_2 extraction of oil from vegetable substrates, but this exhibits considerable variation. The highest reported cost is 17.2 USD/kg oil for the extraction of palm tree (containing 7.5-15% oil) using SC CO_2 at 40-55 ºC and 20-30 MPa (Prado *et al.*, 2010). The lowest reported value is 0.633 USD/kg (estimated from data of Bravi *et al.*, 2002, using an exchange rate of 0.946 USD/€ for 2002; Oanda.com, 2011) for the extraction of oil from sunflower seeds (containing 49.2% w/w oil) using SC CO_2 at 40 ºC and 28 MPa. Authors believe this low cost is questionable for several reasons. Bravi *et al.* (2002) proposed using an unreasonably large superficial velocity (32.8 mm/s) that would fluidize particle as large as 12.4 mm in diameter (particle diameter was not reported), and claimed extraction completion in 10 min. This short time, however, is deemed insufficient to complete the stages involved in the reconditioning of an industrial extraction vessel (Quirin, 2010).

Although some of the variation may be due to differences in the substrate (oil content), there are differences in extraction cost for the same substrate as well. The cost of grape seed (containing 12% w/w oil [30]) oil decreases from USD 11.9/kg for SC CO_2 extraction at 40 °C and 35 MPa (Prado *et al.*, 2012) to 4.45 USD/kg (estimated using an exchange rate of 0.745 USD/€ for 2010, www.oanda.com) for SC CO_2 extraction at 60 °C and 55 MPa (Fiori, 2010). Part of the difference is explained by the difference in extraction pressure, because the extraction cost is lower at 55 MPa than at 30 MPa (Fiori, 2010). Another part of the difference is explained by economies of scale because estimates are based on annual oil productions of 66.4 ton when using an industrial two-vessel (0.5 m^3 capacity each) SCF plant (Prado *et al.*, 2012) or 306 ton when using a three-vessel (0.8 m^3 capacity each) plant (Fiori, 2010). The SC CO_2 extraction cost reported by Fiori (2010) for grape seed approaches the one reported Mezzomo *et al.* (2011) for peach kernel (USD 4.64/kg oil) that contains about the same amount of oil (13.2%, Mezzomo *et al.*, 2009). This result is surprising because the estimate of Mezzomo *et al.* (2011) assumed that extractions were carried out at lower

pressure (40 °C and 20 MPa) in a smaller industrial two-vessel (0.4 m^3 capacity each) SCFE plant.

The operational cost in the present study is difficult to compare with reported SC CO_2 extraction costs for other oil-containing vegetable substrates in literature, not only because of differences in the substrate and its pretreatment, extraction conditions, and industrial SCFE plant size, but also because in this study capital costs were not included (*i.e.*, the total extraction cost is above the USD 4.081-8.149/kg oil values reported in here). Authors would like to stress relevant differences under the prism of results reported in here. 1) Bulk densities (from 600 kg/m^3, Fiori, 2010; to 950 kg/m^3, Prado *et al.*, 2012) are larger than assumed in here. 2) Particle diameters as below recommended in here for industrial SCFE plants having three or more extraction vessels; Fiori (2010) proposes using 0.4-mm particles. 3) Superficial CO_2 velocities are up to one order of magnitude below recommended in here (0.26 mm/s in the study of Prado *et al.*, 2012), which is especially relevant considering the use of small particles.

4. SUPERCRITICAL CO_2 OILSEED EXTRACTION IN MULTI-VESSELPLANTS. 2. EFFECT OF NUMBER AND GEOMETRY OF EXTRACTORS ON PRODUCTION COST

Abstract

This work presents the production costs for the supercritical CO_2 extraction of oilseed (packed bed with particles of 2 mm) in a 2 m^3 industrial multi-vessel plant operating at 40 °C and 30 MPa, using a fully predictive mass transfer model to simulate the process. This work analyses the effect of geometry of the plant (aspect ratio, $3 \geq L/D \geq 8$), superficial CO_2 velocity ($2.71 \geq U \geq 10.4$ mm/s) and number of extraction vessel (2, 3, or 4) on optimal extraction time and minimal production cost. Authors proposed a mathematical expression to estimate the capital cost of a supercritical CO_2 extraction plant, identifying separately the contribution of the extraction vessels and the solvent cycle to the total cost of the plant. The range for the capital cost estimated was MM$ 4.5-6.4. Keeping other variables constant, the production cost decreases when the number of extraction vessels increases, and optimal extraction time presents a maximum for three-vessel plants, comparing with two- and four-vessel plants. The lowest production cost observed in this work was USD 7.808/kg oil for a mass flow rate of 6000 kg/h (U = 10.4 mm/s) in a four-vessel plant (aspect ratio, L/D = 6).

Keywords: Capital cost; extraction; industrial plant; optimal extraction time; production cost; prepressed oilseed; supercritical CO_2.

4.1 Introduction

The decision to apply SuperCritical Fluid Extraction (SCFE) to recover commercially high-value compounds from selected biological substrates demands accurate cost estimates. del Valle *et al.* (submitted) demostrated the usefulness of mathematical simulation for the optimization of extraction time in the supercritical (SC) CO_2 extraction of vegetable oil from prepressed oilseed in the 1-m^3 vessel of an

industrial multi-vessel SCFE plant operating at 40 °C and 30 MPa. The authors used a fully predictive shrinking-core mass transfer model to minimize the operational cost as a function of particle diameter ($0.5 \leq d_p \leq 4$ mm), superficial CO_2 velocity ($2.75 \leq U \leq 11.0$ mm/s), and number (n) of extraction vessel (2, 3, or 4). They observed that the operational cost diminishes as particle diameter decreases, and as the number of extraction vessels increases (del Valle *et al.*, submitted). However, because of a sharp transition wave that develops when extracting small (≤ 1 mm) particles that separates fully extracted (downstream) from virtually unextracted (upstream) substrate within extractors, del Valle *et al.* (submitted) suggested using industrial two-vessel SCFE plants for small particles, and three- or four-vessel plants for medium-to-large (≥ 2 mm) particles. Finally, del Valle *et al.* (submitted) observed that the optimal superficial CO_2 velocity increases as particle diameter decreases so that, within the studied region, best superficial CO_2 velocities are 11.0 mm/s for particles smaller than 1-to-2 mm, 2.75 mm/s for particles larger than 3-to-4 mm, and 5.50 mm/s for particles in between.

del Valle *et al.* (submitted) estimated an operational cost in a per-batch basis, and excluding the expense of purchasing, installing, and starting-up the industrial SCFE plant, which is adecuate in the situation where the plant has iddle capacity and the plant owner offers toll processing services to third parties. This chapter expands that work (Chapter 3) to include the capital cost component of the production cost, which is more relevant in situations where informed decisions on investment should be taken.

The objective of this work was to study the production cost of the SC CO_2 extraction of oil from prepressed oilseeds in industrial multi-vessel SCFE plants, including capital costs. The analysis focuses here in unveiling the effect of the number and shape (length-to-diamerer, L/D, ratio) of the extraction vessels on the annual cost.

4.2 Cost of industrial supercritical extraction plants

Based on data collected by Separex over several years, Perrut (2000) proposed that the cost of a SCFE plant for solid substrates is a function of its size defined as the

product of the total capacity of the extraction vessels (V_T, in liters), and the capacity of the CO_2 pump (Q, in kilograms of CO_2 per hour), Eq. (4.1):

$$I \propto \left(Q \cdot V_T\right)^{m'} \tag{4.1}$$

In Eq. (4.1), *m'* is a scaling factor that characterizes economies of scale or the reduction in cost when increasing the size of a manufacturing facility; in chemical engineering plant design and economics the most commonly used scaling criteria is the six-tenth rule (Peters *et al.*, 2003), which is an empirical relationship stating that as the size of a facility increases, its cost increases proportionally less, *e.g.*, as the plant size doubles (100% increase in plant size), its cost increases approximately 52% (estimated using Eq. (4.1) with *m*' = 0.6). Perrut (2000) reported *m*' = 0.24 for plants for the extraction of solids, fractionation of liquids, impregnation of solids, and atomization of particles using supercritical fluids and ranging from laboratory to industrial size.

Using Eq. (4.1) to estimate plant cost is problematic because of three reasons. (1) It is useless without the cost of a reference plant of known total capacity of extraction vessels and known capacity of CO_2 pump. Perrut (2000) did not include this information in his manuscript. (2) It suggests that the cost of the plant does not depend on operating pressure, but it should increase steeply as the design pressure increases. (3) It suggests that the cost of the plant does not depend on the number (n) or shape (L/D ratio) of the extraction vessels, but it should decrease as n decreases, and be less for slim (large L/D ratio) than thick (small L/D ratio) extraction vessels.

To tackle the first problem, the cost of a reference plant can be estimated by referring to reports in literature or direct quotes from plant manufacturers (del Valle *et al.*, 2005). To tackle the second problem, all values should be re-estimated for plants with a common pressure rating (P_n, in MPa) by using historical currency exchange rates, Chemical Engineering Plant Cost Index (CECPI) values, and pressure-correction factors to account for variations brought about by differences in currency exchange rate, inflation, and pressure rating. The CEPCI is an economical index (base value in 1957 =

100), that weighs several factors affecting the cost of erecting a process plant in the US including machinery, buildings, installation, and skilled supervision, and that is published monthly in *Chemical Engineering* journal (Vatavuk, 2002).

In this manuscript authors hypothesize that the cost of the plant can be split in two items shown in Fig. 4-1: the constituents of the solvent cycle, that would depend mainly on Q, and the extraction vessels, interconnecting elements, and elements connecting them with the solvent cycle, that would depend on the number (n), volume (V_E, in liters), and shape (L/D) of the extraction vessels, as suggested by Eq. (4.2).

$$I \propto \alpha\left(Q\right)^{m_1} + \beta\, n\left(V_E\right)^{m_2} \tag{4.2}$$

where β is a function of the L/D ratio. If the scaling factor for the solvent cycle (m_1) and the extraction vessels (m_2) coincide, then Eq. (4.2) can be written as follows:

$$I \propto \left[\alpha + \frac{\beta\, n}{\left(Q/V_E\right)^m}\right]\left(Q\right)^m \tag{4.3}$$

In Eq. (4.3), the term Q/V_E is proportional to the specific mass flow rate of CO_2 (q), in kilograms per hour per kilogram of substrate, defined by Eq. (4.4). Term $(Q)^m$, on the other hand, is defined by Eq. (4.5):

$$q = \frac{Q}{\rho_b V_E} \tag{4.4}$$

$$\left(Q\right)^m = \left(Q \cdot Q\right)^{m/2} = \left(Q \cdot q\ \rho_b V_E\right)^{m/2} = \left(q\ \rho_b Q \cdot \frac{V_T}{n}\right)^{m/2} = \left(\frac{q\ \rho_b}{n}\right)^{m/2} \left(Q \cdot V_T\right)^{m/2} \tag{4.5}$$

where ρ_b is the bulk density of the pretreated substrate. Replacing Eq. (4.4) and Eq. (4.5) in Eq. (4.2), the latter can be written as follows:

$$I \propto \left(\frac{q\ \rho_b}{n} \right)^{m/2} \left[\alpha + \frac{\beta\ n}{\left(q\ \rho_b \right)^m} \right] \left(Q \cdot V_T \right)^{m/2} \tag{4.6}$$

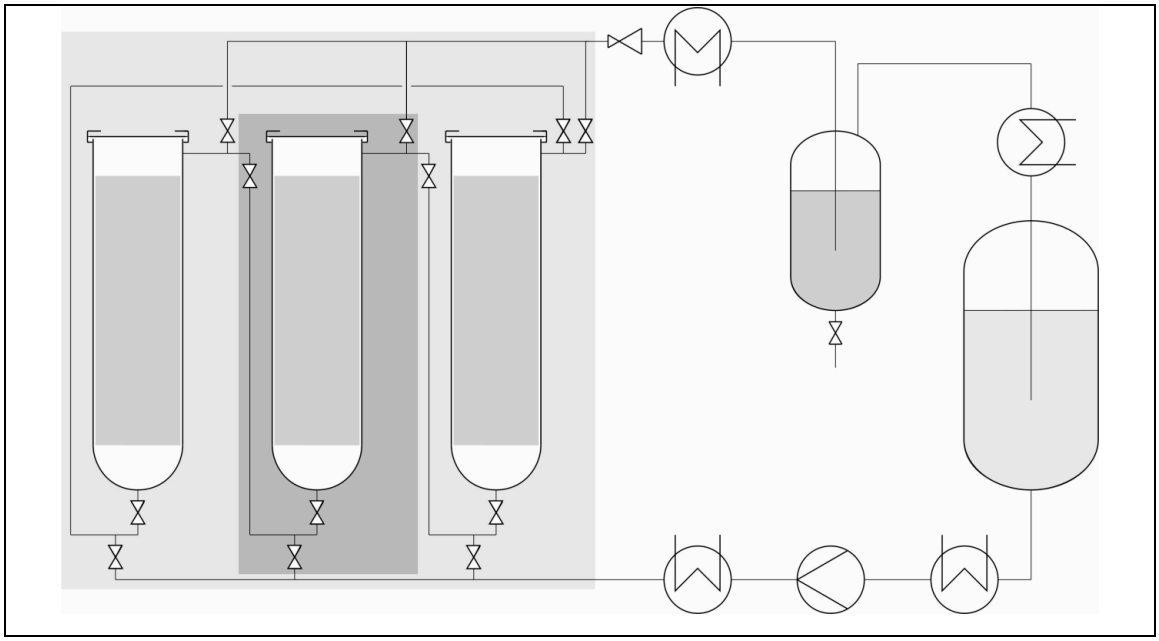

Figure 4-1: Flow diagram of a supercritical fluid extraction plant differentiating the constituents of the solvents cycle, on one hand, and the extraction vessels, interconnecting elements, and elements connecting them with the solvent cycle (under-layered in grey), on the other hand. The extraction vessels part in this example is constituted of three identical units, similar to the one in the middle under-layered in darker grey.

Eq. (4.1) and Eq. (4.6) can fortuitously coincide if the product of the first two terms on the right of Eq. (6) is constant and $m' = m/2$. The value $m' = 0.24$ reported by Perrut (2000) then implies $m = 0.48$ as the scaling factor for SCFE plants. Thus, in this manuscript authors hypothesized a scaling factor for industrial SCFE plants between 0.48 and 0.60 (six-tenth rule). Keeping constant the packing of the substrate in the extraction vessels (ρ_b) and the specific mass flow rate of CO_2 (q) contributes to a

fortuitous coincidence between Eqs. (4.1) and (4.6). Eggers (1996) recommends values of q between 10 and 50 kg/h of CO_2 per kg substrate for the SCFE of oilseeds. Considering this analysis, we used Eq. (4.2) to correlate literature and other information on SCFE plant costs, which was re-written as follows:

$$\frac{I}{I_r} = \frac{\alpha}{\alpha + \beta\, n_r}\left(\frac{Q}{Q_r}\right)^{m_1} + \frac{\beta\, n}{\alpha + \beta\, n_r}\left(\frac{V_E}{V_r}\right)^{m_2} \tag{4.7}$$

where I_r is the cost of a reference plant having n_r extraction vessels of V_r liters capacity each and a CO_2 pump capacity of Q_r. For calculation purposes we used a **2×1000** / **6000** / **39** SCFE plant as reference where the code indicates two (n_r = 2) extraction vessels of 1 cubic meter capacity each (V_r = 1000 L), one pump capable of moving 6000 kilograms of CO_2 per hour (Q_r = 6000 kg/h), and a design (nominal) pressure P_n = 39 MPa where, in absence of further information, P_n is 30% above the extraction pressure (P_E = 30 MPa in our case).

