
AIX-MARSEILLE UNIVERSITE

TITRE

**DEVELOPMENT OF TOOLS FOR THE IMPLEMENTATION OF
AN INDUSTRIAL-SCALE SUPERCRITICAL FRACTIONATION
PROCESS**

THESE

pour obtenir le grade de

DOCTEUR DE L'UNIVERSITE AIX-MARSEILLE

Faculté de Sciences Techniques

Discipline : Génie des Procédés

Présentée et soutenue publiquement par :

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Le 05/05/2015

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Acknowledgments

I would like to express my deepest thanks to all the people who have in any way helped through this research. First of all, I wish to thank the members of the jury for accepting to evaluate this work, particularly to Prof. Jean-Stéphane Condoret and Prof. María José Cocero for their examination. I would like to express my gratitude to Michel and Vincent Perrut for their collaboration and for generously providing us the fish esters for our research. I also wish to thank Thomas Lasserre for his work and passion throughout the Salinalgue Project.

Je souhaite à présent remercier les personnes qui m'ont permis d'arriver à ce stade. Premièrement, je voudrais remercier Elisabeth Badens, Christelle Crampon et Frédéric Charton, non seulement pour leurs apports scientifiques mais particulièrement pour m'avoir permis de développer mes compétences dans une ambiance humaine et encourageante. Je voudrais remercier aussi très particulièrement Jean-Paul Nisteron, sans qui je n'aurais jamais pu démarrer aucune expérience. Je reconnais aussi l'appui et l'aide des doctorants et du personnel permanent du laboratoire, particulièrement à Amine Toudji et Salah Akkache qui m'ont toujours permis d'aller plus loin grâce à leurs apports théoriques et discussions. Je remercie aussi Adil Mouahid pour son aide et support. Finalement, je remercie tout le laboratoire M2P2 pour une expérience enrichissante, pour leur amitié et encouragement constant.

Quisiera también agradecer el apoyo de mi familia, particularmente de mis padres, mi tía y a mi abuela que desde siempre me han sostenido en el camino que he elegido, siempre incitándome a expresar al máximo mis capacidades. A pesar de la distancia han sabido ser un apoyo invaluable. También quisiera agradecer particularmente a mi hermano, Dario Pieck, quien me permitió acceder a esta tesis, me mostró el camino y me acompañó con sus consejos y ayuda. Finalmente quisiera agradecer a Dios, quien me ha llenado de gracias y me ha dado fuerzas para seguir adelante en los momentos más difíciles.



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Nomenclature

Acronyms

<i>CFD</i>	Computational Fluid Dynamics	<i>GRAS</i>	Generally Recognized As Safe
<i>DHA</i>	DocosoHexaenoic Acid	<i>HETS</i>	Height Equivalent to a Theoretical Stage
<i>EE</i>	Ethyl Ester	<i>HTU</i>	Height of a Transfer Unit
<i>EPA</i>	EicosanoPentaenoic Acid	<i>IS</i>	Internal Standard
<i>EOs</i>	Equation of State	<i>NTU</i>	Number of Transfer Units
<i>FAEE</i>	Fatty Acid Ethyl Ester	<i>SFP</i>	Supercritical Fractionation Process
<i>FAME</i>	Fatty Acid Methyl Ester	<i>VLE</i>	Vapor-Liquid Equilibrium
<i>FID</i>	Flame Ionization Detector		

Latin symbols

a	Surface area	m^{-1}	$a = \frac{\text{packing surface}}{\text{bed volume}}$
A_p	Packing element surface	m^2	
$AARE$	Average Absolute Relative Error	—	$AARE = \frac{1}{N} \sum \left \frac{x_i^{exp} - x_i^{calc}}{x_i^{exp}} \right $
Bo	Bond number	—	$Bo = \frac{\rho_L g}{a^2 \sigma}$
c_G	Capacity factor	$m^{1/2} s^{-1}$	$c_G = u_{GF} \left(\frac{\rho_G F_P}{\Delta \rho} \right)^{1/2}$
c_G^*	Dimensionless capacity factor	—	$c_G^* = u_{GF} \left(\frac{\rho_G F_P}{\Delta \rho g} \right)^{1/2}$
c'_G	Corrected capacity factor	—	$c'_G = u_{GF} \left(\frac{\rho_G F_P}{\Delta \rho g} \right)^{1/2} \left(\frac{\mu_L}{\mu^o} \right)^{0.1}$
D_P	Equivalent particle diameter	m	$D_P = \left(\frac{6V}{\pi} \right)^{1/3}$
e	Extract mass flow rate	$kg s^{-1}$	
e_i	Extract mass flow rate of component i	$kg s^{-1}$	$e_i = e \cdot x_i^E$
E	Extract solvent-free mass flow rate	$kg s^{-1}$	$E = \frac{e}{1 - x_{CO_2}^E}$
F_P	Packing factor	m^{-1}	$F_P = \frac{a}{\varepsilon^3}$
F_V	Vapor capacity factor	$m s^{-1}$	$F_V = u_{GF} \left(\frac{\rho_G}{\Delta \rho} \right)^{1/2}$
g	Acceleration of gravity	$m s^{-2}$	$g = 9.81 m \cdot s^{-2}$
h	Liquid holdup	—	
K_i^*	Overall distribution ratio	—	$K_i^* = \bar{K}_i \neq f(X_i)$
L	Liquid solvent-free mass flow rate	$kg s^{-1}$	
ℓ	Vapor load	—	$\ell = 1 - y_{CO_2}$
m_i	Mass of i	kg	
M	Solvent-to-non-solvent ratio in the liquid	—	$M_i = \frac{x_{CO_2}}{1 - x_{CO_2}}$
N	Solvent-to-non-solvent ratio in the vapor	—	$N_i = \frac{y_{CO_2}}{1 - y_{CO_2}}$
n	Number of theoretical stages	—	
o	Overhead mass flow rate	$kg s^{-1}$	

o_i	Overhead mass flow rate of component i	$kg\ s^{-1}$	$o_i = o \cdot x_i^O$
O	Overhead solvent-free mass flow rate	$kg\ s^{-1}$	$O = \frac{o}{1-y_{CO_2}^O}$
r	Raffinate mass flow rate	$kg\ s^{-1}$	
r_i	Raffinate mass flow rate of component i	$kg\ s^{-1}$	$r_i = r \cdot x_i^R$
R	Raffinate solvent-free mass flow rate	$kg\ s^{-1}$	$R = \frac{r}{1-x_{CO_2}^R}$
S	Solvent mass flow rate	$kg\ s^{-1}$	
S'	Recovered solvent mass flow rate	$kg\ s^{-1}$	
S_i	Stripping factor	—	$S_i = K_i^* \varepsilon$
s_{12}	Solubility of FAEE mixture in the solvent	—	$s_{12} = x_{FAEE}^O$
s_{21}	Solubility of the solvent in the raffinate	—	$s_{21} = x_{CO_2}^R$
t_R	Relative retention time	—	
u	Velocity	$m\ s^{-1}$	$u = \frac{\text{mass flowrate}}{\text{cross section} \times \text{density}}$
V	Solvent-free vapor flow rate	$kg\ s^{-1}$	
V_p	Packing element volume	m^3	
x_i	Mass fraction in the liquid	—	
X_i	Solvent-free mass fraction in the liquid	—	$X_i = \frac{x_i}{1-x_{CO_2}}$
y_i	Mass fraction in the vapor	—	
Y_i	Solvent-free mass fraction in the vapor	—	$Y_i = \frac{y_i}{1-y_{CO_2}}$
z	Feed mass flow rate	$kg\ s^{-1}$	
z_i	Feed mass flow rate of component i	$kg\ s^{-1}$	$z_i = z x_i$
Z	Solvent-free feed mass flow rate	$kg\ s^{-1}$	$Z = \frac{z}{1-x_{CO_2}}$

Greek symbols

α_{ij}	Solvent selectivity	—	$\alpha_{ij} = \frac{Y_i X_j}{X_i Y_j}$
ε	Extraction yield	—	$\varepsilon = \frac{E}{Z}$
ε_b	Bed void fraction	—	$\varepsilon = \frac{\text{void volume}}{\text{bed volume}}$
μ	Viscosity	$kg\ m^{-1}\ s^{-1}$	
ρ	Density	$kg\ m^{-3}$	
σ	Interfacial tension	$kg\ s^{-2}$	
ϕ_s	Particle sphericity	—	$\phi_s = \left(36\pi \frac{V_p^2}{A_p^3}\right)^{\frac{1}{3}}$
$\phi_{s,i}$	Stripping loss	—	$\phi_{s,i} = \frac{r_i}{z_i}$
ψ	Flow parameter	—	$\psi = \frac{u_L}{u_G} \left(\frac{\rho_L}{\rho_G}\right)^{\frac{1}{2}}$
Ω	Solvent-to-feed ratio	—	$\Omega = \frac{S}{Z}$

1. Introduction

1.1. Context: The Salinalgue FUI project

The work presented here is but one aspect of the Salinalgue FUI* project. Salinalgue was the largest European project for the production of biofuels and biosourced products derived from the culture of microalgae. The project aim was to develop an economically-viable production and refining of an endemic microalgae on the underexploited salt fields in Southern France, starting by the salt fields at Gruissan.

The first stage of the project consisted in the production of *Dunaliella salina* in four 250 m³ raceways and the exploration of different valorization strategies. A heavy emphasis in the sustainability and environmental responsibility was put. Hence, the use of supercritical processes was envisioned as an alternative to more conventional processes with a heavier environmental footprint.