To estimate parameters α, β, m_1, m_2, and I_r in Eq. (4.7) authors used a two-step procedure. First we used price index (I/I_r) data for SCFE plants in Fig. 1 of Perrut (2000) for a preliminary estimate of α, β, m_1, and m_2. To do this, authors assigned values of n, V_E, and Q of extraction plants commercialized by Separex S.A. (Champigneulles, France) identified in their R&D multipurpose lab and pilot plants (Separex, 2011a) and their reference list of equipment (Separex, 2011b) sold up to 2000. Of the 18 data points, we identified fourteen corresponding to two SF 0.2, two SF 0.5, and one SF 3 laboratory units, one SF 10, one SF 50, and one SF 100 pilots plants, and two SF 50 (**2×50** / **200** and **3×50** / **200**) industrial (multi-vessel) plants among the standard solutions (Separex, 2011a), and a **3×300** / **1600** plant sold to a pharmaceutical company in Italy in 1993, a **4×350** / **2000** plant sold to a food company in Italy in 1994, a **4×400** / **1750** plant sold to a pharmaceutical company in France in 1996, and a **2×500** / **3000** plant sold to a toll processing company in France in 2000 among industrial plants sold (Separex, 2011b). In the case of the laboratory units, Separex reports pump capacity in volume by time units (Separex, 2011a) that we corrected by assuming a CO_2 density ρ = 909.9 kg/m^3 for

typical oilseed extraction conditions (T_{ext} = 40 ºC, P_{ext} = 30 MPa). Most aforementioned plants are rated for P_{ext} = 30 MPa, and the price indexes are in a common basis to account for differences in exchange rate and inflation (Perrut, 2011), and because of these reasons we did not include corrections to the values of I/I_r in Fig. 1 of Perrut (2000). Although values of q for the laboratory units or pilot plants ranged 8 to 30 kg/h of CO_2 per kg substrate (assuming ρ_b = 500 kg/m^3), values of q for industrial plants were in a narrower range (8-12 kg h^{-1} kg^{-1}), as assumed in our analysis. Values of q relate to the superficial velocity of CO_2 according to Eq. (4.8):

$$U = q\left(\frac{\rho_b}{\rho}\right)L \tag{4.8}$$

where L is the length of the extraction vessel. Eggers (1996) recommends values of U between 1 and 5 mm/s for the CO_2 extraction of oilseeds. Eq. (4.8) suggests using proportionally smaller values of q in tall industrial extraction vessels than in short laboratory extraction vessels.

In this first step (calibration step), authors minimized the percent discrepancies between actual values I/I_r, read in Fig. 1 of Perrut (Perrut, 2000), and fitted values (referred to the average of the two) of as a function of α and β using different combinations of m_1 (0.48, 0.52, 0.56, or 0.60) and m_2 (0.48, 0.52, 0.56, or 0.60). Because values of independent variables (V_E, Q) span several log cycles (0.2 to 500 L, 3 to 3000 kg/h of CO_2), we privileged the minimization of percent discrepancies for industrial as compared to pilot plants, and of pilot plants as compared to laboratory units (weighing coefficients of 1, 4, and 16 for laboratory, pilot plant, and industrial units, respectively). Optimal values of m_1 and m_2 coincided (0.48) as assumed when analyzing the validity of Eq. (4.2) or Eq. (4.7) to correlate plant cost values.

Having preliminary best-fitting estimates of α, β, m_1, m_2 for data of Perrut (2000), the value of I_r was estimated by referring to additional reports in literature informing plant costs, and to quotes provided by plant manufacturers on request

(validation step). Literature values included the costs of a **2×487** / **1693** / **33** industrial SCFE plant for flavoring material (Novak and Robey, 1989), a **4×2000** / **5000** / **72.5** industrial SCFE plant for deoling of peanut halves (Passey, 1994), a **2×209** / **2160** / **32.5** industrial SCFE plant for an "economically interesting" oil from oilseeds (Clavier *et al.*, 1996), a **2×1950** / **18889** / **33** industrial SCFE plant for soil remediation (Montero *et al.*, 1996), a typical **3×500** / **6000** / **84.5** industrial SCFE plant for the extraction of nutraceuticals (Chordia and Robey, 2000), a **2×200** / **345** / **26** industrial SCFE plant for clove bud oil and ginger oleoresin (Rosa and Meireles, 2005), and a **2×200** / **51** / **39** industrial SCFE plant for herbaceous material (Shariaty-Niassar *et al.*, 2009). Körner (1993) informed the effect of plant size on the cost of industrial SCFE plants (**3×100** / **2000**, **3×167** / **4000**, and **3×333** / **8000** all for a nominal pressure 39 MPa) for the extraction of spices. Chemac, Inc. (Upper Saddle River, NJ) quoted in 1996 a **2×200** / **300** / **65** industrial plant for the SCFE of solid substrates. Natex Prozesstechnologie (Ternitz, Austria) quoted in 2003 a **1×80** / **800** / **71.5** pilot plant and a **2×850** / **1700** / **71.5** industrial plant for the SCFE of solid substrates. Assuming ρ_b = 500 kg/m^3, values of q for these pilot and industrial plants ranged 0.50 to 48 kg/h of CO_2 per kg substrate, which illustrates a large heterogeneity in their design compared to the one of Separex's plants informed by Perrut (2000). Except as indicated, the cost of the plants is informed in US dollars with the exceptions of the plants of Clavier *et al.* (1996, French francs), Körner (1993, Deutsch marks), and the plants quoted by Natex Prozesstechnologie (Euros). We re-estimated the cost of each of the fourteen plants in US dollars of March, 2011, for the same pressure rating (P_n = 39 MPa) by using historical currency exchange rates from the internet (Oanda.com, 2011), and CECPI values from *Chemical Engineering* journal (CEPCI = 575.9 in March, 2011). To account for differences in pressure rating, we adopted the suggestion of Hederer and Heidemeyer (1985) who proposed that the cost of high-pressure components (*e.g.*, extraction vessels capable of withstanding ≥10 MPa) increases 50% for each increase in pressure rating of 10 MPa. Generally, we assumed that the nominal pressure of the plant is 30% above the extraction pressure for the plant, but in two cases we adopted the design pressure of the

plants informed by the authors (Montero *et al.*, 1996; Novak and Robey, 1989). Considering the values of n, V_E, and Q of the plants, and best-fitted (preliminary) values of α, β, m_1, and m_2, a value of I_r can be estimated for each of the aforementioned plants using Eq. (4.9):

$$I_r = \frac{I}{\frac{\alpha}{\alpha + 2\,\beta}\left(\frac{Q}{3000}\right)^{0.48} + \frac{\beta\, n}{\alpha + 2\,\beta}\left(\frac{V_E}{1000}\right)^{0.48}} \tag{4.9}$$

Percent discrepancies between best-fit and true values of I/I_r differed considerably more in this second step than the first one, as expected. The assumptions of the designs, the procedure to cost components, the cost structure of the companies that quoted units, the effect of technological development and competition in costs among industrial plant manufacturers (that may be unaccounted for by CECPI indexes) (Perrut, 2011), and the need to introduce pressure corrections, among other factors, may all affect plant costs. In the case of data in Fig. 1 of Perrut (2000) there are no discrepancies brought about by some of these factors. Because of these reasons, in this second step we discarded from further consideration in data fitting the SCFE plants (considered as outliers) that provided the two lowest and two highest estimates of I_r using Eq. (9). As the last step, authors best-fitted values of α, β, m_1, m_2, and I_r to fourteen data points of Perrut (2000) for values I/I_r, and ten data points from other sources for values of I. Fig. 4-2 summarizes the results of our fitting procedure.

The fraction of the total cost associated with the solvent cycle ranged about 40-80% in all SCFE plants of Separex (average = 66%) and about 25-65% in the thirteen industrial SCFE plants reported by others (average = 55%) and included in Fig. 4-2. Weighted averages of percent discrepancies between best-fit and true values of I/I_r in Fig. 4-2 were 11% for the fourteen SCFE plants of Perrut (Perrut, 2000) and 42% for the other ten plants included in data correlation. The maximal discrepancy was 90% in the last case, which compares to 75-120% for the four outliers. Eq. (4.7), with best-fit parameters in Fig. 4-2, predicts discrepancies of 12 to 59% for the cost of industrial

SCFE plants informed by Pereira and Meireles (2007a; 2007b), Pereira *et al.* (2007), Leal *et al.* (2008), Comim *et al.* (2010), Prado *et al.* (2010), and Mezzomo *et al.* (2011).

4.3 Problem statement and solution

This section describes the industrial multi-vessel SCFE plants selected in this study and their costs; the estimation of annual extraction costs as a function of plant configuration and extraction time, that determines the number of batches per year; and the mathematical simulations used to select extraction times and the operation conditions analyzed in this work.

4.3.1 Selection of industrial SCFE plants, and estimation of plant costs

In this work we estimated the cost of several plants designed to carry out extraction at 40 °C and 30 MPa, which covered a wide range of configurations with minimal variations in the extraction vessels and solvent cycle parts of the plants. Two solvent cycles were selected (3000 and 6000 kg/h of CO_2).

Table 4-2 summarizes the cost of the SCFE plants in Table 4-1, which were estimated using Eq. (4.7), with best-fit parameters in Fig. 4-2. To account for the effect the shape of the extraction vessels on plant cost, authors considered that the cost of a vessel is proportional to the amount of steel using in manufacturing it. The amount of steel was estimated using standard formulae to estimate thickness of walls to withstand an inner pressure of 39 MPa in the side wall (cylindrical) and top and bottom heads (hemispherical) of the extraction vessels (Bednar, 1996). In practice differences were all associated to the top and bottom heads as the increased thickness of the cylindrical portion of the larger diameter vessels was compensated exactly by their decreased height. For capital cost estimates, authors used a single value for the cost of installing in its final placement, and starting up the plant, which is about 20% of the cost of the plant. Finally, authors rounded costs to the nearest number in USD 50 thousand units because of the uncertainty of estimated values, *cf.* Fig. 4-2. According to Table 4-2, the cost of reducing the aspect ratio from 8 to 3 is only about 6 to 7%.

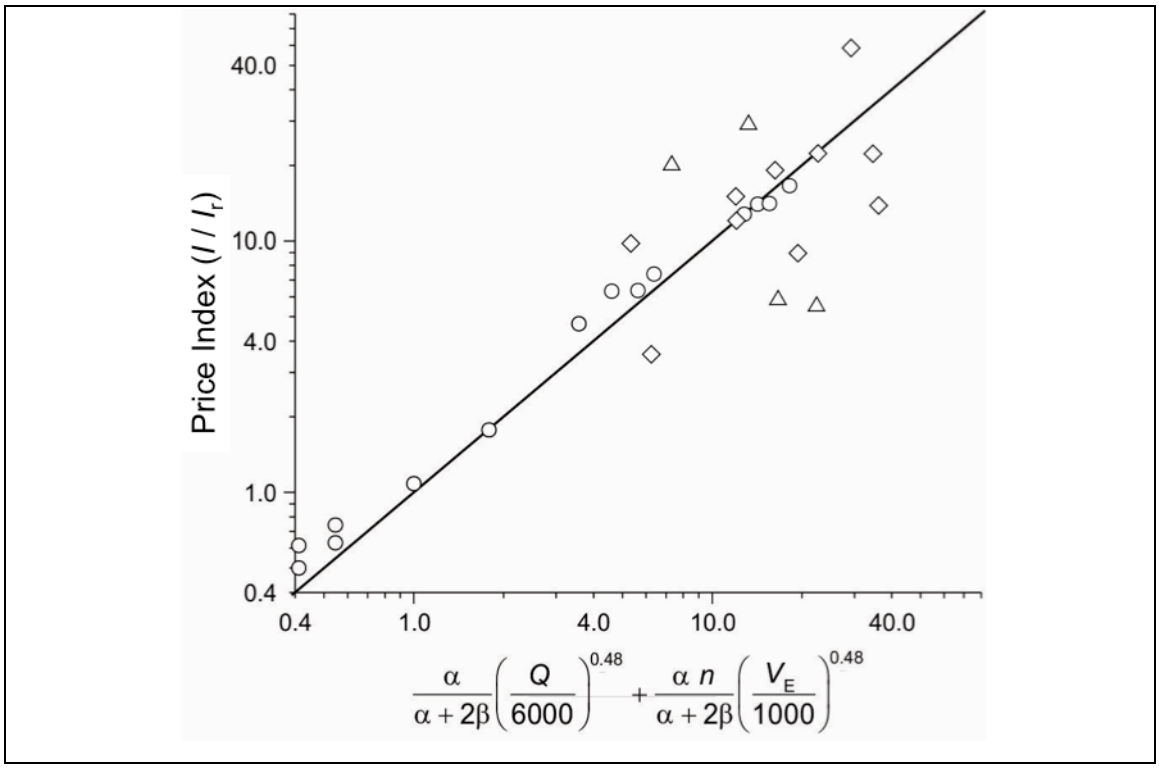

Figure 4-2: Estimated cost index of a supercritical fluid plant that can operate at 30 MPa as a function of the number and volume of extraction vessel and F_{CO2}. The price index are (○) Perrut's (2000) plant cost data; (△) plant cost (calibration data); and (◇) plant cost (validation data)

For the extraction vessels, five inner diameters (47.3, 52.1, 54.2, 59.6, and 65.6 cm) were selected. Because all plants have a total inner volume of 2 m^3 of extraction vessels, the cylindrical part of those vessels was obtained by segmenting a tube-like segment (11.38, 9.38, 8.67, 7.17, and 5.92 m, respectively) into two, three, or four equal-length pieces. The aspect (length-to-diameter) ratio of, and superficial velocities in the selected extraction vessels are summarized in Table 4-1. In most cases, the aspect ratio of the extraction vessels ($3 \leq L/D \leq 8$) is within the interval recommended by Eggers (1996) ($4 \leq L/D \leq 6$). On the other hand, the SC CO_2 superficial velocity in the extraction vessels ($2.71 \leq U \leq 10.4$ mm/s) is within about the same interval previously covered by the authors (del Valle *et al.*, submitted) ($2.75 \leq U \leq 11.0$ mm/s).

On the other hand, the cost of increasing the number of extraction vessels increases about 9 to 13% from two to three and 7 to 11% from three to four. Lastly, the cost of doubling CO_2 mass flow rate from 3000 to 6000 kg/h is about 13 to 17%.

Table 4-1. Aspect (length-to-diameter, *L*/*D*) ratio of extraction vessels, and superficial velocity (*U*) of CO_2 in the supercritical fluid extraction plants considered in this work. All plants had a total capacity of 2 m^3 ($n \times V_E$).

Plant characteristic	Vessel inner diameter (*D*, cm)				
	47.3	52.1	54.2	59.6	65.6
	L / *D* ratio (–)				
$n = 2$ ($V_E = 1000$ dm^3)	–	–	8.00	6.00	4.50
$n = 3$ ($V_E = 667$ dm^3)	8.00	6.00	5.33	4.00	3.00
$n = 4$ ($V_E = 500$ dm^3)	6.00	4.50	4.00	3.00	–
	U (mm/s)				
$Q = 3000$ kg/h of CO_2	5.22	4.30	3.97	3.29	2.71
$Q = 6000$ kg/h of CO_2	10.4	8.60	7.95	6.57	5.42

4.3.2 Estimation of annual costs

The annual cost includes a SCFE-plant-specific capital (or investment) cost (C_I), that was estimated using Eq. (4.10) by assuming an annual discount rate (r) of 6%, and that plants had a null residual value after 10 years (plant life):

$$C_I = I\left[r\frac{(1-r)^{10}}{r^{10}-1}\right] \tag{4.10}$$

where I is the cost of the installed SCFE plant (Table 4-2).

Table 4-2. Cost (in USD) of the installed supercritical fluid extraction plants considered in this work (Table 4-1).

Plant characteristic	Vessel inner diameter (D, cm)				
	47.3	52.1	54.2	59.6	65.6
Q = 3000 kg/h of CO_2					
n = 2 (V_E = 1000 dm^3)			4.500.000	4.550.000	4.650.000
n = 3 (V_E = 667 dm^3)	4.900.000	4.950.000	5.000.000	5.100.000	5.250.000
n = 4 (V_E = 500 dm^3)	5.300.000	5.450.000	5.500.000	5.650.000	
Q = 6000 kg/h of CO_2					
n = 2 (V_E = 1000 dm^3)			5.250.000	5.300.000	5.400.000
n = 3 (V_E = 667 dm^3)	5.650.000	5.700.000	5.750.000	5.850.000	6.000.000
n = 4 (V_E = 500 dm^3)	6.050.000	6.200.000	6.250.000	6.400.000	

The annual cost also includes a labor cost (C_L = 424,000 USD) that was estimated assuming that 8 workers were required to operate in three 8-h-daily shifts (2 workers/shift), each being paid USD 4,417 per month (Lack and Seidlitz, 2001). We considered SCFE plants operating continuously, three 8-h-shifts per day, required the personnel to feed four shifts.

The annual cost of the solvent cycle (C_{SC}) corresponds to the cost of energy to pump, heat, cool, or condense CO_2 and that are proportional to mass flow rate of CO_2 and the total operational time (7200 h considering continuous operation for 300 days a year), Eq. (4.11). Authors used the specific cost informed by del Valle *et al.* (submitted) for extraction of prepressed oilseeds at 40 °C and 30 MPa, separation of the extracted oil at 60 °C and 8 MPa for, holding of CO_2 at 25 ºC and 6.4 MPa (saturated liquid) in a buffer vessel, and precooling of CO_2 to 15 ºC before the main pump (positive displacement compressor).

$$C_{SC} = 5.94 \cdot 7200 \cdot Q_{CO_2} \tag{4.11}$$

Authors used the specific cost informed by del Valle *et al.* (submitted) for extraction of prepressed oilseeds at 40 °C and 30 MPa, separation of the extracted oil at 60 °C and 8 MPa for, holding of CO_2 at 25 ºC and 6.4 MPa (saturated liquid) in a buffer vessel, and precooling of CO_2 to 15 ºC before the main pump (positive displacement compressor).

The annual cost of the extraction batches (C_B) corresponds to the costs of prepressed oilseeds, vented CO_2 (considering that following completion of extractions, the pressure of the extraction vessels equalize with the one of the buffer vessel), energy to depressurize extraction vessels, and energy to repressurize the extraction vessels. The specific values of these costs depend on the size of the extraction vessel (Table 4-1), and were estimated using the calculation procedures proposed by del Valle *et al.* (submitted). The annual cost also depends on the total number of extraction batches (N), that it turn depends on the extraction time (t, h) and number of vessels in the plant (n), Eq. (4.12):

$$C_B = \left(250 + 40 + 0.9\right) \cdot V_E \cdot N \tag{4.12}$$

The last item of the annual cost is that of the (dissolved) CO_2 lost with the oil recovered in the separator, which depends on the total amount of vegetable oil produced by the SCFE plant that, in turn, depends on the extraction-time-dependent oil yield (E, obtained by simulation), the size of the extraction vessels, and the number of extraction batches in the year. Eq. (4.13) assumes that 0.1 kg of CO_2 are lost for each kg of recovered oil that is saturated with SC CO_2 at the separation conditions (60 °C and 8 MPa) (Klein and Schulz, 1989).

$$C_{SD} = 0.4 \cdot 0.1 \cdot E \cdot N \tag{4.13}$$

Finally we computed the total annual cost, Eq. (4.14), adding up the annual costs of investment, labor, energy expenditure in the solvent cycle, and depressurization and represurization operations, prepressed oilseeds, and CO_2 vented from extraction vessels or lost with the oil recovered in the separator, and added up and extra 5% to the

operational cost to account for administration, maintenance, and other minor costs (del Valle *et al.*, submitted).

$$C_T = 0.136 \cdot C_I + 1.05 \cdot \left(424000 + C_{SC} + C_B + C_{SD}\right) \quad (4.14)$$

4.3.3 Optimization of extraction times

Being selected substrate and extraction and separation conditions coincidental, the values of physical properties of CO_2, oil content, solubility at extraction and separation conditions, and effective diffusivity of oil in the substrate at extraction conditions reported in Table 4-2 of del Valle *et al.* (submitted) were used for computations. Considering the recommendation of del Valle *et al.* (submitted) for extraction of prepressed oilseeds in a industrial multi-vessel SCF plant, 2 mm particles were selected that were assumed to form packed bed with bulk density of 500 kg/m^3, interparticle porosity of 0.36, and total porosity (after completing extraction) of 0.60.

Simulations of SC CO_2 extractions of prepressed oilseed particles in two-, three-, and four-vessel SCFE plants were carried out using the MATLAB program of Núñez *et al.* (2011) with modification reported by del Valle *et al.* (submitted) using a shrinking-core hypothesis to mathematically model inner mass transfer in the substrate. Required values of the axial dispersion and film mass transfer coefficients were estimated using the correlations of del Valle *et al.* (2011) and King and Catchpole (1993), respectively. Oil yield and average residual concentration of oil in CO_2 in extraction vessels were estimated as a function of extraction time as described by del Valle *et al.* (submitted). The evolution against extraction time of oil yield and average residual concentration of oil in the CO_2 within the extraction vessel, that in turn determines the complimentary amount of oil that can be recovered from this CO_2 during decompression of the vessel, were computed as described by del Valle *et al.* (submitted). These values were estimated continuously in simulations of two-vessel, but discretly in three- and four-vessel SCFE plant, and used to estimate the total cost of extraction per unit weight of recovered oil, Eq. (4.15):

$$C_{PC} = \frac{C_T}{500 \cdot V_E \cdot E \cdot N} \tag{4.15}$$

In the case of industrial two-vessel SCFE plants, extraction cost was minimized by inspection of curves of cost *versus* extraction time, whereas in the case of the three- and four vessel plant the algorithm of del Valle et al. (submitted) was used for that purpose. The algorithm is as follows. Extraction times were spaced 40 min initially, where an intermediate (middle) time has lower operational cost than the two extremes. When that condition was identified, the two intervals (from the lower to the middle extraction time, and from the middle to the upper extraction time) were halved, new simulations were carried out for these intermediate times, and a new interval containing the minimal was identified. This procedure was repeated three times to identify the 10-min interval where the optimal extraction time was located. If the operational cost for the second simulation was higher than the first simulation, a third simulation was run for an extraction time 40 min below the initial value, and subsequent simulations were run reducing the extraction time 40 min up to identifying an 80 min interval where the optimal was located. Otherwise, the true function of the operational cost *versus* extraction time was explored by increasing extraction time 40 min in each simulation up to locating the 80-min interval containing the optimal. This, together with the mathematical expression for the effect of extraction time on operational cost, (similarly to Eq. 3.3), allowed an accurate description of the true function of the operational cost *versus* extraction time.

4.4 Results

Fig. 4-3 shows that production cost depends critically on extraction time, so that there exist an optimal for which it reaches a minimal. This was shown in our previous contribution (del Valle *et al.*, submitted) in the case of the operation cost, that excludes capital cost associated with the purchase, installation, and start-up of the SCFE plant, and that is also included in Fig. 4-3. The minimal operational cost is not only about USD 4 / kg less than the minimal production cost in the case of the extraction of the oil using

6000 kg/h CO_2 in a two-vessel SCFE plant with broad extraction vessels (L / D = 4.5), but it also occurs for a larger extraction time in a lengthier plateau. This is because capital cost is a major contributor to the production cost, which increases markedly as oil production diminishes. The annual expenses in the capital cost and labor items are fix amounts. The cost items associated with demands electrical power, heat addition, and heat removal are approximately a fix amount that depends on the mass flow rate of CO_2, as the energy demand on unloading and reloading the extraction vessel is much less than the energy demand of the solvent cycle. Consequently, as shown in Fig. 4-3, the contribution of these items (capital, labor, electrical power, heat addition, heat removal) to the production cost increases as extraction time increases because of a monotonous decrease in oil production. This reduction in oil production, in turn, is a consequence of the continuous decrease in the rate of oil extraction as extraction proceeds, Fig. 4-3. On the other hand, the annual expenses in substrate and CO_2, which are proportional to the number of batches decrease as these batches decrease when extraction is extended, with the end result of a reduction of their contribution to the production cost. Also, CO_2 expenses is proportional to the productivity of the SCFE plant and depend on the phase equilibrium at separation conditions (60 ºC and 8 MPa) where the CO_2 is solubilized in the oil about 10% w/w (Klein and Schulz, 1989).

The minimal production cost diminishes as the mass flow rate of CO_2 increases, and the number of extraction vessels of the SCFE plant increases, Fig. 4-4. On the other hand, for a given CO_2 mass flow rate, production cost diminishes slightly when the diameter of the extraction vessel diminishes. The two effects of the reduction in extraction vessel diameter, namely the increase in superficial CO_2 velocity, and the increase in extraction vessel heights, have opposite effects on extraction rate. Extraction rate increases with superficial CO_2 velocity, particularly in the initial stages of the extraction process, when there is a larger effect of external resistances to mass transfer than in the final, inner-mass-transfer-controlled stages. On the other hand, the extraction rate decreases as the CO_2 approaches the exit of taller extraction vessels, when oil

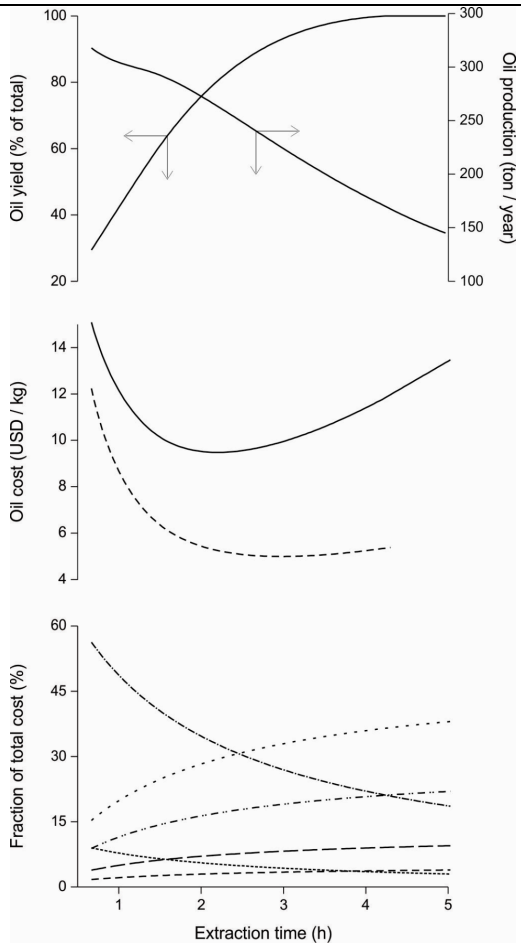

Figure 4-3: Cumulative extraction curve (oil yield versus extraction time), plant productivity curve (oil production versus extraction time), and unitary (——) operational and (– – –) production (operation plus capital) cost as a function of extraction time for the production of vegetable oil in a two-vessel supercritical fluid extraction plant operating with 6000 kg/h of CO_2 at 40 °C and 30 MPa. The 1-m3 extraction vessels have an aspect ratio (L/D) of 4.5. The figure also includes the distribution of the production cost in several items: (–·–·–) capital, (·····) labor, (– ·· –) substrate (prepressed oilseed containing 20% w/w oil); (·------) CO_2; (— —) heat removal; and, (– – –) head addition plus electrical power.

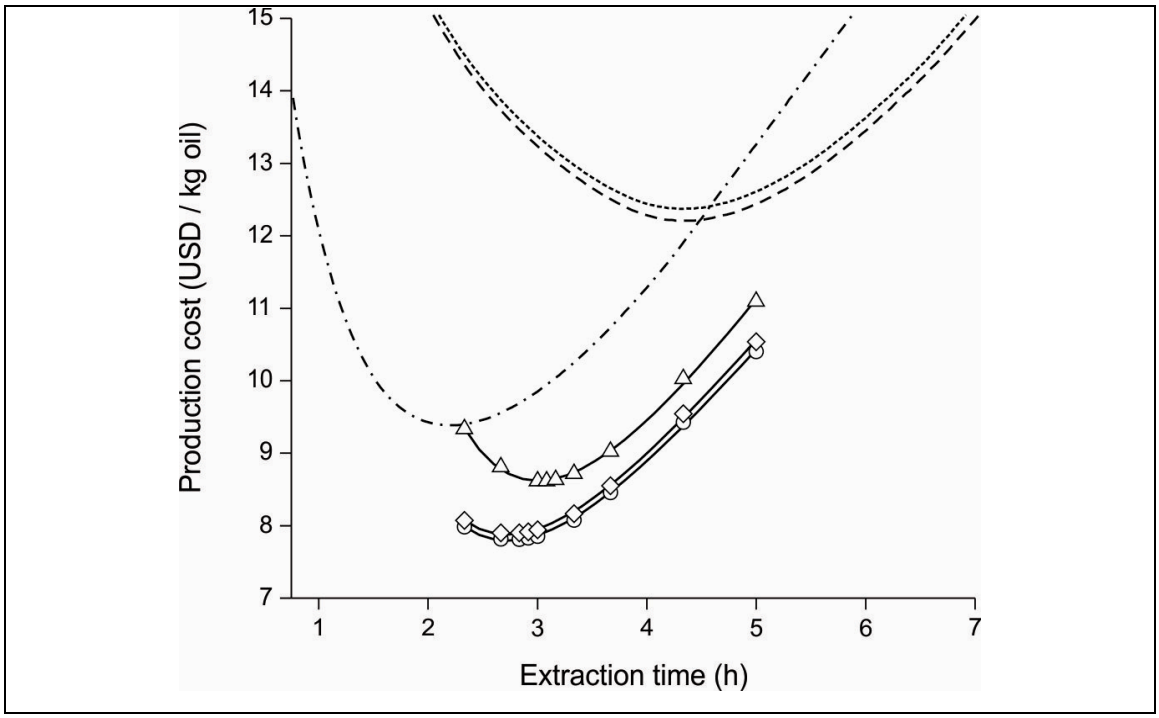

Figure 4-4: Oil production cost as a function of extraction time for selected supercritical fluid extraction plants carrying out extraction of a prepressed oilseed (containing 20% w/w oil) at 40 °C and 30 MPa: two-vessel plants having 1-m^3 extraction vessels of (·····) 65.6 cm or (– – –) 54.2 cm diameter and operating with 3000 kg/h of CO_2; (–·–·–) two (1-m^3), (△) three (0.667-m^3), or (◇) four (0.5-m^3) vessel plants having extraction vessel of 54.2 cm diameter and operating with 6000 kg/h of CO_2, and, (○) three/vessel plants having 0.5-m^3 extraction vessels of 47.3 cm diameter operating with 6000 kg/h of CO_2.

concentration in the CO_2 increases as a result of the faster extraction at the entrance of the extraction vessel.

Particularly, in this case where the extraction vessel volume keeps constant, a decreasing in the extraction vessel diameter also implies an increasing in the extraction vessel length, which will compensate a higher superficial CO_2 velocity, resulting in a residence time within the extraction vessel practically constant.

Table 4-3 summarizes optimal extraction times and minimal production costs, which decrease as a result of an increase in CO_2 mass flow rate or an increase in the number of extraction vessels of the SCFE plant, but remain virtually unaffected by the diameter of the extraction vessel. Variation in minimal production cost with extraction vessel diameter ranged from about 1% for two-vessel SCFE plants to about 3% for three-vessel plants, both operating with 3000 kg/h of CO_2. This result parallels minimal variations in optimal extraction times and oil yields with extraction vessel diameter, which in turn resulted in equivalent oil productivities. There was a larger effect of the number of extraction vessels on minimal production cost, which decreased 8-9% when increasing from two to three vessels of aspect ratio L/D = 6.0, or 9-14% when increasing from three to four vessels of aspect ratio L/D = 6.0. As suggested by Fig. 4-4, optimal extraction times were largest for the three vessel plants, intermediate for the four-vessel plants, and largest for the two vessel plants, which paralleled changes in extraction yield. Optimal oil yield was above 90% for three- and four-vessel SCFE plants, but below 90% for two-vessel plants. On the other hand, oil productivities increased with the number of extraction vessels, mainly as a consequence of the increase in production batches. The largest reduction in minimal production cost was the one resulting from doubling CO_2 mass flow rate; 19% for four-vessel SCFE extraction plants, 23% for two-vessel plants, and 24% for the four-vessel plants. This was mainly a consequence of the increase in extraction rates that resulted in reductions in optimal extraction time of 44 to 50%. This reduction in extraction time was at the expense of a reduction in oil yield, which decreased 4-6%. The effect of the increase in the number of batches prevailed over that of the increase in yield, with the end result of an increase in oil productivity of 71 to 86%.

Table 4-4 summarizes the split of minimal production costs among different items as a function of SCFE plant design. Energy requirements associated mainly with operation of the CO_2 cycle, particularly heat and electricity, the same as CO_2 make-up, make a small contribution to production cost.

Table 4-3: Optimal extraction time and minimal production cost, and oil yield and annual productivity under optimal conditions of supercritical fluid extraction plants considered in this work (Table 4-1).