After grow, harvest and concentration of the microalgae into a paste, the oil targeted for production of biodiesel can be extracted. From this point, and following the biorefinery concept, several different setups were considered in order to recover co-products such as ω -3 concentrated oils, carotenoids such as β -carotene and luteine, phospholipids, biogas and animal fodder.

The diversification of the array of possible products is very important for the economic viability of the project. The production of biodiesel must face the current relatively low prices of petroleum-issued fuels and be able to compete. Hence, the capacity to recover derivative higher-value products becomes an important factor when discussing the economic viability of the project.

* Fonds Unique Interministériel

Supercritical extraction was chosen for the recovery of the algal oil, but the process could also be used to purify carotenoids [1] (which are produced in great quantities by *Dunaliella salina*) or phospholipids [2]. In the context of the Salinalgue project, the extraction by use of supercritical fluids was studied at the M2P2 laboratory but will not be discussed in this dissertation since it addresses a different process. After the extraction of the oil, the supercritical fractionation process becomes an interesting process to consider. In an innovative process as the one proposed by the Salinalgue Project, the amount of possible applications of the fractionation process is immense. Moreover, changes in the feed composition due to its biological source and/or economic factors such as the fluctuation of prices of high-added value products require the designed process to be flexible. The supercritical fractionation process is flexible and can be controlled through process variables such as temperature, pressure, solvent-to-feed ratio and use of cosolvents.

The oil extracted from the microalgae contains many thermosensitive valuable products that are hard to separate. For example, microalgal oil has been reported to be able to contain a large quantity of ω -3 fatty acids depending on the growth conditions [3]. Concentration of ω -3 fatty acids such as the eicosanopentaenoic acid and docosahexaenoic acid (EPA and DHA, respectively) has already been proved feasible through supercritical fractionation [4–10]. Moreover, separation of monoacylglycerols, diacylglycerols and triacylglycerols (MAGs, DAGs and TAGs) could be sought for the valorization of MAGs and DAGs for use as surface agents [11,12].

1.2. Objectives and layout

Scientific research has proved that the envisioned separations are feasible, but most research has been conducted at laboratory-scale and the tools required for the extrapolation of the process are hardly mature. In order to address this problem, this work has focused on the development and validation of engineering tools to reduce the requirements needed for the implementation of a supercritical fractionation process.

First, a bibliographic review of the state of the art in supercritical fractionation is presented in order to give the technical basis for the rest of the discussion.

Then, the fractionation of ethanol-water mixtures at three different scales is addressed in order to validate the scale-up procedure and equilibrium-stage models for a system with known properties and thermodynamic behavior. In this chapter, a comparison is drawn between laboratory, pilot and industrial scale experimental results and the predictions of an equilibrium-stage model.

A theoretical discussion on the flooding phenomenon follows. The flooding capacity of a countercurrent column will define its maximum throughput capacity. Hence, it is very important to be able to estimate it correctly. The set of available flooding data is analyzed and a general correlation is proposed. Possible reasons are discussed for large experimental deviations.

Then, a simplified equilibrium-stage model for constant selectivity mixtures is developed. This model is fitted to our new experimental fractionation data of a complex mixture of fatty acid ethyl esters issued from fish oil.

Finally, some overall conclusions are given. In the aim of improving our knowledge of this process even further, an outline for future works is also proposed.

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2. Bibliographic review

2.1. Introduction

Supercritical fractionation is a unit operation which allows separation and purification of low-volatility and/or thermosensitive mixtures by use of a solvent under supercritical conditions. It is an environmentally friendly alternative to liquid-liquid extraction using classical solvents with great potential for a wide range of industrial applications.

In this section, the scientific literature addressing the conception and dimensioning of supercritical fractionation units is classified and analyzed according to the classical stages involved in the design of a unitary operation.

2.2. Supercritical fluids

Supercritical fluids have received a great amount of interest within the research community over the last decades because of their unique properties which are midway between those of liquid and gaseous phases.

The interest in supercritical fluids comes from the fact that supercritical fluids present gas-like viscosities, diffusion coefficients greater than those of normal liquids and liquid-like solvent power. As an example, Table 2.1 gives the physico-chemical properties of carbon dioxide, the most used fluid for supercritical applications. These properties theoretically allow supercritical fluids to overcome the dynamic restraints of liquid extraction and the equilibrium restraints of gas-liquid contactors. Moreover, the solvent power of a supercritical fluid can vary greatly with relatively small changes of pressure and temperature (*cf.* Figure 2.1). The ability to fine-tune the solvent capacity

by means of these two operational variables is of the most interest for selective extraction operations and later solvent recovery [5,6].

Table 2.1 :Physico-chemical properties of carbon dioxide

Temperature	Pressure	Physical state	Density	Diffusivity	Viscosity
/K	/MPa		[1] /kg m ⁻³	[2] /m ² s ⁻¹	[3] /Pa s
313	0.1	Gas	1.7	5.1×10^{-6}	1.6×10^{-5}
313	10	Supercritical fluid	631.7	1.4×10^{-8}	4.8×10^{-5}
300	50	Liquid	1028.9	8.7×10^{-9}	1.33×10^{-4}

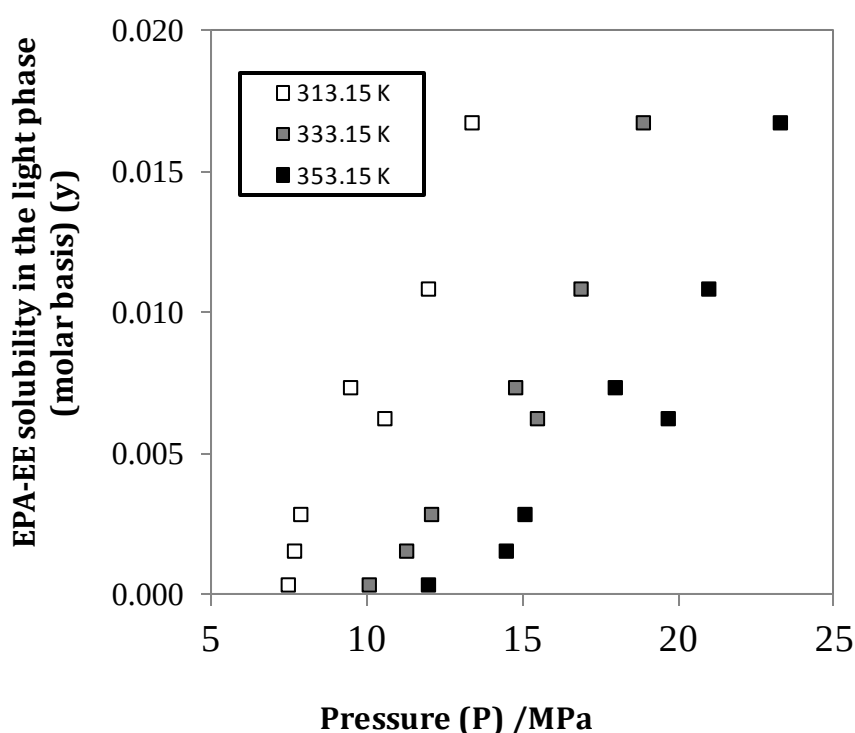


Figure 2.1: Solubility of eicosanopentaenoic acid ethyl ester (EPA-EE) in supercritical carbon dioxide as a function of pressure at different temperatures [4].

2.3. What is supercritical fractionation?

Supercritical fractionation is a hard subject to tackle probably due to the heterogeneity of the works carried out and their few industrial applications to date. Even the name and origins of this unitary operation are presented differently in scientific literature. In this review, the following definition is proposed:

The supercritical fractionation process is the continuous separation process based on the difference in solubility between the components of a liquid feed in a solvent at conditions in which the solvent and the feed are not miscible and beyond the critical pressure and temperature of the pure solvent.

After physical separation and depressurization, each phase will yield a different product: the fraction dissolved by the solvent will yield the *extract* while the rest of the feed components will form the *raffinate*.

In 1978, while reporting the capacity of this process to produce different cod liver oil fractions, Zosel [7] calls it “detraction” for its similarity to both extraction and distillation. Since then, this operation has been commonly referred to as “supercritical [fluid] fractionation” [8,9], “fractionation with supercritical fluids” [10,11], “[dense] gas extraction” [12,13] and “supercritical fluid extraction” [14,15].

The term “fractionation” may also be used for any operation allowing for some separation of any mixture components, meaning that there are many other techniques that have been referenced as “supercritical fractionation” in open literature that does not fit the above definition [16].

Finally, for convenience sake, the terms “vapor” and “liquid” will be used in the following discussion to address the solvent-rich light phase and solute-rich heavy phases in the column although it could be argued that they are not truly a vapor or liquid given their existence beyond the critical point of the solvent.

2.4. Past, present and perspectives

In scientific literature the works of Eisenbach [15] on oil treatment are often referenced as the first application of supercritical fractionation. However, the development of this technique can be traced back further, in the works of Zosel [7,17]. Moreover, a patent from 1939 already described the fractionation of petroleum oil

components using a supercritical solvent [18]. These first studies implemented a semi-continuous setup in which the charge to be treated (the feed) was kept in a high pressure vessel while a continuous stream of solvent was used to remove the soluble compounds.

From an industrial point of view, the first practical application of the process was part of the Biomedical Test Materials Program [19]: it used a semi-continuous process to pre-concentrate EicosanoPentaenoic Acid (EPA) and DocosaHexaenoic Acid (DHA) from fish oils for medical research purposes. The final pure product was obtained by preparative chromatography. Nowadays, the process is still used for commercial EPA and DHA production, dealcoholization of beverages and extraction of limonene from citrus oil but more detailed data is hard to come by. Several similar processes have been implemented at industrial scale at near-critical conditions such as the Solexol process (vegetal oil fractionation with propane) [20,21], and the ROSE [22], DeMex [23] and Solvahl processes [24] (deasphalting of heavy petroleum residues with recovery of the solvent under supercritical conditions).