Vessel number	*L*/*D* ratio (-)	Optimal extraction time (h)	Oil yield (%)	Oil production (ton/year)	Production cost (USD/kg oil)
Q = 3000 kg/h of CO_2					
2	8.00	4.358	85.9	141.9	12.21
2	6.00	4.358	85.0	141.9	12.26
2	4.50	4.358	85.8	141.8	12.37
3	8.00	5.940	98.0	158.3	11.24
3	6.00	5.942	98.0	158.2	11.29
3	5.33	5.943	98.0	158.2	11.33
3	4.00	5.946	98.0	158.1	11.43
3	3.00	5.949	98.0	158.0	11.57
4	6.00	4.997	95.9	207.0	9.682
4	4.50	4.999	95.8	206.9	9.791
4	4.00	5.001	95.8	206.8	9.827
4	3.00	5.003	95.8	206.7	9.937
Q = 6000 kg/h of CO_2					
2	8.00	2.211	80.8	263.1	9.384
2	6.00	2.194	80.4	263.8	9.418
2	4.50	2.217	80.8	262.5	9.480
3	8.00	3.038	92.4	291.9	8.559
3	6.00	3.039	92.4	291.7	8.588
3	5.33	3.040	92.4	291.6	8.614
3	4.00	3.040	92.3	291.4	8.669
3	3.00	3.143	94.0	287.0	8.764
4	6.00	2.754	91.2	357.3	7.808
4	4.50	2.797	91.9	354.7	7.874
4	4.00	2.753	91.1	357.1	7.895
4	3.00	2.753	91.0	356.8	7.960

SCFE plant purchase, installation, and start up, labor, and substrate, on the other hand, make a major contribution to production cost. Capital cost is 44-105% higher than labor cost with the difference increasing with the diameter of extraction vessels, their number, or the mass flow rate of CO_2. For SCFE plants operating with 3000 kg/h of CO_2, capital cost is 33-76% higher than substrate cost, with the difference being the largest for three-vessel plants, the lowest for four-vessel plants, and increasing as extraction vessel diameter increases. On the other hand, capital cost is 10-16% smaller than substrate cost for two- or four-vessel SCFE plants using 6000 kg/h of CO_2 with this difference generally decreasing as the diameter of the extraction vessels increases. However, for the three-vessel plants using 6000 kg/h of CO_2 capital and substrate costs are about the same; the fraction of production cost associates with SCFE plant purchase, installation, and start-up increases from 97 to 107% of the fraction associated with pretreated substrate purchase as the diameter of the extraction vessel increases from 47.3 to 65.6 cm.

For a comparable superficial CO_2 velocity, the production cost in three- and four-vessel SCFE plants decreases as volume of the extraction vessel increases or their aspect ratio increases, Fig. 4-5. Minimal production cost decreases as extraction rate increases when superficial velocity increases.

This increase in extraction rate decreases the optimal extraction time with the end result of an increase in the number of annual batches. On the other hand, the optimal extraction time increases as the volume of the extraction vessel increases. Under optimal operation conditions, SCFE plants with 1-m^3 vessels allowed as high or higher oil yields than reported in Table 3; 97-99% for the three-vessel plant and 96% for the four-vessel plants. Productivity of these 1-m^3-vessel SCFE plants increased with superficial CO_2 velocity (from 163 to 305 ton/year of oil in the three-vessel plant when increasing U from 2.71 to 5.41 mm/s, and from 411 to 679 to/year of oil in the four vessel plant when increasing U from 5.41 to 10.8 mm/s) and number of extraction vessel (a 35% increase at U = 5.41 mm/s when increasing from 3 to 4 extraction vessels), as expected.

Table 4-4: Distribution of the production cost in several items of supercritical fluid extraction plants considered in this work (Table 4-1) operating under optimal conditions (Table 4-3).

Vessel number	*L*/*D* ratio (-)	Contribution of item to production cost (%)					
		Capital cost	Labor	Substrate	CO_2	Removed heat	Added heat and electrical power
Q = 3000 kg/h of CO_2							
2	8.00	35.3	24.5	23.8	3.82	5.28	2.21
2	6.00	35.5	24.4	23.7	3.80	5.26	2.20
2	4.50	36.0	24.2	23.5	3.77	5.22	2.18
3	8.00	37.4	23.8	22.7	3.63	5.15	2.15
3	6.00	37.7	23.7	22.6	3.62	5.13	2.14
3	5.33	37.9	23.6	22.5	3.60	5.11	2.13
3	4.00	38.3	23.5	22.3	3.57	5.07	2.11
3	3.00	39.0	23.2	22.1	3.53	5.01	2.09
4	6.00	35.9	21.2	26.9	4.31	4.57	1.93
4	4.50	36.6	20.9	26.6	4.27	4.52	1.91
4	4.00	36.8	20.9	26.5	4.25	4.51	1.90
4	3.00	37.4	20.6	26.3	4.20	4.46	1.88
6000 kg/h of CO_2							
2	8.00	28.9	17.2	33.0	5.28	7.42	3.09
2	6.00	29.0	17.1	33.0	5.29	7.37	3.08
2	4.50	29.5	17.0	32.6	5.22	7.36	3.07
3	8.00	30.7	17.0	31.6	5.06	7.33	3.06
3	6.00	30.9	16.9	31.5	5.05	7.31	3.05
3	5.33	31.1	16.9	31.4	5.03	7.29	3.04
3	4.00	31.5	16.8	31.2	5.00	7.25	3.02
3	3.00	32.4	16.9	30.3	4.86	7.28	3.03
4	6.00	29.5	15.2	35.1	5.62	6.57	2.76
4	4.50	30.2	15.2	34.6	5.53	6.56	2.75
4	4.00	30.1	15.0	34.8	5.57	6.50	2.73
4	3.00	30.6	14.9	34.5	5.52	6.45	2.71

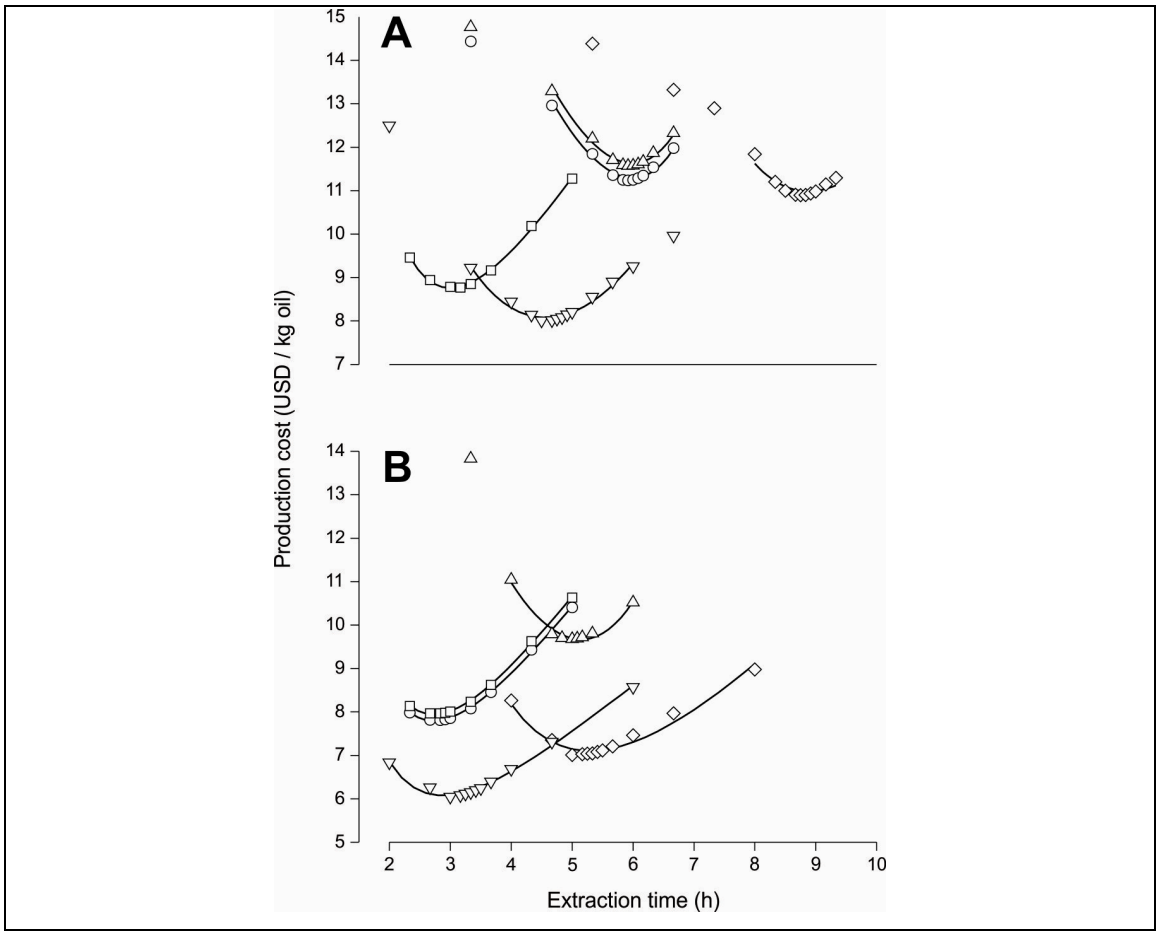

Figure 4-5: Oil production as a function of extraction time for selected (**A**) three-vessel or (**B**) four-vessel supercritical fluid extraction plants carrying out extraction of a prepressed oilseed (containing 20% w/w oil) at 40 °C and 30 MPa. The three-vessel plants have 1-m^3 vessels of an aspect ratio (L/D) 4.5 operating at a superficial CO_2 velocity (U) of (◇) 2.71 mm/s or (△) 5.41 mm/s, or 0.667-m^3 vessels of L/D = 3.0 operating at (△) U = 2.71 mm/s or (□) U = 5.41 mm/s, or (○) L/D = 8.0 operating at U = 5.22 mm/s. The four-vessel plants have 1-m^3 vessel of L/D = 4.5 operating (◇) U = 5.41 mm/s or (▽) U = 10.8 mm/s, or 0.5-m^3 vessels of L/D = 6.0 operating at (△) U = 5.22 mm/s or (□) U = 10.4 mm/s, or (○) L/D = 3.0 operating at U = 6.57 mm/s.

The negative effect of an increase in aspect ratio can be compensated by an increase in superficial velocity, with this compensation near perfect when the mass flow rate of CO_2 is kept constant, Fig. 4-4 and Table 3.

4.5 Discussion

Production cost diminishes when decreasing the aspect ratio of extraction vessels, increasing superficial CO_2 velocity (possibly above the top 5 mm/s value suggested by Eggers, 1996), or increasing the number of extraction vessels.

It is apparent that when the specific solvent rate is kept constant (Q_{CO2}/M_o), which is equivalent to keeping the residence time in the extraction vessel constant, the optimal extraction time and oil yield remain approximately constant, and consequently economics do not change. Thus, using as scale-up criteria a constant residence time may be a reasonable one. In literature there are works that have studied the scaling-up of the process using the ratio Q_{CO2}/M_o constant (Eggers and Sievers, 1989; Mezzomo *et al.*, 2009; Prado *et al.*, 2011). Eggers and Sievers (1989) analyzed this criterion and marked that is not useful because the increasing of the solvent mas flow with the height of the extraction vessel could provoke a compaction of the starting material. Mezzomo *et al.* (2009) scaled-up the extraction of peach almond oil with SC CO_2 using four criteria, keeping constant the following ratios: (i) solvent mass-to-substrate mass (M_{CO2}/M_o = 109.5 g/g); (ii) CO_2 flow rate-to-substrate mass (Q_{CO2}/M_o = 1.3 g/g min); (iii) M_{CO2}/M_o = 104.1 g/g and Q_{CO2}/M_o = 17.3 g/g min; and (iv) Re = 7.8×10^{-7}, m_{solv}/M_o = 104.1 g/g, and Q_{CO2}/M_o = 17.3 g/g min. Their results indicated that SC CO_2 extraction of peach almond is controlled by diffusion. Also, the extraction curves were quite similar for small and large scales (particularly the mass transfer coefficients estimated for their mathematical model). Thus, they concluded that the second and third criteria were adequate to represent the extraction curves at industrial scale. Prado *et al.* (2011) applied successfully the scaling-up (extraction vessel ratio equal to 1:15) of the extraction of both clove and sugarcane residue keeping $M_{CO2}/M_o \approx 3.6$. The shape of the extraction curves and yield in both raw materials were slightly higher (20% for clove and 15% for

sugarcane residue) in pilot plant than in laboratory scale, which is according with manufacturer information instead of literature information. Also, they applied a combined criterion to scale-up keeping both M_{CO2}/M_o and Q_{CO2}/M_o constants, but changing Q_{CO2}/M_o they obtained the same results, concluding that its simple criterion was good enough. Prado *et al.* (2012) also applied M_{CO2}/M_o constant (= 8.2) as criterion to scale-up (1:15) the extraction of grape seeds with SC CO_2 with good results, where extraction curves at different scales practically overlapped. From the costing standpoint, the extraction of grape seed with SC CO_2 at 40 ºC and 35 MPa, extraction time of 240 min and a M_{CO2}/M_o ratio of 6.6 resulted in the best combination between yield and cost (manufacture or production cost of 12.08 USD/kg of grape seed oil).

Regarding the economics in SC CO_2 extraction of oil from vegetable substrates, there are works in literature that reported manufacture or production costs that included capital cost in their estimates. Bravi *et al.* (2002) reported a production cost of 0.633 USD/kg of oil (value updated; Oanda.com, 2011) for the extraction of sunflower seed (C_o = 49.2% w/w) using SC CO_2 at 40 ºC and 28 MPa. Authors think that this value is too low and questionable because the huge superficial velocity (32.8 mm/s) and short extraction times (10 min), which probably would be insufficient to complete the reconditioning steps in an extraction vessel (Quirin, 2010). Prado *et al.* (2010) reported a cost of 17.2 USD/kg of oil for the extraction of palm tree (C_o = 7.5-15% w/w) using SC CO_2 at 40-55 ºC and 20-30 MPa. This cost is too high compared with Bravi *et al.* (2002) due to the different substrates, but it would be more realistic considering other works about it in literature. More comparable, there are works that studied the economics in the oil extraction with SC CO_2 from grape seed. Fiori (2010) reported 7.82 USD/kg of oil (value updated, Oanda.com, 2011) for the extraction of grape seed (C_o = 12% w/w) with SC CO_2 at 60 ºC and 55 MPa compared with 11.9 USD/kg (updated value, Oanda.com, 2011) for the grape seed extraction with SC CO_2 at 40 ºC and 35 MPa (Prado *et al.*, 2012). From both results we can conclude that pressure has a positive effect on the production cost, as our results. Economies of scales also explained the difference because the first work had an oil production of 306 ton/year (3×0.8 m^3 plant) (Fiori,

2010) and the last one obtained an oil production of 66.7 ton/year (2×0.5 m^3 plant) (Prado *et al.*, 2012). Despite of above, Mezzomo *et al.* (2011) reported a production cost of 4.64 USD/kg of oil for peach kernel extraction with SC CO_2 at 40 ºC and 20 MPa for a initial oil content (C_o = 13.2% w/w) similar to Fiori (2010), which is contradictory with our evidence given that Mezzomo *et al.* (2011) did the extraction at lower extraction pressure [20 MPa *versus* 35 MPa for Fiori (2010), at the same extraction temperature] in a smaller plant [2×0.4 m^3 plant *versus* 2×0.5 m^3 plant for Fiori (2010)].

In this work, production cost estimated for oil extraction from rapeseeds (C_o = 20% w/w) with SC CO_2 at 40 ºC and 30 MPa were in the range 7.808-12.37 USD/kg of oil. Comparing with this work, the optimum production cost reported by Fiori (2010) (7.82 USD/kg oil) is practically the same that minimum production cost. However, the main difference between that work and ours is in the bulk density was larger [600 (Fiori, 2010) *versus* 500 kg/m^3) and particle size was shorter [0.4 (Fiori, 2010) *versus* ≥0.5 mm], which would contribute to decrease costs in the process (del Valle *et al.*, submitted). On the other side, manufacture cost reported for Prado *et al.* (2012) (11.9 USD/kg oil) is within the range of production cost estimated in this work, but considering a larger bulk density (950 kg/m^3) and lower superficial velocity (0.26 mm/s). This last is relevant when the bed has small particles, where lower superficial velocities will avoid its fluidization (del Valle *et al.*, submitted).

Production cost range estimated in this work were 52.3-65.9% higher that the operational cost range (4.081-8.149 USD/kg oil) estimated by del Valle *et al.* (submitted), being the main difference the capital cost. In this work capital cost meant at least 28.9% of the whole production cost. In literature, the contribution of capital cost (or investment) to production cost is in a wide range. Bravi *et al.* (2002) considered that capital cost represented in average about 58.2% of production cost. Prado *et al.* (2012) reported that the contribution of investment on manufacture cost was 45.9-51.0%. In the case of Fiori (2010), the capital cost in the case was a 46.5% of production cost. And Mezzomo *et al.* (2011) considered 30.4% of cost of manufacturing corresponded to the fraction of investment (or capital cost).

The requirement of CO_2 make-up for the SCFE plants considered in this work was 177-428 ton of CO_2/year. CO_2 losses produce when an extraction vessel is vented to the environment (up to 100 kg/batch) and the CO_2 dissolved in the oil, which was estimated in 10% w/w (del Valle *et al.*, submitted). Bravi *et al.* (2002) estimated a CO_2 make-up of 628 kg of CO_2/h for the optimized case (equivalent to 4.5 ton/year if it is considered a continuous production of 7200 h/year). Fiori (2010) considered that CO_2 is lost only when extraction vessels are opened and evaluated by void fraction in the bed and the CO_2 density at 1 MPa, resulting in a CO_2 make-up of 54 ton/year. Prado *et al.* (2012) considered a CO_2 loss of 2% of the total CO_2 used in the process, resulting in a CO_2 consumption of 320-1000 ton/year. Finally, Mezzomo *et al.* (2011) also considered a CO_2 loss of 2%.

Results suggest economies of scale in the sense that production cost increases when the size of the extraction vessels increases as shown here in the case of three- and four-vessel plants. This should be further explored, systematically.

5. PRODUCTION COSTS OF SUPERCRITICAL CO_2 OILSEED EXTRACTION IN MULTI-VESSEL PLANTS. 3. EFFECT OF PRESSURE AND PLANT SIZE

Abstract

In previous works authors studied the effects of several parameters (particle size, mass flow rate of CO_2, aspect ratio of the extraction vessels, total volume of a supercritical extraction plant) on operational and production costs for the oil extraction from prepressed oilseeds at 40 ºC and 30 MPa in an industrial multi-vessel plant. This work presents the effect of the pressure on production cost in an industrial plant for the supercritical CO_2 extraction of prepressed rapeseeds (20% residual oil content) by process simulation. This system was selected because a fully predictive mass transfer model exists based on shrinking core hypothesis. The extractions were simulated at 40 ºC and 30, 50, and 70 MPa for 33 supercritical extraction plants having 2, 3, and 4 extraction vessels, and different total volumes. A range of production cost of 6-12 USD/kg oil was estimated. For the same total volume of extraction vessels, the cost decreases when the extraction pressure increases from 30 to 50 MPa, and it increases slightly when it increases from 50 to 70 MPa, despite of the capital cost increased with pressure. The number of extraction vessels has a positive effect on production costs, and the economies of scale allow a decreasing in cost when plant size increases.

Keywords: extraction pressure effect; industrial plant; optimal extraction time; production cost; prepressed oilseed; supercritical CO_2; total volume of extraction.

5.1 Introduction

Extract production from vegetable substrates using supercritical CO_2 (SC CO_2) as solvent is an excellent alternative, mainly because these extracts have high quality and are practically solvent-free (Brunner, 2005). For long time, SC CO_2 extraction has not been considered competitive due to its high cost, especially because of the high capital cost. However, this technology could be competitive for certain added-value products such as

specialty oils whose market price would justify high investments. Authors have studied previously both operational (del Valle *et al.*, submitted) and production costs (Núñez and del Valle, submitted) for oil extraction from prepressed oilseeds at 40 ºC and 30 MPa, showing that it is possible to optimize extraction time from the cost standpoint, using process simulation.

del Valle *et al*. (submitted) estimated the operational cost in function of extraction time for a 1 m^3-extraction vessel placed in a SuperCritical Fluid Extraction (SCFE) plant with two, three, or four extraction vessels, for the case when the SCFE plant has idle capacity and could offer toll processing. Authors evaluated the effect of particle size ($0.5 \leq d_p \leq 4$ mm), mass flow rate of CO_2 ($3000 \leq Q \leq 12000$ kg of CO_2/h) and number of extraction vessels (n = 2, 3, and 4). From the operational cost standpoint, the best operational conditions found by del Valle *et al*. (submitted) were 6000 kg/h of CO_2 (corresponding to a superficial velocity, U, of 5.50 mm/s) for a particle size of d_p = 2 mm. Operational costs reported were in the range of USD 4.08-8.15/kg of oil (del Valle *et al.*, submitted).

Núñez and del Valle (submitted) estimated production costs in function of extraction time and proposed a methodology to estimate the capital cost (one of the bigger uncertainties in cost estimates) for 2 m^3-SCFE plant processing particles of 2 mm and using two mass flow rates (Q = 3000 and 6000 kg/h of CO_2). They evaluated the effect of geometry of the extraction vessel by modifying the aspect ratio (L/D) of the vessels between 3 and 8, and number of extraction vessels (n = 2, 3, and 4). Production cost diminished when increasing L/D and U, this last one even above the limit recommend by Eggers (1996) of 5 mm/s. Also, results of Núñez and del Valle (submitted) suggest that there are economies of scale where production cost decreases with an increasing of both size of the extraction vessels and n (going from 2-to-3 and 3-to-4 extraction vessels). The production costs estimated were in the range 7.96-12.4 USD/kg of oil.

This work follows the above contributions. Specifically the objective of this work was to determine the effect of extraction pressure (at 30, 50, and 70 MPa) on production cost by process simulation for the rapeseed oil extraction in an industrial SCFE plant.

5.2 Problem statement and solution

This section presents the effect on production cost of extraction pressure at the same total volume of SCFE plant; extraction pressure for SCFE plant having the same productivity, resulting in different plant sizes; total volume of the SCFE plant; and number of extraction vessels.

5.2.1 Productivity estimation in a SCFE industrial plant using process simulation

Núñez *et al.* (2011) and del Valle *et al.* (submitted) describe in detail an industrial SCFE plant with three extraction vessels, which can be divided in two parts: (i) solvent cycle and (ii) extraction vessels operation. Solvent cycle starts with a buffer vessel (CO_2 as saturated liquid at 25 ºC and 6.4 MPa). CO_2 stream coming from the buffer tank is pre-cooled before a pump, pumped up to extraction pressure (30, 50, or 70 MPa) and adjusted at extraction temperature by a heat exchanger (at 40 ºC). After the extraction step, the CO_2 stream with the solute is expanded in a separator (at 60 ºC and 8 MPa), where the solute precipitates, and the gas phase of CO_2 is recovered by condensation and stored in the buffer tank to recirculate it again to the solvent cycle. On the other hand, in a SCFE plant with n extraction vessels, (n -1) are connected in series and working in the process, and the last one is reconditioning steps (consisting of depressurization from extraction pressure to buffer tank pressure; unloading of exhausted substrate; loading of fresh substrate, and repressurization up to the extraction pressure).

Productivity was estimated using the algorithm proposed by Núñez *et al.* (2011). This algorithm uses a predictive model to simulate the inner mass transfer in a packed bed based on the shrinking-core hypothesis. The original algorithm was programmed in MATLAB to describe the pseudo-steady-state operation in a three-vessel SCFE plant (Núñez *et al.*, 2011). Outputs of the simulation included the yield and residual concentration of oil in CO_2 in the extraction vessel as a function of extraction time.

For the simulation purposes, values of physical properties and mass transfer parameters were calculated or estimated as Núñez *et al.* (2011). The physical properties (ρ and μ) of CO_2 (pure) were estimated using NIST Database (Lemmon *et al.*, 2010). Authors

assumed that prepressed oilseeds contained 20% oil (C_o = 0.20 kg oil per kg substrate), and a bed porosity ε_b = 0.36 and a bulk density ρ_b = 500 kg/m^3. For mass transfer parameters, the effective diffusivity of oil in the substrate ($D_e = F \cdot D_{12}$) was calculated as the product of the microstructural factor (del Valle *et al.*, 2006) and the binary diffusivity (D_{12}) that was estimated using the correlation of Funazukuri *et al.* (2009). The axial dispersion coefficient (D_L) was estimated using the correlation of del Valle *et al.* (2011) and the film mass transfer coefficient (k_f) that was estimated using the correlation of King and Catchpole (1993). Finally, the saturation concentration (C_{sat}) of oil in CO_2, and the saturation concentration of oil in CO_2 at separation conditions (C_{sep}) were estimated using the correlation of del Valle *et al.* (2012a).

In this work the following parameters were modified that affect extraction rate besides the extraction pressure: number of extraction vessel (n = 2, 3, and 4); and total volume of the SCFE plant ($0.394 \leq V_T \leq 5.860$ m^3). To determine the total volume of the SCFE plants, this work used two 2 m^3-SCFE plants operating at 30 and 50 MPa, respectively, as base cases. By process simulation, authors established the total volume for SCFE plants whose productivity were the same than the base cases and replicated those volumes at extraction pressures considered in this work, resulting in 33 SCFE plants operating at 30, 50, or 70 MPa with 2, 3, or 4 extraction vessels, for processing of 2 mm particles using a superficial CO_2 velocity 6.57 mm/s (del Valle *et al.*, submitted; Núñez and del Valle, submitted).

5.2.2 Operational cost in in the SCFE plant

Operational cost could be divided in two categories: i) costs associated with solvent cycle; and, ii) costs associated with the batch process. Costs associated to the solvent cycle correspond to the energy cost to pump, heat, and cool (to condense CO_2), which are proportional to the flow rate of CO_2 and extraction time, and can be estimated as the weighted average of the energy requirements and the costs of heat. Energy requirements in the solvent cycle were estimated using a *T-s* diagram for pure CO_2 similarly to del Valle *et al*. (submitted). Costs associated with the batch process include the cost of prepressed oilseeds (0.5 USD/kg, Lack and Seidlitz, 2010), CO_2 make-up (0.4 USD/kg, Lack and

Seidlitz, 2001), and energy to depressurize and re-pressurize an extraction vessel (depending on extraction pressure and volume of extraction vessel). The amount of CO_2 lost at the end of the extraction was estimated with its density at 40 ºC and 6.4 MPa (166.7 kg/m^3, Lemmon *et al.*, 2010) and the final porosity ($\varepsilon_b = 0.6$) resulting from the removal of oil. Table 5-1 shows the energy costs in the solvent cycle used in this work in function of extraction pressure.

Also, the annual operational cost include the following costs: labor of 53,000 USD/year-man (Lack and Seidlitz, 2001) (two operators per 8-h shift, continuous operation); and other minor costs (administration, maintenance, and energy requirement of closure systems of extraction vessels, among others), which were assumed to account for 5% of the operational costs. Finally, authors considered occupancy of the SCFE plant of 7200 h per year.

Table 5-1: Energy costs in the solvent cycle in function of the extraction pressure

Item cost (USD/kg CO_2)	Extraction pressure (MPa)		
	30	50	70
Heating	193	190	186
Cooling	222	243	262
Electric power	35	62	89

5.2.3 Capital cost for the SCFE plant

In this work the capital cost was estimated with the expression proposed by Núñez and del Valle (submitted) (Eq. 5.1).

$$I = I_r \left(\frac{\alpha}{\alpha + 2\beta} \left(\frac{Q}{6000} \right)^{0.48} + \frac{\beta \, n \, f_v}{\alpha + 2\beta} \left(\frac{V_E}{1000} \right)^{0.48} \right) \tag{5.1}$$

where I (USD) is the cost of purchase a SCFE plant; α, β, and I_r are the parameters of the Eq. (5.1); I_r (USD) is the cost of a reference 2×1000 L SCFE plant with a CO_2 pump

capacity of 6000 kg/h; n (-) is the number of extraction vessels; V_E (L) is the capacity of extraction vessels; f_v is the shape factor, considering the aspect ratio of the extraction vessel. In Eq. (5.1), the term relative to the extraction vessel was weighted by a pressure correction factor according with Hederer and Heidemeyer (1985) who showed that cost of an extraction vessel increases 0.5-fold every 10 MPa. More details about it are explained in Chapter 4 above (Núñez and del Valle, submitted).

5.2.4 Estimation of the production costs and optimization of extraction time

Authors estimated the equivalent annual cost to the capital cost (C_I, USD/year) as indicates Eq. (5.2) (similar to Eq. 4.10) and the production cost (C_{PC}) as USD per kilogram of oil extracted as indicates Eq. (5.3) (other form for Eq. 4.15). Total oil extracted includes the remained oil at the end of the extraction, which is recovered when the extraction vessel is depressurized from extraction pressure to buffer tank pressure:

$$C_I = \left[r \frac{(1-r)^a}{r^a - 1} \right] I \tag{5.2}$$

$$C_{PC} = \frac{C_{CP} + 1.05 \times C_{OC}}{E_A} \tag{5.3}$$

In Eq. (5.2) a indicates a 10-year time horizon and r = 0.06 is the discount rate. In Eq. (5.3), C_{OC} (USD/year) is the annual operational cost including costs associated to solvent cycle, batch process, and labor (factor 1.05 indicates the 5% for minor costs); and E_{annual} (kg oil per year) is the annual productivity of the SCFE plant.

The minimization of production cost for two-vessel SCFE plants was done by inspection of the curves of cost *versus* extraction time. For three- and four- vessel SCFE plants the minimal production cost was found by using the algorithm of del Valle *et al.* (submitted) where the optimum extraction time was determined in a 10-min interval in the curve of cost *versus* time. For more detail about production cost estimation see sections 4.3.2 and 4.3.3 (Núñez and del Valle, submitted).

5.3 Results

Fig. 5-1 shows the positive effect of extraction pressure on the production costs for two-vessel SCFE plants (extraction vessel volume V_E = 1 m^3). Optimal extraction time per batch is longer for SCFE plant operating at lower extraction pressures. In this case, when extraction pressure is 30 MPa the optimal extraction time (2.192 h) is 2- and 3-times longer that plants operating at 50 MPa (1.056 h) and 70 MPa (0.725 h). On the other hand, production cost in the SCFE plant operating at 50 MPa is slightly lower than the one operating at 70 MPa (difference of 0.078 USD/kg of oil), and evidently lower than the one operating at 30 MPa (difference of 1.154 USD/kg of oil). This implies that for SCFE plant with the same total capacity ($2m^3$ in this case) an increasing in extraction pressure from 30 to 50 MPa decreases the production cost in a 13%, but the decreasing of the extraction pressure from 50 to 70 MPa practically has not effect on production cost.

Comparing SCFE plants with the same annual productivity (550 ton/year of oil), the minimum production cost is reached at the lowest pressure considered in this work (30 MPa). This can be seen in Fig. 5-2 that shows the production cost of two-vessel plants operating at 30 MPa (total volume V_T = 5.860 m^3), 50 MPa (V_T = 2 m^3) and 70 MPa (V_T = 1.204 m^3). This result indicates that economies of scale compensate longer extraction time at low pressures that in turn determine fewer annual batches of the plant. In this case, optimal extraction times for the plant operating at 30 MPa is 3.414 h, which is 3 and 5 times longer than plants operating at 50 MPa (1.056 h) and 70 MPa (0.564 h).

Besides of this, the change in the SCFE plant sizes was not proportional with the increasing of extraction pressure. When pressure increased from 30 to 50 MPa (increasing of 67%), the plant size diminished 66%, but when pressure increased from 50 to 70 MPa (67%), plant size diminished only 40%.

Confirming that economies of scale apply to SCFE processes, Fig. 5-3 presents the effect of the total volume on production cost for two-vessel SCFE plants operating at 40 ºC and 50 MPa. The larger is the SCFE plant, the lower is the production cost, but at expense of a longer optimal extraction time.