One of the most promising industrial uses of supercritical fractionation is the replacement of petroleum-issued solvents by supercritical carbon dioxide for recovery and purification of valuable compounds [5,25]. Other supercritical solvents have been studied, principally light paraffins such as methane [26], ethane [26–29] and propane [30–34], but carbon dioxide presents several key advantages:

- 1) Carbon dioxide has a low critical temperature (31°C) compared to classical solvents, i.e. water (374°C), methanol (239°C), ethanol (240°C), chloroform (263°C), benzene (289°C) and hexane (234°C) [35]. This property allows use of this solvent in order to treat thermo-sensitive products and reduces heating costs.
- 2) Contrary to light paraffins, carbon dioxide is not flammable, explosive or toxic under normal concentrations, and it is generally non-reactive.

- 3) Carbon dioxide is recognized by the U.S. Food and Drug Administration as a GRAS (Generally Recognized As Safe) solvent, meaning that it can be used for food processing without premarket review and approval [36].
- 4) Carbon dioxide has a low cost and is abundant, since it is primarily obtained as a by-product in the ammonia and hydrogen production processes [37].
- 5) Being gaseous at ambient temperature and pressure, the solvent can be separated, recovered and recycled by simple depressurization (though this is not specific to carbon dioxide).

For these reasons, carbon dioxide has been used as a working solvent in most of the reviewed articles.

Being a high or at least medium pressure process, supercritical fractionation is expected to induce higher investment costs than classical unitary operations. Hence, most research into supercritical fractionation has targeted the separation and purification of relatively high added-value compounds from natural matter that could not be treated by distillation methods or to achieve products of superior quality. Indeed, supercritical fractionation may be able to operate under mild temperatures and medium pressures in cases in which distillation processes cannot be carried out without product degradation. Also, the recovery of the solvent in supercritical fractionation is simpler compared to liquid-liquid extraction processes. Furthermore, even if the separation between the product and carbon dioxide is practically total, the eventual presence of traces of residual carbon dioxide in the extract or raffinate carries no product degradation or health hazards, contrary to classical organic solvents.

Table 2.2 shows that the separation tasks that have received the most attention from the research community include the purification or concentration of EPA and DHA from fish oil, generally after transesterification of the corresponding triglycerides

with methanol or ethanol [9,38–43]; breaking of azeotropes, i.e. ethanol/water [44–46], 2-propanol/water [47,48]; dealcoholization of beverages [49–55]; the separation of heavy waxes from petroleum residues; the deterpenation of citrus oils [56–65] and the recovery of high added-value products from natural matter (principally α -tocopherol [66–68] and squalene [69–75]). In most cases, carbon dioxide is used as the working solvent. Temperatures have been varied from 296 K (subcritical conditions) up to 380 K, with most of the data found between 313 and 353 K. The working pressure ranges from 7 to 44 MPa, with most articles using pressures between 9.5 and 30 MPa. Hence, the reduced temperature is in the 0.97 – 1.25 range and the reduced pressure is varied from 0.94 to 6. Other solvents investigated include ethane, propane, pentane and toluene. For these solvents, the reduced temperature used is usually in the 0.95 – 1.15 range while pressures show much bigger scattering, with reduced pressures ranging from 0.5 to 3.3 in the case of toluene and from 3 to 15 in the case of propane. It can be seen that overall, the solvent to feed ratio varies greatly since it depends on the specific system. Indeed, the lower the product solubility, the more solvent will be required for the separation.

Another factor to take into account is that most of the scientific literature is focused on feasibility studies at laboratory or pilot scale. Only the studies of Fleck et al. [38] and Catchpole et al. [76] have put more emphasis in a multi-scale approach. Studies addressing the hydrodynamic behavior, transfer rates or modeling of the process are less common and will be discussed in more detail in the following section.

Supercritical fractionation presents many similarities with supercritical extraction processes that rely on the ability of supercritical fluids to selectively recover targeted compounds from solid matrices. Supercritical extraction has been successfully implemented at industrial scale for many applications, including the extraction of

caffeine from coffee and extraction of bitter compounds from brewery hops [77]. Given the presence of a solid matrix, extraction is a batch operation while fractionation can be carried out continuously. The current tendency for supercritical extraction is to increase the pressure as high as technically possible in order to increase efficiency and solubility of the extracted compounds. In contrast, fractionation processes cannot be carried out beyond a certain pressure since an increase in the overall pressure reduces the density difference between the light phase and the heavy phase, hampering their physical separation.

Despite the aforementioned advantages and the various systems studied, no widely implemented large-scale industrial application is found even if industrial fractionation units exist. Although an increased research interest is shown, the industrial implementation of supercritical fractionation lags far behind. So, is the scientific knowledge mature enough for the conception and wide industrial application of supercritical fractionation units? The aim of this chapter is to group the existing scientific data for the conception and design of supercritical fractionation units in order to come forward with some design guidelines for the process conception, design, optimization, and scale-up and identify research needs.

Table 2.2: Selected experimental works

Year	Author	System (Solute/Diluent)	Solvent (Cosolvent)	Temperature /K	Pressure /MPa	Solvent- to-feed ratio (Ω)	Mode ^a	Setup ^b	Gradient ^c
1987	Lahiere [47]	2-propanol / Water	CO ₂	298* - 308	8.2 – 10.2	5 – 10	C	ST	
		Ethanol / Water	CO ₂	313	10.2	13 – 22			
1989	Krukonis [78]	PCBs / Fish Oil	CO ₂	343	17 – 44	70 – 125	S	EV	T
	Nilsson [9]	EPA, DHA Ethyl Esters / Fish Oil FAEE	CO ₂	313 – 373	10.8 – 15		S	EC	
1992	Eckert [31]	Non-ionic surfactants	CO ₂ (Methanol, Ammonia, Propane)				S	EV	
1995	Lim [44]	Ethanol / Water	CO ₂	308 – 323	9.1 – 12.2		C	SP	
	Schaffner [66]	alpha-tocopherol / alpha-tocopherol acetate	CO ₂	323 – 343	17 – 20			MS	
1996	Pratt [32]	Poly(ethylene-co-acrylic acid) copolymers	Propane	393 – 423	48.2 – 64.7		S	EV	
			Butane	428 – 433	44.8 – 63.6				
			Dimethyl ether	408 – 413	19.9- 61.8				
1997	Goto [56]	Limonene / Linalool, Orange oil	CO ₂	333	8.8 – 9.8	20 – 80	C	PC	T X T
	King [79]	MAG, DAG, TAG fractionation	CO ₂	338 – 368	17.2 – 34.5		S	PC	
	Reverchon [57]	Citrus Peel Oil	CO ₂	313 – 353	7.5 – 9	60 – 120	C	PC	
	Sahle-Demessie [80]	MAG, DAG, TAG fractionation	CO ₂	340 – 380	20.7 – 34.5		S	PC	
	Shen [81]	Rice Bran Oil Fractionation	CO ₂	313 – 323	8.6 – 11.2	300 – 330	C	PC	
	Shi [82]	Petroleum vacuum residue	Pentane	513 – 523	4 – 12		S	PC	
1998	Fleck [38]	EPA-DHA ethyl esters / Fish oil FAEE	CO ₂	333 – 353	14.5 – 19.5	70 – 180	C	PC	TX
	Laitinen [45]	Ethanol / Water	CO ₂	313	10	6.5 – 13	C	RD	
	Sato [58]	Orange oil deterpenation	CO ₂	313 – 333	8.8 – 9.8	20 – 80	C	PC	
1999	Budich [59]	Terpenes / Citrus oil	CO ₂	333	10.7 – 11.3	50 – 100	C	PC	
	Laitinen [48]	1-butanol / Water	CO ₂	313	10	0.7 – 2.7	C	OR	

Table 2.2: Selected experimental works (continuation)