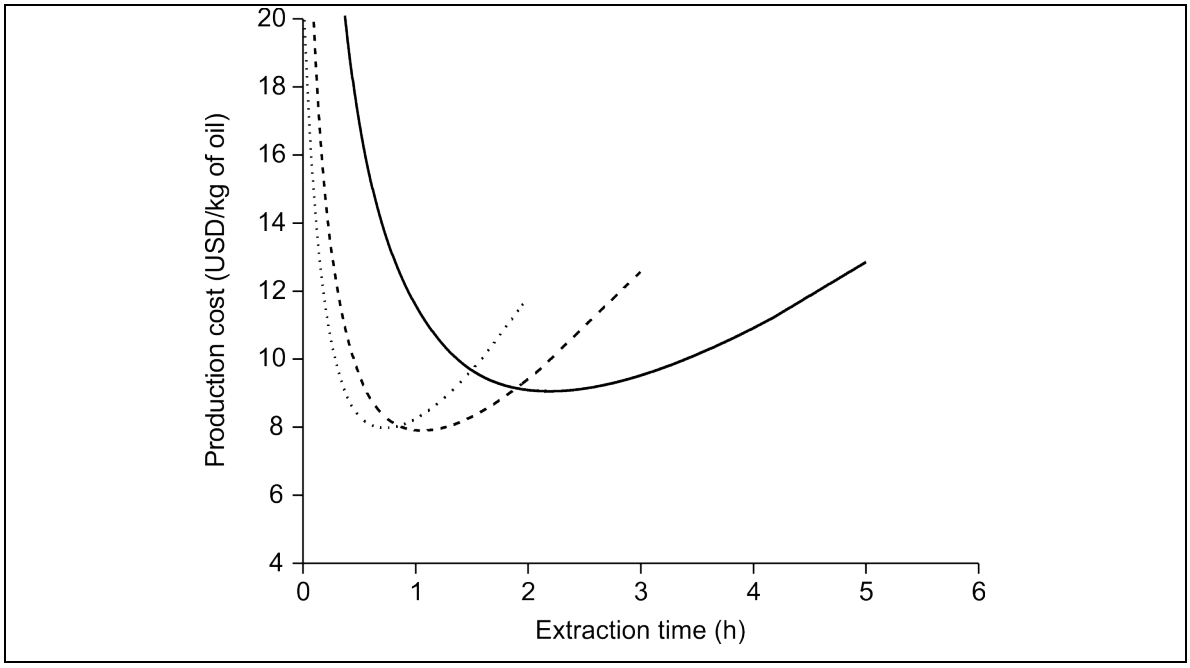

Figure 5-1: Positive effect of extraction pressure on production cost in function of extraction time for two-vessel SCFE plants (Total extraction volume of 2 m^3) operating at 40 ºC. Extraction pressures in the plot are (——) 30 MPa, (– – –) 50 MPa, and (· · · · ·) 70 MPa.

These optimal extraction times were proportionally shorter as the plant size decreased, being 1.1, 0.8, and 0.6 h those times for total volume of the plant 2, 1.202, and 0.680 m^3, respectively. Results in Figs. 5-2 and 5-3 show the convenience to operate plants with bigger capacities. The only caution is the optimal extraction times reached at 70 MPa, which could be shorter than the time that takes to put an extraction vessel again into the cycle.

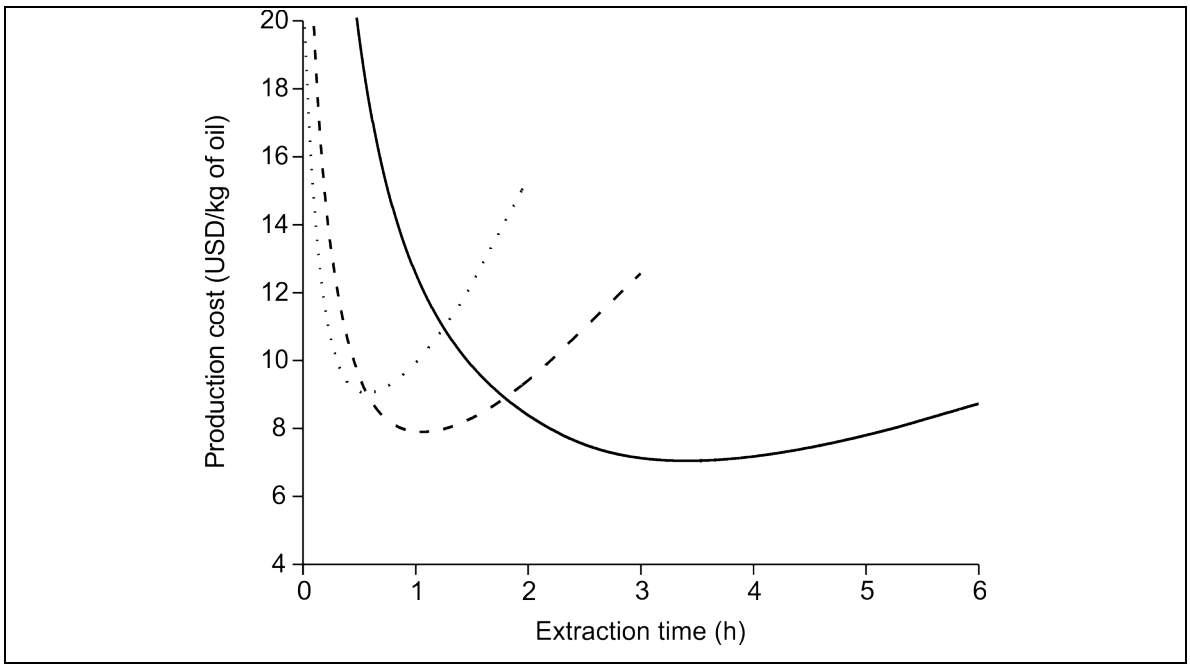

Figure 5-2: Production cost comparison among two-vessel SCFE plants with the same annual productivity (550 ton of oil per year), operating at 40 ºC, resulting in different combinations of extraction pressure and total volume of plant. The combinations of extraction pressure and extraction vessel volume are the following: (——) 30 MPa and 2.93 m^3, (– – –) 50 MPa and 1 m^3, and (· · · ·) 70 MPa and 0.602 m^3.

Fig. 5-4 shows the effect of extraction pressure on production cost for SCFE plants with (A) three and (B) four vessels (extraction vessel volume is V_E = 1 m^3 in each case). For both types of plants the tendency is the same: the lower is the extraction pressure, the longer is the optimum extraction time. In fact, the SCFE plant operating at 30 MPa has at least an optimal extraction time twice longer that the other ones. On the other hand, the minimum production cost for three- and four-vessel SCFE plants corresponds to 50 MPa as extraction pressure, being slightly lower than the production cost for the plant operating at 70 MPa. This result differs from the case of two-vessel SCFE plant, where the minimal production cost was reached at 70 MPa). As showed del Valle *et al.* (submitted), optimal extraction time for three-vessel plant is shorter than four-vessel plant. Minimal

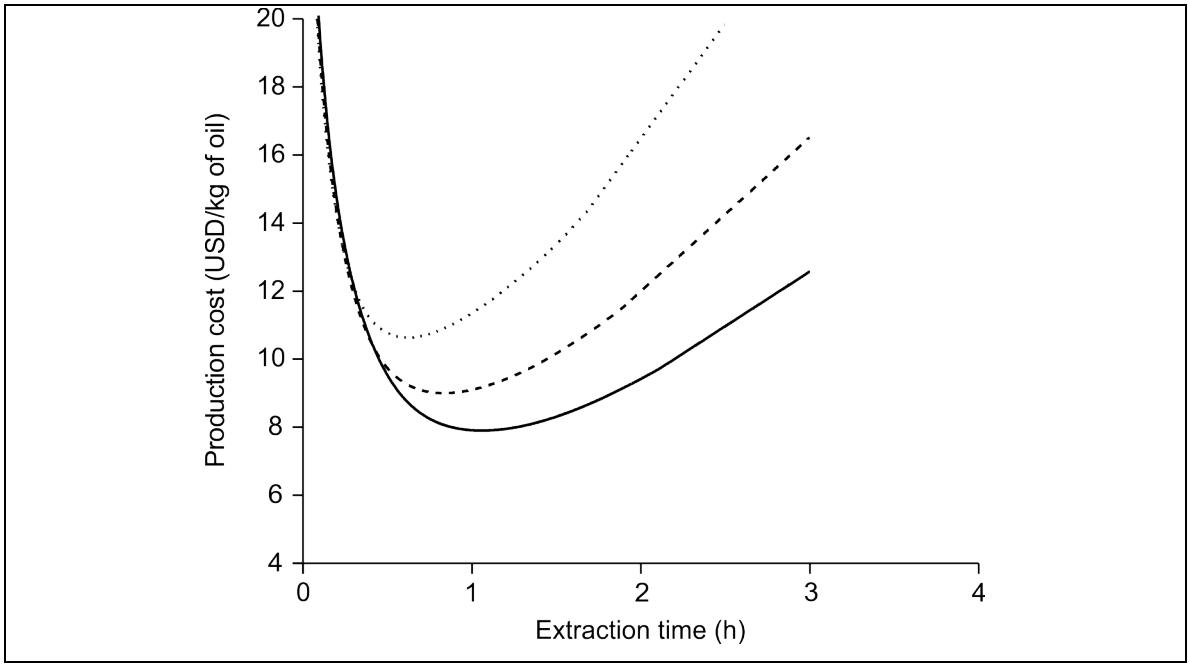

Figure 5-3: Positive effect of plant size on production cost in function of extraction time, for two-vessel SCFE plant operating at 40 ºC and 50 MPa, having total extraction volume of (——) 2, (– – –) 1.202, and (· · · ·) 0.680 m^3.

extraction time for a three- and four-vessel plant operating at 50 MPa is 2.2 and 2.5 h, the minimal production costs are 7.31 and 6.61 USD/kg of oil, respectively. However, Núñez and del Valle (submitted) obtained a different result, where the optimal extraction time was shorter for four- than three-vessel plant. This could due to the particular extraction conditions used by Núñez and del Valle (submitted) (Chapter 4).

Fig. 5-5 shows the effect of number of extraction vessel (n = 2, 3, and 4) on the production cost in function of extraction time in SCFE plants with extraction vessels of 1 m^3 operating at 40 ºC and 50 MPa. Similarly to above result (Fig. 5-4), the number of extraction vessels affects positively the production cost, which is according with the assumption that the larger is n, the closer to a counter-current process is the SCFE process where the mass transfer is more efficient. Besides having lower production costs in a four-vessel SCFE plant, the performance of a four-vessel SCFE plant also is better where the

productivity is 842.9 ton/year of oil, comparing with two- and three-vessel plants whose productivity are 546.3 and 640.1 ton/year of oil, respectively.

Table 5-2 summarizes the production cost estimated for SCFE plant processing prepressed rapeseeds with particle size of 2 mm and operating at 40 ºC and 30, 50, or 70 MPa. All plants operate with the same superficial CO_2 velocity (U = 6.57 mm/s), which results in a range of mass flow rates depending on the plant capacity (2,337 < F_{CO2} < 12,313 kg/h of CO_2). Production costs estimated in this work are in the range 5.881-12.74 USD/kg of oil, and capital cost estimated are between $3.800 and $23.75 millions. The lowest production cost was estimated for a 4×2.930 m^3 SCFE plant operating at 40 ºC and 30 MPa, which confirms the convenience of having bigger plants from the cost standpoint. Keeping constant all other parameters, an increasing of the extraction pressure from 30 to 50 MPa means a decreasing of 11.6% (average) in production cost. On the contrary, an increasing of extraction pressure from 50 to 70 MPa results in a decreasing of 1.6% (average) in production cost. On the other hand, the extraction yields (52.1-87.8%) for plants with two vessels are too low according with the previous works (del Valle *et al.*, submitted; Núñez and del Valle, submitted) considering that the lowest extraction yield estimated was 80.4%. However, it keeps the tendency that the substrate is partially exhausted in two-vessel plants, and almost exhausted for three- (88.9-98.7%) and four-vessel plants (94.1-97.7%). Finally, the lowest production cost was estimated for a 4×2.930 m^3 SCFE plant operating at 40 ºC and 30 MPa, which confirms the convenience of having larger plants.

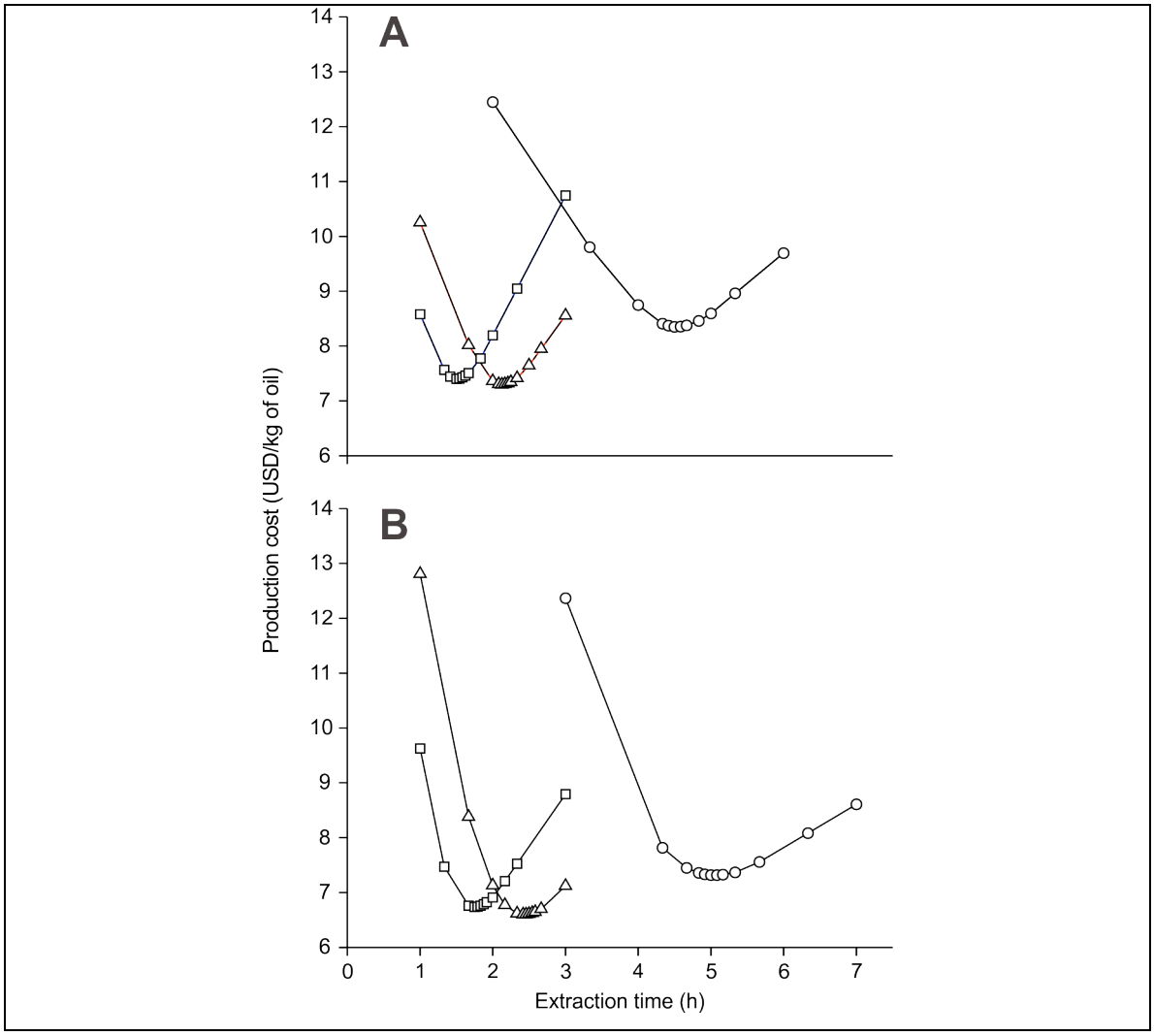

Figure 5-4: Effect of extraction pressure on production cost in function of extraction time for SCFE plant with (A) three and (B) four 1-m^3-vessels, operating at 40 ºC. the curves represents extraction at (○) 30, (△) 50, and (□) 70 MPa.