Year	Author	System (Solute/Diluent)	Solvent (Cosolvent)	Temperature /K	Pressure /MPa	Solvent-to-feed ratio (Ω)	Mode ^a	Setup ^b	Gradient ^c
2000	Camy [83]	DMC / Water	CO ₂	325	20		S	EV	
	Catchpole [76]	Vitamin A palmitate / Cod liver oil	CO ₂ (ethanol)	333	20 – 30		C – H	PC	
	Catchpole[69]	Squalene / Shark liver oil	CO ₂	333	25		C	MS/PC	
		Squalene / Olive Oil Deodorizer Distillate	CO ₂	313 – 333	10 -25	13 – 70			
	Crause [84]	2-methylnaphtalene / Hexadecane	CO ₂	353	12.5	10 – 15	C	PC	
	Kondo [60]	Bergamot oil deterpenation	CO ₂	313 – 353	7.8 – 10.8	10 – 45	S – C	PC	T
	Köse [61]	Origamun oil deterpenation	CO ₂	311 – 328	7 – 8.5		S	PC	T
	Laitinen [85]	Pyridine / Water	CO ₂	313	10	2.75-4.6	C	OR	
	Riha [39]	Fish oil FAEE fractionation	CO ₂	313 – 353	9 – 20	75 – 130	C	PC	X
2001	Benvenuti [62]	Terpenes / Lemon peel oil	CO ₂	316	8 – 8.5		S	EV	
	Kubat [63]	Origamun oil deterpenation	CO ₂	311 – 328	7 – 8.5		S	PC	T
	Markom [86]	Crude palm oil TAGs	CO ₂	313 – 333	11 – 20		S	EV	
	Ruivo [70]	Squalene / Methyl oleate	CO ₂	313	11.5	2 – 80	C	PC	TX
	Señoráns [49]	Brandy aroma	CO ₂	303 – 353	7 – 30	2 – 20	C	PC	
	Señoráns [50]	Flavonoids / Orange juice	CO ₂	313	16	3 – 11	C	PC	
	Señoráns [51]	Ethanol / Brandy	CO ₂	313	10 – 20	13.5	C	PC	
	Stockfleth [87]	Olive oil deodorizer distillates	CO ₂	313 – 373	8 – 30		C – H	PC	
2002	Kondo [64]	Lemon oil deterpenation	CO ₂	313 – 333	8.8 – 9.8	18 – 64	S	PC	T
	Mendes [88]	Vitamine E / Soy Oil Deodorizer Distillate	CO ₂	313 – 353	9 – 17		S	EV	
	Persson [89]	Phenolic compounds / Water	CO ₂	313 – 343	15 – 20	1.67	C	PC	
	Ruivo [71]	Squalene / Methyl oleate	CO ₂	313	11.5	2 – 80	C	PC	TX
	Simó [90]	Orange juice	CO ₂	313	16	3 – 11	C	PC	
	Simões [74]	Squalene / Deep-sea shark liver oil	R134a	333 – 353*	6	25 – 100	C	PC	
	Zhuang [91]	Petroleum pitch	Toluene	614	5.2 – 13.8	2	C	MS	

Table 2.2: Selected experimental works (continuation)

Year	Author	System (Solute/Diluent)	Solvent (Cosolvent)	Temperature /K	Pressure /MPa	Solvent-to-feed ratio (Ω)	Mode ^a	Setup ^b	Gradient ^c
2003	Dunford [92]	FFA – Phytosterol Ester/ Crude Rice Bran Oil	CO ₂	318 – 353	14 – 27.5	7	C	PC	
	Señoráns [52]	Ethanol / Brandy	CO ₂	313	20		C	PC	
2004	Fang [93]	Oxygenated compounds / Bergamot oil	CO ₂	313 – 348	8.5 – 14.5	22 – 40	C	PC	T
	Hurtado-Benavides[94]	Vitamine E, Sterols / Olive oil	CO ₂	313	20	23 – 42	C	PC	
	Tabera [95]	Olive leaves hexane extract	CO ₂	308 – 323	7.5 – 20	12.5	C	PC	
2005	Gast [67]	Tocopherols / Crude palm oil	CO ₂	340 – 370	20 – 30	25 – 65	C	PC	X
		Squalene / Soy Oil Deodorizer Distillate	CO ₂	353 – 363	23 – 26	33 – 171			
	Gironi [65]	Lemon oil deterpenation	CO ₂	315 – 333	8.4 – 10.5	58 – 138	S	PC	X
2006	Chuang [96]	Minor components / Crude palm oil FAMES	CO ₂	333	14	14 – 31	C	MS	
	Edwards [97]	Petroleum pitch	Toluene	603 – 653	3.5 – 11.1	5 – 60	C – S	PC	T
	Gironi [40]	Fish oil FAEE fractionation	CO ₂	315 – 343	10.1 – 17.2		S	EV	
2007	Eller [98]	Hexane / Soy Bean Oil	CO ₂ (He, N ₂ , Ar)	298 *	9.3		S	PC	
	Fatouh [99]	Buffalo butter oil	CO ₂	323 – 343	10.9 -40.1		B	EV	
	Fernandes [72]	Squalene / Methyl oleate	CO ₂	313 – 333	11.5 – 18.5	10 – 20	C	PC	
	Gracia [100]	Sugar cane spirit aroma extraction	CO ₂	313 – 333	10 – 25		B	EV	
	Perretti [41]	EPA, DHA Ethyl Esters / Fish Oil FAEE	CO ₂	313 – 333	10 – 30		S	PC	T
	Rincón [33]	Waste lubricant oil recovery	Propane	353 – 368*	30	2 – 6	C	EC/PC	T
	Schwarz [34]	Alcohol ethoxylates	Propane	389 – 402	12.5 – 15	21 – 66	C	PC	
2008	Chang [42]	EPA-DHA / Soft Shell Turtle Oil FAEE	CO ₂	333 – 353	20	250 – 1000	C	PC	
	Chen [101]	gamma-oryzanols / Rice Bran Oil	CO ₂	343 – 363	20 – 30	70 -200	C	PC	
	Danielski [102]	Mandarin peel oil deterpenation	CO ₂	323 – 333	8.5 – 10	34 – 82	C	PC	X

Table 2.2: Selected experimental works (continuation)

Year	Author	System (Solute/Diluent)	Solvent (Cosolvent)	Temperature /K	Pressure /MPa	Solvent- to-feed ratio (Ω)	Mode ^a	Setup ^b	Gradient ^c
2008	Eller [103]	Ethyl Ferulate, FAEE / TAGs	CO ₂	296 – 298 *	11	3 – 50	C	PC	
	Fornari [73]	FFA / Lampante olive oil		313	18 – 25	20			
		Sunflower oil deodorizer distillate	CO ₂	338	10 – 21	15 – 30	C	PC	
		Squalene / Olive oil deodorizer distillate esterification residue		343	15 – 23	13			
	Gironi [104]	Lemon oil deterpenation	CO ₂	323 – 343	8.7 – 11.2	25 – 70	C	PC	
	Ruivo [105]	Squalene / Oleic acid	CO ₂	313	18		C	M	
			CO ₂	313 – 323	18	8 – 40	C	PC	
	Varona [106]	Lavandin essential oil	CO ₂	313 – 333	9 – 11	30 – 200	C	PC	
	Vázquez [107]	NEAKG / Shark liver oil ethyl esters	CO ₂	318 – 338	14 – 18	15	C	PC	T
	Zacchi [108]	FFA / Rapeseed oil	CO ₂	333 – 338	20 – 26	20 – 50	C – H	PC	
2009	Kawashima [109]	Biphenyl compounds / Rapeseed oil	CO ₂	323 – 343	15 – 30	12 – 72	C	PC	
2010	Da Porto [53]	Ethanol / Grape spirit	CO ₂	323	10	7 – 20	C	PC	
	Rincón [110]	Used frying oil recovery	CO ₂ (Ethanol, Methanol, Acetone, Hexane)	298* - 353	30 – 40		S	EV	
	Ruiz-Rodriguez [54]	Ethanol / Wine	CO ₂	308	9.5 – 18	9 – 30	C	PC	X
	Schwarz [111]	Alcohol ethoxylates	Propane	386 – 404	13 – 15	51 – 94	C	PC	T
2011	Bonthuys [27]	Tetradecane / 1-Dodecanol	CO ₂	313 – 343	9 – 12.5	25 – 50			
			Ethane	313 – 343	6 – 9	18 – 30	C	PC	
	Gañán [112]	Essential oils deterpenation	CO ₂	313 – 323	6 -12		B	EV	
	Rezayat [113]	Triacetin / Acetyl glyceride mixture	CO ₂	321 – 345	10 – 14		S	PC	T
	Rincón [29]	Used frying oil recovery	Ethane	298* - 353	15 – 25	40 – 55	S – C	PC	
	Schwarz [28]	Tetradecane / 1-Dodecanol	Ethane	315 – 354	6.3 – 9.2	18 – 38			
			CO ₂	312 – 354	8.2 – 15	27 – 106	C	PC	TX

Table 2.2: Selected experimental works (continuation)

Year	Author	System (Solute/Diluent)	Solvent (Cosolvent)	Temperature /K	Pressure /MPa	Solvent-to-feed ratio (Ω)	Mode ^a	Setup ^b	Gradient ^c
2012	Al-Darmaki [75]	Squalene / Palm fatty acid distillate	CO ₂	313 – 353	10 – 20	10 – 35	C	PC	T
	Brunner [10]	Palmitic acid / Palm fatty acid distillates	CO ₂	333 – 373	20 – 29	50 – 350	C	PC	
	Cervo [14]	Petroleum pitch	Toluene	623 – 673	7	5 – 12	C	PC	T
			Pentane	513 – 533	7	5 – 12			
	Lopes [43]	EPA, DHA / Fish oil	CO ₂	306 – 333	10 – 30		S	EV	
	Ruiz-Rodriguez [55]	Ethanol / Wine	CO ₂	313	9.5 – 18	9 – 30	C	PC	
		Aroma / Wine	CO ₂	313	9.5	2 – 4			
2013	Esguerra [114]	Polycyclic aromatic hydrocarbon pitch	Toluene (NM2P)	603 – 653	2 – 8		S	PC	T
	Peretti [115]	Lycopene / Tomato pomace	CO ₂	313 – 333	10 – 30		S	PC	T
2015	Gañán [116]	Peppermint essential oil	CO ₂	313	8.5		S	EV	

*: Temperature range below the solvent critical point.

^a: B: Batch; S: Semicontinuous; C: Continuous; H: hydrodynamic study.

^b: ST: Sieve-tray column; EV: Extraction vessel; EC: Empty column; SP: spray column; M: membrane separation; MS: mixer-settler; PC: packed column; RD: rotating disk column; OR: Oldshue-Rushton extractor.

^c: T: Temperature gradient (Internal reflux); X: External reflux.

DGDG: Digalactosyldiacylglycerol; DHA: Dodecahexaenoic acid; DMC: Dimethylcarbonate; EPA: Eicosanopentaenoic acid; FAEE: Fatty acid ethyl esters; FAME: Fatty acid methyl esters; FFA: Free fatty acids; NEAKG: Non-esterified alkoxyglycerols; NM2P: N-methyl-2-pyrrolidone ; PCB: Polychlorinated biphenyls; TAG: Triacylglyceride; R134a: 1,1,1,2-tetrafluoroethane

2.5. The design stages and modeling

In this review, the relevant scientific literature is classified and analyzed from three points of view corresponding to the classical stages involved in the design of a Supercritical Fractionation Process (SFP):

- 1) *Exploratory research*: the first stage to any SFP implementation is the validation of its feasibility through a thermodynamic study, generally carried experimentally.
- 2) *Overall process design*: Once a process validation has been carried out, process variables are determined. Optimization is carried over the long term costs (mostly through minimizing the operation energy consumption and solvent-to-feed ratio).
- 3) *Equipment design*: With the process conditions fixed, the contactor can be dimensioned according to hydrodynamic and transfer models. Computational fluid dynamics (CFD) could be use for the optimization of packing geometry, liquid distributors, etc.

2.5.1. Exploratory research

Supercritical fractionation as a separation and/or purification process relies on the capacity of a solvent under supercritical conditions to force an asymmetric partition of the feed components between a solvent-rich vapor and diluent-rich liquid phase that can be physically separated by their density difference.

Two thermodynamic variables will have a great impact on the process and contactor design: the *solvent selectivity* and the *solvent load*. The solvent selectivity is the ratio between the solute and diluent concentrations in the solvent phase divided by the ratio between the solute and diluent concentrations in the feed phase. The solvent load represents the amount of both solute and diluents in the solvent phase, which is

directly related to the solvent-to-feed ratio required for the separation. These two parameters can be determined from phase equilibrium measurements. In the case of a countercurrent column, a low selectivity will increase the column height, whereas a low solvent load will increase the column cross section. In order for the process to be practically viable, minimum selectivity and solvent load values exist and will depend on the system and contactor type.

2.5.1.1. Solvent selection

Although the selection of the solvent is technically the first stage of process conception, for the reasons stated in the introduction section, carbon dioxide is nearly always used. Given the influence of temperature and pressure on carbon dioxide solvent power, it is often preferable to explore different operating conditions rather than use other solvents.

2.5.1.2. Choosing the working conditions

There is only a limited region on a temperature-pressure diagram for which the operation will be feasible. Since this process relies on the uneven partition of the solutes into two phases, if the feed is miscible with the solvent, the fractionation is impossible. If the system presents a three-phase equilibrium region, no purification may be achieved under those conditions since only the phase relative proportions may vary. The extent of the region in which fractionation can be accomplished may be determined experimentally by trial-and-error or by considering the thermodynamic fluid phase behavior.

Once the feasible temperature, pressure and global composition range are known, the operation pressure and temperature are chosen in order to maximize the solvent selectivity and solvent load.

Another parameter that needs to be accounted for in the choice of the working conditions is the density ratio between the overhead and raffinate. As the pressure and temperature approach the mixture critical pressure and temperature, the solvent load increases drastically, but the density of the overhead and raffinate converge, rendering the physical separation difficult. For this reason, fractionation by supercritical carbon dioxide is generally conducted under pressures lower than 30 MPa (cf. Table 2.2).

Experimental approach

Studies for the determination of the extent of the biphasic zone (including solubility or dew and bubble point studies) are common. They can be used to determine the range of feasible temperature and pressure conditions and to feed a semi-predictive thermodynamic model to predict the solvent load and selectivity. Experimental determination of the equilibrium compositions of the vapor and liquid in equilibrium at a given temperature and pressure are more rare and difficult to carry but provide direct empirical values for the solvent selectivity and load. The experimental phase data available at high pressures have been thoroughly reviewed elsewhere and will not be presented here [117–120].

For the prediction of extract and raffinate compositions under the assumption of thermodynamic equilibrium most studies reviewed relied on empirical correlations based on experimentally determined vapor and liquid equilibrium compositions [10,46,67,72,76,31,94,121]. A simple model can be derived from experimental vapor and liquid compositions by assuming a constant partition ratio [34,94].

Fluid-phase behavior via Equations of State (EoS)

The development of predictive or semi-predictive thermodynamic models has been addressed in order to avoid the experimental determination of the fluid-phase behavior. However, fluid-phase equilibria prediction and correlation under high

pressure by Equations of State (EoS) proved to be a complex problem. Much research has been carried out in this subject, as it is of great interest for the future development of supercritical processes. As an example, Fornari et al. [122] reported more than a hundred articles addressing the use of cubic EoS in phase composition prediction under supercritical conditions between 2003 and 2010. For supercritical fractionation studies, van der Waals-type EoS such as the Peng-Robinson EoS [58,123], its Stryjek-Vera modification [106] and the Soave-Redlich-Kwong model [124] with classical mixing rules for mixtures have been used. Group Contribution EoS (GC-EoS) have also been used [112,116]. Although EoS interaction parameters were fitted to experimental data, authors tended to consider EoS deviations as the principal source of error in their models. Fonseca [125] and Valderrama [126] have presented good reviews on phase equilibrium prediction under high pressures.

Rules of thumb

Despite the difficulty in predicting phase behavior equilibrium, some general tendencies can be noted. For example, if the feed components present negligible interactions with each other, their solubility in supercritical carbon dioxide can be considered inversely proportional to their molecular weight and polarity. Solubility generally increases with increasing pressure and solvent density, which in turns decreases the solvent selectivity.

A temperature increase at constant pressure plays a two fold role: it decreases the solvent density and increases the solute vapor pressure. The first effect is more significant under lower pressures, giving place to the retrograde solubility zone; where increasing the solvent temperature decreases its solvent power. If the feed components present strong interaction between them, their solubility will be strongly affected by the feed composition and no generalization is possible.

In the case of fatty acids, the solubility decreases as the chain length increases and increases with an increased unsaturation degree.

2.5.1.3. Exploratory fractionation studies

Based on the previous rules of thumb, some exploratory studies directly screen different temperature, pressure and flow conditions for a separation assumed to be feasible. They primarily address natural complex systems for which the determination and modeling of the vapor-liquid equilibrium is not possible. Many complex natural mixtures have been screened in order to assert the supercritical fractionation purification capacity of high added-value natural products. In the case of natural products, exact compositions and phase behavior under high pressure are not well-known and mixtures are often represented either by their principal components or by lumping them into pseudo-components.

This type of studies are more straightforward but somewhat incomplete: the feasibility of the process is confirmed if a given separation can indeed be carried out but if not, it is difficult to identify the source of the problem. Many factors play a non-negligible role in the operation of a two-phase multicomponent contactor as will be discussed further, such as the hydrodynamic conditions and mass transfer phenomena: a simple change on any of these aspects could render the desired operation possible.

Case study: The quest for anhydrous ethanol

In order to understand the importance of phase equilibrium studies, the ethanol-water fractionation will be discussed. In the 80's, some studies concluded that supercritical fractionation of aqueous ethanol mixtures with carbon dioxide cannot overcome the normal pressure water-ethanol azeotropic composition [127,128]. Later, Budich and Brunner [46] pointed out that those conclusions were drawn from conditions at which carbon dioxide and ethanol are miscible. With a better choice of

conditions, this separation may be possible. If ethanol is taken as the solute, water as the diluent and carbon dioxide as the supercritical solvent, both cases are presented in Figure 2.2. It can be seen that the concentration of the extract cannot overcome the limit imposed by the critical curve in a Type I system, i.e. no fractionation may occur in the miscibility region. However, by changing the pressure and/or temperature, the same system can evolve to a Type II system, in which ethanol can be theoretically extracted with an arbitrary purity.

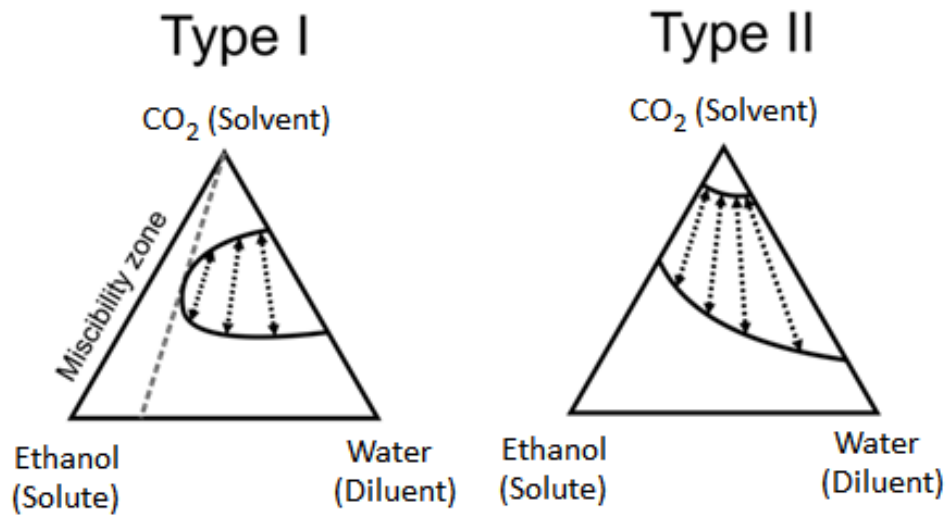


Figure 2.2: Type I and Type II phase diagrams for the ternary system Solute/Diluent/Solvent

In conclusion, the extent of the biphasic equilibrium region is a key parameter that can be obtained from phase equilibrium studies. As mentioned earlier, in order for the operation to be feasible, all global compositions in the contactor have to lie inside the biphasic equilibrium region as shown in Figure 2.3.