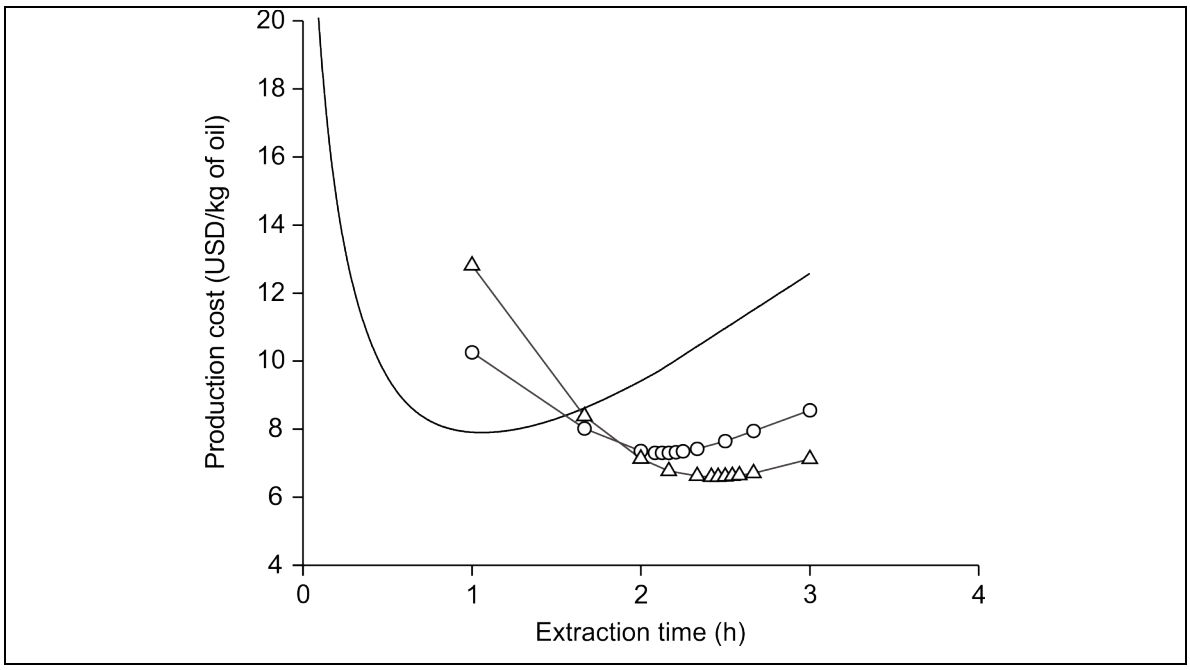

Figure 5-5: Effect of number of extraction vessel on production costs in function of extraction time for a SCFE plant with extraction vessel of 1 m^3 operating at 40 ºC and 50 MPa. Curves represent the number of extraction vessels: (——) 2, (○) 3, and (△) 4, where symbols indicates discrete points for three- and four-vessel plants.

Table 5-2: Minimal production cost, capital cost, annual productivity, optimal extraction time, oil yield for plants considered in this work (d_p =2 mm, U = 6.57 mm/s).

Vessel number (-)	Extraction pressure (MPa)	Total plant volume (m^3)	Optimal extraction time (h)	Oil yield (%)	Oil production (ton/year)	Capital Cost (M USD)	Production cost (USD/kg oil)
2	30	5.860	3.414	87.8	546.5	7,600	7.049
	30	2.000	2.192	79.4	264.1	5,300	9.055
	30	1.202	1.700	73.0	188.6	4,550	10.55
	30	0.680	1.267	65.5	129.1	3,800	12.74
	50	2.000	1.056	77.9	546.3	11,300	7.901
	50	1.202	0.833	72.2	387.1	9,450	9.000
	50	0.680	0.625	64.8	263.8	7,800	10.63
	70	2.000	0.725	73.8	766.5	17,400	7.979
	70	1.202	0.564	67.5	545.7	14,500	9.051
	70	0.680	0.417	59.9	374.8	11,900	10.58
	70	0.394	0.303	52.1	263.7	9,850	12.42
3	30	8.790	6.167	98.3	674.9	9,050	6.516
	30	3.000	4.500	95.9	308.1	6,200	8.352
	30	1.803	4.000	95.2	206.9	5,200	9.819
	30	1.020	3.250	91.9	139.3	4,350	11.81
	50	3.000	2.167	95.6	640.1	13,300	7.307
	50	1.803	1.917	94.2	429.3	11,050	8.400
	50	1.020	1.583	91.4	285.7	9,000	9.813
	70	3.000	1.583	95.0	873.1	20,600	7.429
	70	1.803	1.417	93.9	580.8	17,000	8.523
	70	1.020	1.167	90.6	386.0	13,750	9.897
	70	0.591	1.000	87.0	252.3	11,300	11.90
4	30	11.72	6.750	97.5	915.6	10,550	5.881
	30	4.000	5.083	96.7	411.8	7,050	7.318
	30	2.404	4.500	95.6	276.7	5,900	8.491
	30	1.360	3.750	93.5	184.3	4,850	10.06
	50	4.000	2.500	97.1	842.9	15,350	6.612
	50	2.404	2.208	95.7	565.9	12,650	7.501
	50	1.360	1.917	95.2	368.1	10,200	8.682
	70	4.000	1.833	96.6	1,146.2	23,750	6.759
	70	2.404	1.625	95.1	766.7	19,450	7.650
	70	1.360	1.417	94.3	494.5	15,650	8.866
	70	0.788	1.292	93.5	314.3	12,750	10.63

5.4 Discussion

Extraction pressure has a positive effect on production cost, which is minimum for the highest extraction pressure (70 MPa) in a two-vessel SCFE plant (Fig. 5-1). However, for three- and four-vessel plants the minimum production cost is practically the same for plants operating at 50 and 70 MPa (Fig. 5-4, Table 5-2). In these cases it is not clear what extraction condition would be better, but if it combined with the annual productivity of the plant could help to determine the best extraction pressure. For example, comparing a $3\times1m^3$-the plant operating at 50 or 70 MPa the productivity estimated are 546.3 and 766.5 ton/year of oil, respectively. From the profit standpoint, this could represent an important difference.

On the other hand, the optimal extraction time is limited by the time necessary to complete the reconditioning steps (unloading of exhausted substrate; depressurization of the vessel; pressurization of the vessel; and loading of fresh substrate) in an extraction vessel. In this work, optimal extraction time estimated reaches values as low as 18 minutes (or 0.303 h) for a 2×197 m^3 SCFE plant. It is possible that extraction vessels of that sizes cannot complete the reconditioning steps in 18 minutes, considering that a 1 m^3-extraction vessel can be depressurized around 40-50 minutes (Lack and Seidlitz, 2010). Even this problem would be worse in a multi-vessel plant (n = 3 or 4) where the CO_2 stream must flows through two or three extraction vessel before entering to the separator, and the switch times are shorter (one-half and one-third for three- and four-vessels SCFE plants) than extraction times (Núñez *et al.*, 2011). One possibility to circumvent this problem would be to extend the extraction time and reach an exhaustion grade of the substrate greater than 52%, but the plant would operate in a non-optimal point. Indeed, this constrain must be considered when it making a decision about what extraction condition is the best for an industrial plant.

Regarding the size of the SCFE plant, the larger is the plant, the lower is the production cost keeping constant all other parameters. For a two-vessel SCFE plant operating at 30 MPa, production cost decreases 44.7% for an increasing of 8.6-fold (from 0.680 to 5.860 m^3) in the size of the SCFE plant (Table 5.2). Moreover, the lowest

production cost estimated in this work was 5.881 USD/kg of oil for the biggest SCFE plant considered in this work (4×2.930m^3) operating at 40 ºC and 30 MPa (Table 5-2). Despite of the extraction rate is slower in this case than a higher extraction pressures (50 or 70 MPa), with longer optimal extraction times (6.750 h), the combination between total cost in the plant (MM$ 5.4) and its annual productivity (915.6 ton/year of oil) give a low production cost comparing to smaller plants at the same extraction pressure or other plants operating at higher extraction pressures. Therefore, economies of scale help to decrease the costs in the process, confirming that is convenient larger plants at industrial scale.

Together with the above, an increasing in the number of the extraction vessels contributes to the economies of scale. But even more importantly, it helps to improve the mass transfer by contacting the CO_2 with the substrate in a more efficient way (simulating a counter-current process) and resulting in CO_2 saving (Núñez *et al.*, 2011). Fig. 5-5 clearly shows that production cost decreases when the number of extraction vessels increases, but at the cost of longer optimal extraction times. In SCFE plants with extraction vessels of 1 m^3 operating at 40 ºC and 50 MPa, an increasing of n from 2 to 4 implies a decreasing of 16.3% in the production cost, despite of the higher capital cost. Thus, for the same extraction condition, it would be preferable to operate with four-vessel SCFE plants.

In literature, most of the works about economics in SCFE processes estimate production cost for plant operating around 30 MPa. Previously, Núñez and del Valle (submitted) did a detailed comparison between their results for the extraction of prepressed oilseeds at 40 ºC and 30 MPa and production cost reported in literature for the supercritical CO_2 extraction of oilseed at extraction pressure between 25 and 35 MPa. The only work that reported production cost for the oilseed supercritical CO_2 extraction at higher pressure was Fiori (2010), who estimated a production cost of 7.82 USD/kg of oil (value updated, Oanda.com, 2011) for the extraction of grape seed (C_o = 12% w/w) in a 3×0.8 m^3 SCFE plant with SC CO_2 at 60 ºC and 55 MPa. In this work, the production cost estimated for the supercritical CO_2 extraction of prepressed rapeseed (d_p = 2 mm) in a comparable plant (3×1 m^3, operating at 40 ºC and 50 MPa) with that of Fiori (2010) is 7.307 USD/kg of oil, which is in the same order of magnitude. The small differences between production costs estimated in both works can be explained by the slightly higher extraction conditions

considered by Fiori (2010). The main difference is the annual productivity reported in each work, being 306 ton/year of grape seed oil in the case of Fiori (2010) and 640.1 ton/year of rapeseed oil in this work. This indicates that the total cost estimated in this work is twice higher that the one estimated by Fiori (2010), which probably is due to the capital cost estimation in each case. Fiori (2010) estimated a capital cost of $5.3 million using the expression proposed by Lack *et al.* (2001), and this work estimated a capital cost of $13.3 million using the expression proposed by Núñez and del Valle (submitted).

6. CONCLUSIONS AND PERSPECTIVES

This thesis showed that simulation aids to optimize the process from both operational and economical (costs) standpoints. The main motivation of this endeavor was to contribute to the state of the art with a new methodology for the design and optimization of supercritical CO_2 extraction processes of solid substrates based on (i) minimal experimental information; (ii) mathematical modeling of the mass transfer in the packed bed and process simulation to scale-up the process; and (iii) costs estimation. Particularly, this thesis studied both operational and production costs in a supercritical CO_2 extraction of prepressed oilseeds process at industrial scale using a novel simulation algorithm.

The simulation algorithm presented in this thesis (Chapter 2) is based on the predictive shrinking core model for the inner mass transfer of the supercritical CO_2 extraction of prepressed oilseeds at 40 ºC and 30 MPa, which estimates the cumulative oil extraction curves in a multi-vessel (three or four extraction vessels) supercritical CO_2 extraction plant. This situation is numerically difficult to solve, given that the CO_2 stream leaving an extraction vessel enters to the next one in the cycle with a history of oil concentration, which affects the mass transfer in the following extraction vessels. The results showed that the supercritical CO_2 extraction of prepressed oilseed process reaches a pseudo-steady-state condition after three iterations in the simulation of the extraction process in one batch (Fig. 2-3). This means that the cumulative extraction curve obtained after that three iterations is representative of any batch that is carried out in the plant, which, in turn, allows estimating the productivity of a plant in function of extraction time and other relevant parameters that can be modified in the algorithm programmed in MATLAB. Among those operational parameters are the following: particle size, bulk density, and porosity of the packed bed; superficial velocity or flow rate of CO_2; extraction conditions (extraction and separation conditions); and the geometry of the supercritical extraction plant, including the size, form (aspect ratio, L/D), and number of the extraction vessels (that in turn determine the total volume of an industrial plant).

With respect to the scaling-up of a supercritical extraction process, this thesis proposes simulation as a versatile tool to evaluate changes in parameters affecting the

extraction rate. This would avoid doing experiments to many different extraction conditions and, hence, it would allow savings in resources and time. In literature, there are reported two main scaling-up criteria for the supercritical CO_2 extraction processes: (i) use the cumulative extraction curve obtained experimentally in laboratory, predicting the performance of the plant at large scale, and (ii) keeping constant the CO_2 flow rate-to-mass of substrate ratio, which is equivalent to keep constant the residence time in the extraction vessel. The first criterion has the problem that the extraction rate at industrial level is not the same as laboratory (generally is slower) and, therefore, the productivity could be overestimated leading to erroneous results regarding the costs of this technology. On the other hand, the second criterion applies only if the extraction is carried out in one extraction vessel at time, *i.e.*, only for two-vessel plants. This happen because the cumulative extraction curve changes for multi-vessel plant (n = 3 or 4) respect of the simpler case, so it is recommended caution at the moment to apply the residence time constant as scaling-up criterion (Fig. 2-5).

Regarding the costing of the supercritical CO_2 extraction process, this thesis studied both operational (Chapter 3) and production cost (Chapters 4 and 5). Operational costs include the following items: (i) costs associated to the batch (extraction itself), which include substrate, CO_2 make-up due to the losses when the extraction is finished and the remained CO_2 is vented to the environment, and energy to depressurize and pressurize the extraction vessel; (ii) costs associated to the solvent cycle, which include heating and cooling to adjust the CO_2 stream conditions by means of heat exchangers, and electric power to pump the CO_2, (iii) labor, and (iv) other minor costs expressed as the 5% of the sum of all previous costs. On the other hand, the production costs include the operation cost (as explained before) and the capital cost. Capital cost refers to the investment in the supercritical CO_2 extraction plant (main equipment, buildings, etc.). This thesis studied the effect number and geometry (L/D) of extraction vessels, extraction pressure, and plant size on production costs.

Operational costs estimated in this thesis are in the range of 4.081-8.149 USD/kg of oil, for a supercritical CO_2 extraction plants processing prepressed oilseeds (C_o = 20% w/w with extraction vessels of 1 m^3 operating at 40 ºC and 30 MPa (Chapter 3). This thesis

studied the effect on extraction rate of particle size (d_p = 0.5, 1, 2, 3, 4 mm), superficial CO_2 velocities (2.76, 5.52, and 11.0 mm/s), and number of extraction vessels (n= 2, 3, and 4). Operational cost decreases when the particle size decreases, keeping other parameters constant (Fig. 3-3). However, packed beds with smaller particles (d_p = 0.5 and 1 mm) are not practical for multi-vessel plants because in just one batch the packed bed is almost exhausted, being unnecessary the use of other extraction vessel connected in series (Fig. 3-4). So, the analysis for three- and four-vessel plants corresponds to particle sizes ≥ 2 mm. On the other hand, the effect of superficial CO_2 velocity on operational cost depends on the particle size (Fig. 3-5). For intermediate particle sizes ($1 \leq d_p < 3$ mm) most convenient superficial CO_2 velocity is the intermediate value considered in this work (5.52 mm/s), and for large particle sizes the best superficial CO_2 velocity is 2.71 mm/s. This trend is seen in all simulated plants. Considering a particle size of 2 mm, an increasing in superficial CO_2 velocity from 2.71 to 5.52 mm/s produces a decreasing in operational cost and optimal extraction time. However, when superficial CO_2 velocity increases from 5.52 to 11.0 mm/s, optimal extraction time decreases, but operational cost increases slightly. So, there is a minimum operational cost using a superficial CO_2 velocity of 5.52 mm/s for particles of 2 mm (Fig. 3-6). Finally, operational cost decreases when the number of extraction vessels increases, but at expenses of an increasing in optimal extraction time (Fig. 3-8).

For estimation of production costs, capital cost is the item that presents major uncertainties. In literature there is little information about costing a supercritical CO_2 extraction plant and this know-how is generally associated to plant manufacturers. This thesis proposes a mathematical expression to determine the capital cost based on information available in the literature and direct quotations of plants (Eq. 4.9). The expression notes separately the contribution of the solvent cycle (up to 65%, proportional to the flow rate of CO_2) and the extraction vessels (aspect ratio and number of extraction vessels) on the capital cost (Fig. 4-2).

A consequence of including capital cost in the analysis is that optimal extraction time does not coincide for operational and production cost (Fig. 4-3). In general, and keeping constant all parameters, the optimal extraction time is shorter for production cost than operational cost. It is very important to keep in mind this point depending on which

decision is made. If it were an investment decision, the relevant value to compare with other alternatives would be the production cost, but if the decision were about the optimal point of operation of an existing plant (especially if this plant has idle capacity), the relevant value to take in count would be the operational cost.

Considering the effect of the number (n = 2, 3, and 4) and geometry ($3 \leq L/D \leq 8$) of the extraction vessels, production costs estimated in this thesis are in the range of 7.808-12.37 USD/kg of oil (including capital cost). These production costs were obtained for supercritical CO_2 extraction plants whose total extraction volume was 2 m^3, processing prepressed oilseeds (C_o = 20% w/w and d_p = 2 mm) at 40 ºC and 30 MPa. This resulted in superficial CO_2 velocities between 2.71 and 10.4 mm/s, considering two mass flow rate of CO_2 (3000 and 6000 kg/h). For the plants considered in this part, capital costs estimated were between USD 4.5 and USD 6.4 millions. The major contributions to the production cost are the capital cost (28.9-39.0%), substrate (22.1-35.1%), and labor (14.9-24.5%). Minimal production cost depends on residence time and decreases when superficial CO_2 velocity increases. Also, for a given CO_2 velocity, an extraction vessel with a low aspect ratio performs better than a slender one. Similarly to the operational cost analysis, production cost decreases with an increasing of number of extraction vessel. And this also implies that economies of scale allow decreasing the production costs. In addition, there are other factors besides production cost that should be accounted for to make investment recommendations as the oil yield or exhaustion grade of the substrate, and the annual productivity of the plant. This last factor is very important when the objective is to maximize the profitability of the industrial plant.

Now, considering the effect of the extraction pressure (P_{ext} = 30, 50, and 70 MPa) and the total volume of the plant ($0.394 \leq V_T \leq 11.72$ m^3) of the extraction vessels, production costs estimated in this thesis are in the range of 5.881-12.74 USD/kg of oil (including capital cost). These production costs were obtained for supercritical CO_2 extraction plants of 2, 3, and 4 extraction vessels, processing prepressed oilseeds (C_o = 20% w/w and d_p = 2 mm) at 40 ºC using a superficial CO_2 velocity of 6.57 mm/s. The resulting mass flow rates of CO_2 were in the range 2,337-12,313 kg/h. Capital costs for the plants considered in this work were in a wide range between USD 3.95 and USD 23.8

millions. For two-vessel plants, production cost decreases when extraction pressure increases. However, for multi-vessel plants, the minimum production cost is reached at 50 MPa, although this production cost is slightly lower than at 70 MPa (Fig. 5.1 and 5.4). In last case, together with the production cost the annual plant productivity can be other factor helping to make investment decisions. On the other hand, when supercritical CO_2 plants has the same annual productivity, the size of the SFE plant has more influence than extraction pressure on production cost (Fig. 5-2). Moreover, for plant operating at the same extraction conditions, the larger is the plant, the lower is the production cost. Even more, an increasing in the number of extraction vessel also implies a decreasing in the production cost (Fig. 5-5). All this confirms that economies of scale apply to a supercritical CO_2 extraction process and allow decreasing the costs in the process.

Finally, the methodology presented in this thesis can be extrapolated to other substrates by collecting a minimal amount of experimental information to determine the relevant mass transfer parameter (microstructural factor, F, for a particular substrate, which is a function only of the pretreatment, that in turn it determines the effective diffusivity of the solute in the solid matrix), and adapting the mass transfer model to the simulation algorithm. For example, this methodology was applied to estimate the production cost for the supercritical CO_2 extraction of oil from rosehip seeds (F = 0.0996) at different extraction conditions (results not reported). This is an specialty oil whose selling price reaches 55 USD/kg. The highest production cost estimated with this methodology was 14.86 USD/kg of rosehip oil, which compared with the selling price gives a good margin for a possible profitable business (to estimate that production cost, the supercritical CO_2 extraction of rosehip seeds was simulated in a 2×1 m^3 plant, with a capital cost of USD 4.7 millions, and the following extraction conditions: particle size of 0.5 mm, extraction conditions at 40 ºC and 30 MPa, using a superficial CO_2 velocity of 3.8 mm/s, obtaining a optimal extraction time of 1.1 h, oil yield of 97,3% per batch, and a annual productivity of 360 ton/year of rosehip oil). This indicates that supercritical CO_2 extraction could be a competitive technology from the economical standpoint for specialty oils or other value-added products (*e.g.*, carotenoids).

NOMENCLATURE

Variables and parameters

a_p Superficial area-volume ratio of the particles ($m^2 \cdot m^{-3}$)

C Oil concentration in the supercritical phase (kg oil$\cdot m^{-3}$ CO_2 or kg$\cdot$oil kg^{-1} CO_2)

C_o Initial oil content in the substrate (kg oil$\cdot m^{-3}$ CO_2 or kg$\cdot$oil kg^{-1} CO_2, C_o = 0.2 kg oil$\cdot kg^{-1}$ prepressed rapeseed)

C_p Oil concentration in the solid particle pores (kg$\cdot m^{-3}$)

C_{sat} Oil solubility in the supercritical fluid at extraction conditions (kg$\cdot m^{-3}$ or g oil$\cdot kg^{-1}$ CO_2, C_{sat} = 7.915 g oil$\cdot kg^{-1}$ CO_2 at 40 ºC and 30 MPa).

C_{sep} Oil solubility in the supercritical fluid at separation conditions (kg$\cdot m^{-3}$ or g oil$\cdot kg^{-1}$ CO_2, C_{sep} = 0.164 g oil$\cdot kg^{-1}$ CO_2 at 60 ºC and 8 MPa)

d_p Particle diameter (m)

D Extraction vessel inner diameter

D_{12} Binary diffusivity of the solute in the supercritical fluid ($m^2 \cdot s^{-1}$)

D_e Solute effective diffusivity within the solid substrate ($m^2 \cdot s^{-1}$)

D_L Axial dispersion coefficient ($m^2 \cdot s^{-1}$)

E Extraction yield (kg solute$\cdot kg^{-1}$dry solid)

E_A Annual extraction yield in a SCFE plant (ton-oil $year^{-1}$)

F Microstructural correction factor (-)

F_{CO2} CO_2 mass flow (kg$\cdot s^{-1}$ or kg$\cdot h^{-1}$)

h Enthalpy of the CO_2 stream (kJ kg^{-1})

k_f External mass transfer coefficient ($m \cdot s^{-1}$)

L Extraction vessel (or packed bed) height (m)

L/D Aspect ratio

m Scaling factor for SCFE plant

m' Scaling factor for SCFE plant ($0.5 \times m$)

M Mass of the substrate (kg)

M_{CO2} Mass of CO_2 (kg)

M_o Initial mass of the substrate (kg)

M_r Oil recovery at the end of extraction (kg)

n Number of extraction vessels in a SCFE plant (-)

n_r Number of extraction vessels of a reference SCFE plant (-)

N Number of annual batches (-)

P_{ext} Extraction pressure (MPa)

P_n Design or nominal pressure of a extraction vessel (MPa)

P_{sep} Separation pressure (MPa)

q Specific mass flow rate of CO_2 ($m^3\ kg^{-1}\ s^{-1}$)

Q_{CO2} CO_2 volumetric flow ($L \cdot min^{-1}$)

r Radial position in the particle (m)

r_c Radial position of the rich-solute core radius (m)

R Particle radius (m)

t Extraction time (s or h)

t_c Cycle time (h)

t_s Switch time (h, = $t_e \times (n\text{-}1)^{-1}$)

T_{ext} Extraction temperature (K)

T_{sep} Separation temperature (K)

u Interstitial velocity of the supercritical fluid in the packed bed ($=U \cdot \varepsilon^{-1}$, $m \cdot s^{-1}$)

U Superficial velocity of the supercritical fluid in the packed bed ($m \cdot s^{-1}$)

U_{mf} Velocity of incipient fluidization ($m \cdot s^{-1}$)

V_E Extraction vessel volume (m^3 or L)

V_r Volume of a reference SCFE plant (m^3 or L)

V_T SCFE plant volume (m^3 or L)

z Axial position along the extraction vessel (m)

Cost items

a Time horizon for the SCFE plant (=10 years)

C_B Annual cost of the extraction batches (USD)

C_I Specific capital cost or equivalent annuality for the SCFE plant (USD)

C_{OC} Operational cost (USD kg^{-1} of oil)

C_{PC} Production cost (USD kg^{-1} of oil)

C_{SC} Annual cost of the solvent cycle (USD)

C_{SD} Annual cost of the CO_2 dissolved in the oil within the separator (USD)

C_T Total annual cost in a SCFE plant

I Cost of a SCFE plant (USD)

I_r Cost of a reference SCFE plant (USD)

r Discount rate for the equivalent annuality of the SCFE plant (=6%)

Dimensionless groups

b Solute solubility-solute content in the solid ratio (-)

Bi Biot number ($= k_f \cdot R \cdot D_e^{-1}$, -)

Pe Peclet number ($= u \cdot L \cdot D_L^{-1}$, -)

Re Reynolds number ($= d_p \cdot U \cdot \rho \cdot \mu^{-1}$, -)

S Dimensionless extraction yield (-)

Sc Schmidt number ($= \mu \cdot \rho^{-1} \cdot D_{12}^{-1}$, -)

X Dimensionless solute concentration in the solid particle pores (-)

y Dimensionless solute concentration in the supercritical phase (-)

Y Dimensionless solute concentration in the supercritical phase (-)

Vectors

$\mathbf{H}_i$ History vector of the output current of an extraction vessel at stage i

$\mathbf{S}_i$ Extraction yield vector of the output current of an extraction vessel at stage i

$\mathbf{t}_i$ Extraction time vector of the output current of an extraction vessel at stage i

$\mathbf{y}_i$ Solute concentration vector of the output current of an extraction vessel at stage i

$\mathbf{Y}_i$ Solute concentration vector of the inlet current of an extraction vessel at stage i

Greek letters

α Weighting parameter for the solvent cycle in the SCFE plant cost estimation

β Weighting parameter for the extraction vessel geometry in the SCFE plant cost estimation

δ Dimensionless radial position in the particle (-)

δ_c Dimensionless radius of the particle rich-solute core (-)

ρ	CO_2 density ($kg \cdot m^{-3}$)
ρ_b	Bulk density of the packed bed ($kg \cdot m^{-3}$)
μ	CO_2 viscosity ($Pa \cdot s$)
ε_b	Bed porosity (-)
ρ_b	Bed bulk density ($kg \cdot m^{-3}$)
θ	Dimensionless time (-)
τ_e	Dimensionless characteristic external time of the extraction (-)
ζ	Dimensionless axial position (-)

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APPENDIXES

APPENDIX A: DEPRESSURIZATION AND PRESSURIZATION IN AN EXTRACTION VESSEL

This appendix describes the procedure to estimate the energy of both depressurization and pressurization for an extraction vessel. Both processes, together with the unloading of exhausted substrate and loading of fresh substrates, are parts of the reconditioning steps of an extraction vessel, which complete an extraction cycle (sum of the extraction itself and reconditioning steps).

Estimation of depressurization time of an extraction vessel

Depressurization starts at extraction conditions (40 °C and 30 MPa). The assumptions to estimate the depressurization energy were the following assumptions: i) the CO_2 mass decreasing within the vessel (ρV) is equal to the mass flow leaving the vessel ($\dot{m}$); ii) the physical properties of the CO_2 within the vessel are constant for a small mass of CO_2 leaving the vessel; iii) the small CO_2 mass leaving the vessel has the same density as the CO_2 within the vessel (ρ); and, iv) the CO_2 mass flow is constant for a small reduction of the CO_2 mass within the vessel. Eq. (A.1) represents the mass flow of CO_2 leaving the vessel. The volumetric flow in Eq. (A.1) is considered proportional to the pressure difference between the pressure in the extraction vessel (P_1) and the external pressure (P_2) (Eq. A.2). In Eq. (A.2), P_2 corresponds to the pressure of the working tank (saturated conditions at environmental temperature, in this case 6.4 MPa) until the pressure in the extraction vessel and working tank coincides (CO_2 is recovered for recycling to the process). After this, P_2 corresponds to the atmospheric pressure, when CO_2 is vented to the atmosphere. We do not consider another CO_2 recovery step (which typically is done by a compressor up to 0.2-0.5 MPa). Finally, the variation of the CO_2 density for a small mass of CO_2 leaving the vessel in Δt (Eq. A.3) is obtained by solving Eq. (A.1)-(A.3) simultaneously.

$$\dot{m} = \rho \dot{V} \tag{A.1a}$$

$$dm = \rho dV \tag{A.1b}$$

$$\dot{V} = \frac{\Delta V}{\Delta t} = K\left(\frac{P_1 - P_2}{\rho_{m_1}}\right)^{1/2} \quad \text{(A3–1.2)}$$

$$\rho_{m_2} = \rho_{m_1} e^{\left(\frac{\Delta V}{m_1}\rho_{m_1}\right)} \quad \text{(A3–1.3)}$$

On the other hand, if the changes in both potential and kinetic energy are neglected, the energy change in the extraction vessel depends on the enthalpy of CO_2 that leave the vessel (h_{CO2}) and the external heat entering/exiting (dQ) as shows the Eq. (A.4). Eq. (A.4) can be re-writing using Eq. (A.5), assuming physical properties of CO_2 within the extraction vessel are the same than the CO_2 leaving the vessel. Finally, Eq (A.6) describes the heat transfer entering/exiting to/from the extraction vessel per volume unit.

$$d\left(mu_{CO_2}\right) = -dm\,h_{CO_2} + dQ \quad \text{(A.4)}$$

$$\rho u_{CO_2} = \rho h_{CO_2} - P \quad \text{(A.5)}$$

$$Q_V = \int_{h_1}^{h_2} \rho\, dh - \left(P_2 - P_1\right) \quad \text{(A.6)}$$

Eqs. (A.1)-(A.6) were solved using numerical methods implemented in Excel ®.

K in Eq. (A.2) was selected such that the CO_2 within the extraction vessel during the depressurization process never reach a two-phase state, which determine a K value of 6.5×10^{-6}. Eq. (A.2) can be derived of energy balance between the extraction vessel and the working tank Eq. (A.7):

$$\dot{V} = A\left(\frac{2}{K'}\right)\left(\frac{P_1 - P_2}{\rho}\right)^{1/2} \quad \text{(A.7)}$$

In Eq. (A.7) K' is a drop-pressure factor. So, if we suppose that the piping in the system have 40 mm of internal diameter and the K value is 6.5×10^{-6}, the K' results 74×10^{-5}.

Pressurization process in an extraction vessel

The pressurization starts at 40 °C and 0.1 MPa, and proceeds in two steps: (i) vessel is equalized with the working tank (6.4 MPa); and (ii) CO_2 is pumped up to 30 MPa.

We did the following assumptions to solve the Eqs. (A.8)-(A.11): (i) CO_2 is pumped from the working tank (P_1 = 6.4 MPa and 25 ºC) to the vessel; (ii) CO_2 is preheated before entering to the extraction vessel in a heat exchanger up to 40ºC (extraction temperature) (iii) the temperature in the vessel is constant and equal to 40 ºC.

The pump work and heat transfer in heat exchanger were estimated similarly to the Appendix A:

$$dW = \frac{dm\left(h_o - h_i\right)}{\eta_i \eta_e} \tag{A.8}$$

$$dQ = dm\left(h_o - h_i\right) \tag{A.9}$$

Also, density changes and heat transfer in the extraction vessel was estimated analogously to the Appendix A:

$$\rho_{m_2} = \rho_{m_1} e^{\left(\frac{\dot{V}}{m_1}\rho_{m_1}\Delta t\right)} = \rho_{m_1} e^{\left(\frac{\Delta V}{m_1}\rho_{m_1}\right)} \tag{A.10}$$

$$Q_V = \int_{h_1}^{h_2} \rho\, dh - \left(P_2 - P_1\right) \tag{A.11}$$

The leaving the vessel (ΔV) in Eq. (A.10) is equal to $\Delta V = K\left(\left(P_1 - P_2\right)/\rho_{m1}\right)^{1/2} \Delta t$ or 55 L depending on the step (equalization up to working tank conditions or pumping) in the pressurization process.

APPENDIX B: ESTIMATION OF OIL RECOVERY IN THE DEPRESSURIZATION OF A EXTRACTION VESSEL

The oil recovery (M_r) was estimated as the mass of oil dissolved in the CO_2 leaving the extraction vessel when the pressure is reduced from P_1 to P_2 (Eq. A.10). On the one hand, if oil solubility (C_{sat}) is higher than actual oil concentration in CO_2, the oil recovery is determinate by the product between the oil concentration and the CO_2 flow (Eq. B.1). If oil solubility is lower than actual oil concentration in CO_2, the oil recovered is proportional to the CO_2 flow and the oil solubility at T_1 and P_1, (Eq. A.1). The oil solubility in the CO_2 was estimated using the correlation proposed by del Valle *et al.* (2012a). The oil concentration in the beginning of the depressurization was estimated as an average of the oil concentration along to the extraction vessel at the end of the extraction process.

$$M_r = \left(M_1 - M_2\right)\min\left(C_{sat}, C_i\right) \tag{B.1}$$