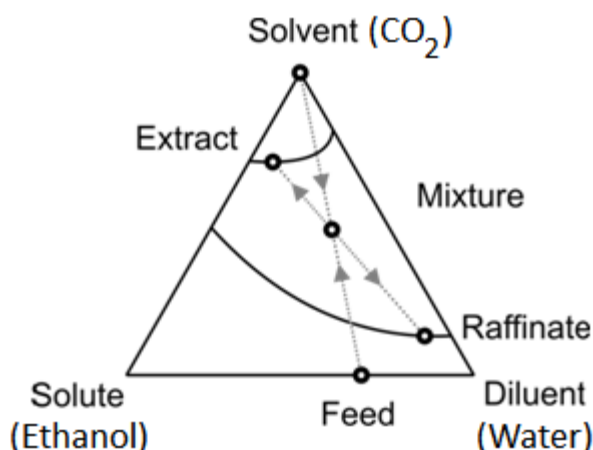


Figure 2.3: Ternary diagram and current compositions in a fractionation process

2.5.2. Overall process design

Once the operation conditions have been chosen in the first design stage, the overall process design is tackled. There are two key aspects in this stage:

- the transfer of the soluble components from the feed to the solvent and physical separation of the liquid and vapor,
- the recovery of the extract from the overhead and solvent recycling.

The first aspect is carried out by the contactor, and must be addressed during its conception and design. The extract recovery and solvent recycling are closely related and are often addressed together and affect the design of the downstream separation and solvent cycle.

Another adoption to be made is whether the operation mode should be continuous or semi-continuous (i.e., batch on the feed side and continuous on the solvent side). In general, the semi-continuous mode is only preferred for small scale units.

2.5.2.1. The contactor

In the case of a semi-continuous operation mode, the feed is kept within a closed vessel swept continuously by the solvent. Being a batch operation on the feed side, the

operation must be stopped in order to recover the final raffinate and replace it with fresh feed material. In its simplest form, this operation mode is akin to supercritical extraction from solids, which has been implemented much easier and at a bigger scale than supercritical fractionation. However, contrary to extraction, total depressurization of the vessel to recover the raffinate and introduce the fresh feed is not required.

The simplest possible contactor is a high pressure cell in which the solvent bubbles through the contained liquid. Some designs are mechanically agitated to improve transfer efficiency. Another refinement of the semi-continuous technique is to impose a temperature gradient on the solvent after contact with the feed to condense part of the extract. In this case, a column is used (empty, packed or with plates) and fixed on top of the vessel, similar to laboratory-scale batch distillation processes. The column is often operated at the retrograde solubility region; hence, the supercritical solvent is heated as it rises through the column so that some of the dissolved compounds condense, creating an internal reflux. The higher contact surface thus created between the rising solvent and the descending liquid improves the operation efficiency. As the solvent load decreases on top of the column, an improvement in the solvent selectivity is generally also achieved. The only drawback of this method is that a decrease in the solvent load yields an increased solvent-to-extract ratio, which in turns gives place to higher investment and operative costs. It is also to note that the maximum extract purity in a semi-continuous operation mode is limited by the feed composition and that the composition of the extract will vary as a function of time as the raffinate is depleted from the more soluble components.

In the case of a continuous process, several contactor types have been studied including spray columns, sieve-tray columns, packed columns, agitated columns (Oldshue-Rushton type), mixer-settler systems and hollow fiber modules (*cf.* Table 2.2). Packed columns with either structured or random packing elements have been the most

common choices. Agitated columns present some advantages in the case of low mass transfer rates and low solvent-to-feed ratios. Mixer-settlers designs may be chosen for applications in which mass transfer rates are slow or the solute and solvent density are too close for gravity-driven designs. Hollow-fiber contactors are a recent development and present a high volumetric efficiency. However, care must be taken when choosing the membrane material and to avoid surpassing the maximum pressure drop across the membrane [129,130].

As stated, the contactor choice will have an impact on the process viability. In the case of countercurrent columns, the separation between the vapor and liquid is achieved by gravity. The maximum operating pressure is set by the difference between the extract and raffinate densities. The solvent load (which in turns affects the solvent-to-feed ratio) will also be of great importance for the choice of the contactor. Patents and papers reported rather good performance with solvent-to-feed ratios from 1 to 250 (reaching even 500 on some accounts) but good results were often found with solvent-to-feed ratios around or above 50. As already stated in the previous section, the required solvent-to-feed ratio is dependent on the specific system and product solubility; hence, care should be taken when comparing different systems. Siebert et al. [131] reported that the most performing contactor for ethanol/water and 2-propanol/water fractionation with carbon dioxide for a bubbling regime were sieve trays, followed by structured packings and random packings. Daurelle et al. [132] confirmed the superior efficiency of sieve trays over Raschig rings and Montz packing for the dehydration of 1-propanol and 2-propanol with supercritical and liquid carbon dioxide under a bubbling flow regime. Spray towers (empty columns) are generally outperformed by all other contactors due to their high backmixing [131].

Finally, continuous processes possess several advantages over semi-continuous process from both a practical and economical point of view [5]. Continuous operations

are generally associated with lower operating costs. Another important factor is that continuous processes can overcome the limitations on the extract purity of semi-continuous implementations by the use of an external reflux. By recycling some of the recovered extract into the top of the column and injecting the original feed somewhere in the middle of it, the column is effectively divided into a bottom stripping and a top enrichment section. The reflux ratio may then be used to regulate the extract composition. Higher reflux ratios give a purer extract but also mean a higher solvent-to-feed ratio [10,46,111].

2.5.2.2. Extract recovery and solvent cycle

The conditions in which the extracted fraction is recovered can also have a great impact on the process feasibility. For example, Brignole et al. [30] studied light paraffins as solvent for the extraction of alcohols from water solutions. They used a high pressure distillation set-up to recover the extract after cooling and partial depressurization of the overhead. They reported *solvent entrainment effects* (i.e. an increase in the vapor pressure of water caused by its immiscibility with the solvent) in the recovery system allowing obtaining pure alcohols despite the limited solvent selectivity at the extraction stage. In order to present an entrainment effect, the solvent volatility in the recovery stage must be between those of the recovered alcohol and water.

Extract recovery is also one of the most important economic factors on any supercritical application. In the case of SFPs, several alternatives have been proposed:

- 1) **Solvent heating and/or depressurization:** widely used for its simplicity, this method allows solvent recovery by drastically reducing solvent power. In addition to depressurization, heat is generally applied. This method entrains high energetic costs. Multiple stages may be used to enhance product recovery or to

recover several distinct fractions. It is the most suitable alternative for semi-continuous operations. In such cases, different extracted fractions can be collected as a function of time. In small scale installations, the solvent can simply be pre-heated, depressurized to ambient pressure and vented.

- 2) **High pressure distillation:** after exiting the column, the overhead is decompressed and/or cooled into its two-phase region before being fed into a secondary high pressure distillation column. This method has lower energetic costs than solvent heating and depressurization but higher investments and complexity and is seldom reported (examples of its use can be found in the works of Brignole et al. [30], Varona et al. [106] and Budich and Brunner [46]).
- 3) **Adsorption, absorption, and membrane filtration:** adsorption of extracted products with activated carbon is used in small capacity installations before recycling the solvent or in cases in which only the raffinate is of value, or when the extract is highly volatile. Absorption by solvents can also be used. Both methods are widely used for the carbon dioxide regeneration and caffeine recovery in the production of decaffeinated coffee [133]. Membrane technologies have been proposed and implemented at pilot scale for the recovery of rice-bran oil from supercritical carbon dioxide [134–136].
- 4) **Cosolvent desorption (de-entrainment):** If a cosolvent is used to increase the solvent extract load, desorption of the cosolvent will entrain the precipitation of the extract. For example, fatty acid solubility in carbon dioxide may be enhanced by the presence of ethanol. After extraction, the ethanol can be absorbed with water in a countercurrent washer. The extracted oil condensates and can be easily recovered from the bottom of the washing column. Ethanol can then be recovered by distillation. The energetic requirements of this method are expected to be lower due to the lack of a depressurization stage, since both

the contactor and the washer can be kept at the same pressure. Birtigh et al. [137], proposed a process scheme in which the cosolvent is also recovered by supercritical fractionation, hence using three contactors: one to fractionate the product, one to recover the extract, then one for the recovery of the cosolvent. The main disadvantage of such process is its complexity.

Once the extract has been recovered, the solvent must be recycled except in the case of small scale laboratory setups in which the added investment outweighs the solvent cost. The resulting solvent cycle can be driven by a compressor or a pump. The extract recovery stage has a strong impact in the solvent cycle conception, as well as the working pressure and the operation scale. In the following analysis, a heating and depressurization scheme is presented since it is the most widely implemented.

A typical pump cycle and its associated temperature-entropy diagram are shown in Figure 2.4. The make-up solvent is usually fed as a saturated vapor (point A). After mixing with the recycled solvent (point 1), the solvent is condensed and sub cooled to avoid cavitation of the pump (point 2). A high pressure liquid pump is used to reach the working pressure (point 3) before heating up to the working temperature (point 4). Once the solvent leaves the contactor, it is depressurized (point 5) and heated (point 6) to recover the extract. The order of these operations may vary depending on the product thermal sensitivity or clogging capacity. In a compressor-driven cycle, the cooling of the solvent is reduced (point 2') and most heating is no longer required in an optimized cycle. However, a small exchanger would be used in a high scale process to level the possible process fluctuations. Depending on the working pressure, compression may require several cooling and compression stages. Additional heating and cooling may be required depending on the solvent, fractionation temperature and pressure and solvent recovery method. Smith Jr. et al. [138] gave a more extensive list of possible cycle configurations.

This simple example shows that the compressor cycle requires less total heat exchanger area and less overall thermal energy input. Overall energy consumption of compressor cycles is generally lower for working pressures under 30 MPa [139]. However, the compressor design parameters are outside of the range of classical practice, adding complexity to its conception [140]. This is why, although most research on process optimization points out compressor cycles to be the most efficient, in all the reviewed literature, experimental fractionation runs have been carried out in a pump-driven cycle.

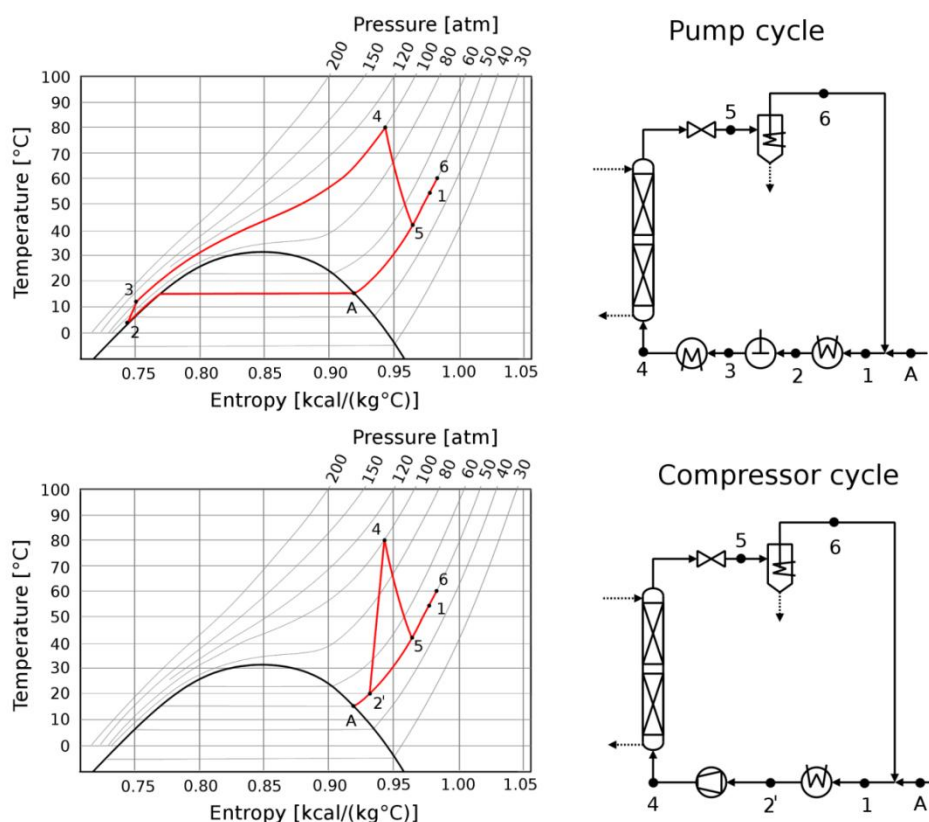


Figure 2.4: Temperature-Entropy diagram of pure carbon dioxide and flow-sheet diagrams for pump and compressor solvent cycles.

2.5.2.3. Process optimization

Once the process flowsheet has been chosen, models based on thermodynamic data are used to assess the optimal fractionation conditions. For complex natural

matrices, it is common to lump various physico-chemically similar compounds into pseudo-components.

The working solvent, temperature and pressure are usually selected as a compromise between the solvent load and selectivity. The reflux rate (if any), solvent-to-feed ratio and recovery conditions are determined by use of equilibrium models. The number of theoretical stages is also used as an indication of the difficulty of the separation.

In equilibrium models, the column is considered to be conceptually equivalent to a series of mixed stages atop of each other, as shown in Figure 2.5. It is generally assumed that both phases leaving a stage are in equilibrium with each other, although this assumption may be replaced by the use of stage efficiencies. In all of the reviewed articles, stage efficiency was not considered.

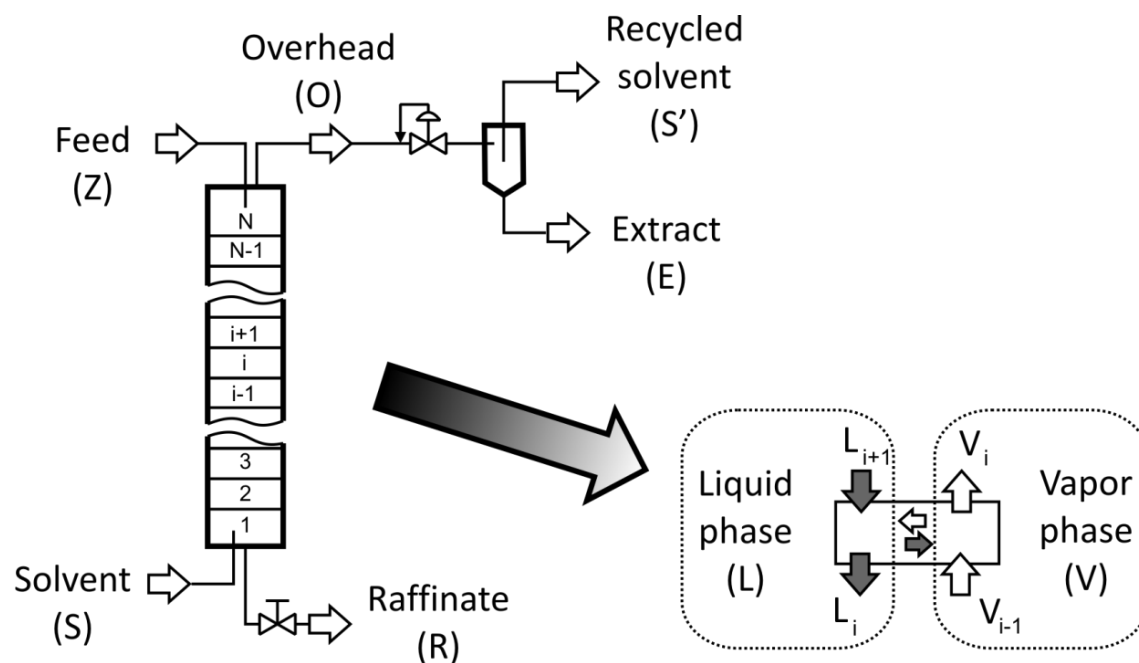


Figure 2.5: Conceptual diagram of equilibrium models.

In the case of binary feed mixtures at constant temperature, the Ponchon-Savarit method, which includes no further assumptions, can be applied by means of Janecke coordinates [10,31,46]. Phase equilibrium data are required to compute the minimum

and operational number of theoretical stages and the optimal solvent-to-feed ratio. For refluxed columns, it is also possible to obtain the required minimum and operational reflux. A graphical construction may be used to solve the design problem [141]. Furthermore, if the solvent load is considered independent on the extract composition, the McCabe-Thiele method can be used. Brunner and Machado applied this method to palm oil deodorizer distillates fractionation, but their choice of the feed state (i.e. the feed saturation degree) was not specified [10]. Finally, if the solvent relative selectivity is also constant, the Kremser equation can be used to directly calculate the required number of stages for a single column section [76,132]. This hypothesis reduces the model to a single equation.

Each method relies on different hypothesis and hence, may give different estimates on the number of stages required. There is no clear criterion to choose one method over the other. Riha and Brunner presented a comparison of Height Equivalent to a Theoretical Stage (HETS) values calculated from experimental data [39]. The ones obtained with the Ponchon-Savarit method presented the lowest standard deviation, which may imply a better reliability for extrapolation purposes.

For multicomponent feeds, the previous methods are not applicable. To overcome this, commercial simulators coupled with user-made modules for equilibrium phase composition prediction have been used. Each stage is simulated as a simple flash operation and the number of stages is determined from the extract and raffinate compositions. The predicted internal composition gradients in a fatty acid ethyl ester fractionation column have been shown to agree well with experimental data [59]. This same methodology was used by Manan et al. for palm oil refining [142].

2.5.3. Equipment Design

The contactor is the only piece of equipment specific to supercritical fractionation. This section will focus on countercurrent packed column type contactors which are by far the most widely studied in the scientific literature.

Two aspects must be distinguished when designing the contactor. First, hydrodynamic data are needed in order to assert the maximum feed flow rate with acceptable efficiency (*maximum column capacity*) in order to obtain the contactor diameter. Secondly, transfer efficiency data are needed to determine the column height. The first aspect has been more developed in literature than the second one.

2.5.3.1. The column hydraulic capacity

In a typical countercurrent column setup, the supercritical solvent is injected at the bottom of the column and flows upward while the liquid is injected in the upper part of the column and flows downward. There are some hydrodynamic restraints in order to achieve such flow state. The density gap between the two phases must be over 150 kg m^{-3} , so that a stable countercurrent flow may be achieved [5,6].

Another important aspect to take into account is the solvent-to-feed ratio. A minimum and maximum solvent-to-feed ratio can be calculated from thermodynamic data, in order to ensure a biphasic system along the column. Moreover, the efficiency of the column will be affected by extreme values, since the solvent-to-feed ratio affects hydrodynamic state of the column. For low solvent-to-feed ratios, agitated columns or mixer-settler contactors should be thought as viable alternatives. For very high solvent-to-feed ratios with low contact times, Venturi washers [141] and static mixer-cyclonic separator systems [5] should be considered. Finally, for column contactors, residence times are imposed by the hydrodynamic regime and cannot therefore be varied independently. If needed, mixer-settler designs allow for independent control of both

phases residence time. In most cases, however, gravity-driven countercurrent columns are used.

A well designed column should be as small as possible to minimize investment costs while remaining large and flexible enough to absorb process fluctuations. Here forth, the term “column” will be used to describe packed and plate columns interchangeably.

Gravity-driven countercurrent gas-liquid columns under normal pressure have been largely studied. Supercritical fractionation columns are expected to present a similar hydrodynamic behavior. It is well known from experimental data for gas-liquid columns that there is a range of gas and liquid flow rates in which the operation achieves maximum transfer capacity, i.e. the volumetric transfer rate reaches a maximum and the size of the required contactor becomes minimal.

A classical experience to determine the flow rates that lead to this maximum transfer efficiency for gas-liquid contactors is to vary the gas feed rate at constant liquid flow rate and measure the effect of the countercurrent liquid on the gas pressure drop along the column. While maintaining a constant liquid feed rate and increasing progressively the gas feed rate at low gas flow rate values, it can be seen that the pressure drop follows the same tendency than a dry packed column but remains higher. Even higher pressure drops are obtained if the experience is repeated at higher liquid flow rates. This is due to the liquid restricting the free flow section for the gas as it flows down through the column. At a certain point, an increase in the gas flow rate will generate a more rapid increase in the pressure drop. This point is called the *loading point*. Before the loading point, the momentum transfer between the gas and liquid is negligible, but once the liquid flow rate surpasses the loading point, the upflowing gas will hamper the liquid downflow by creating waves and entraining liquid droplets. This in turn will increase the volume of liquid accumulated in the column (known as *liquid*

holdup). The liquid holdup is normally expressed as the volume of liquid divided by the column volume. It is divided into a static and a dynamic term. The static holdup corresponds to the amount of liquid retained in dead volumes and gussets by capillary forces. The dynamic holdup corresponds to the increase in liquid holdup measured when the liquid is continuously fed into the column and depends on both the liquid and gas flow rates. The increase in liquid holdup reduces the gas flow section even further, which is the reason for the sudden increase on the gas pressure drop. If the gas flow rate is increased even further, the flooding point will be reached. At this point the gas completely prevents the liquid descent, increasing the holdup dramatically. First, a continuous liquid layer is formed on top of the column and the column will be progressively filled with liquid. At this point, the pressure drop increases drastically.

Before the flooding point, the liquid flows in the form of streams, droplets and jets. This hydrodynamic condition is called *trickling regime*. After the flooding point, the gas rises in the form of bubbles through a continuous liquid layer. This regime is called *bubbling regime*. Transfer capacity is increased beyond the loading point, given the intense contact between the phases, but it drops dramatically once the flooding point is reached due to the loss of interface area. The maximum mass transfer capacity for a countercurrent column is usually found just below the flooding point.

The hydrodynamic state of the column strongly affects its transfer capacity. Figure 2.6 presents the evolution of the Height Equivalent to a Theoretical Stage (HETS) (the height required for a packed column to present the same efficiency as a perfectly mixed contactor) as a function of the gas flow rate for traditional saddles. As discussed, at first, an increase on the gas or vapor flow rate reduces the HETS due to the enhanced contact between the phases. Then, after the loading point, the HETS stabilizes. If the gas flow rate is increased further, as the flooding point is approached,

HETS values decreased further before increasing drastically as the flooding point is reached.

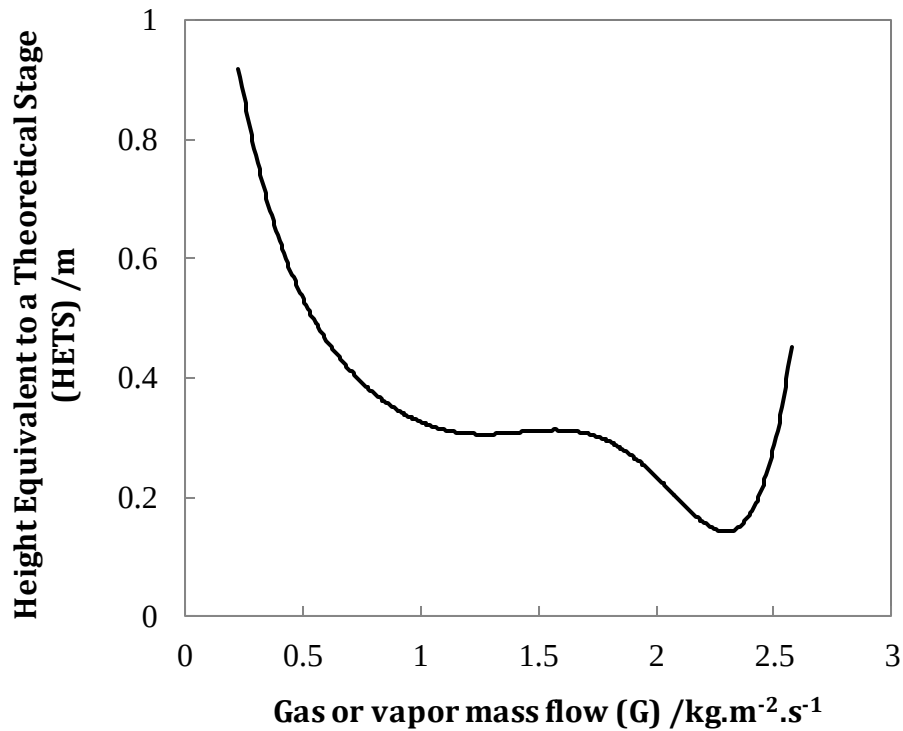


Figure 2.6: Influence of the gas flow rate on the HETS value at normal pressure for 25 mm (1 in) traditional saddles [143]

Studies addressing the hydrodynamic behavior of a column at supercritical conditions are scarce. Loading and flooding phenomena have also been observed under supercritical conditions [13,87,108]. The evolution of the liquid holdup and pressure drop as a function of the liquid velocity at constant vapor velocity is presented in Figure 2.7 for the water/CO₂ system. As in the case of a normal pressure system, it can be seen that both the liquid holdup and pressure loss increase as the liquid and/or vapor velocity increases. The sudden change of slope in the pressure loss and holdup tendencies as the liquid velocity increases is a clear sign of imminent flooding.

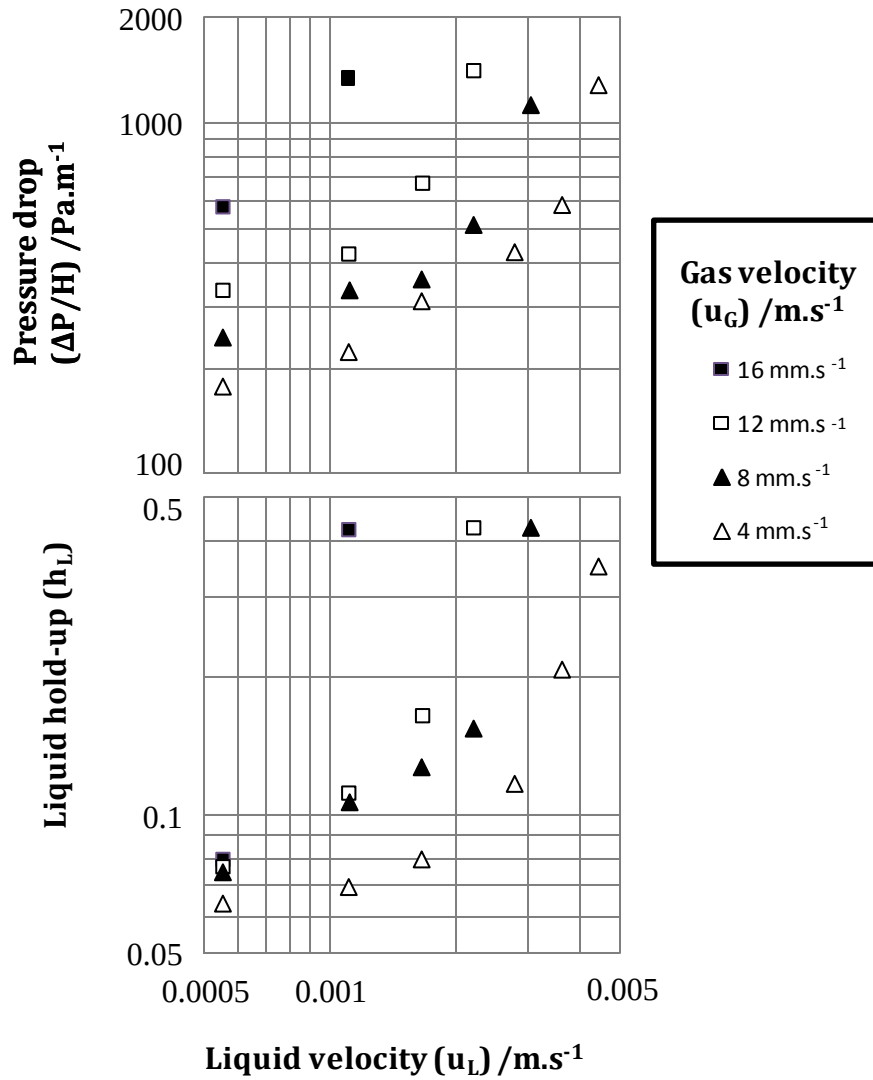


Figure 2.7: Liquid holdup (h_L) and pressure drop ($\Delta P/H$) for the water-carbon dioxide system with 5×0.5 mm glass Raschig rings at 313 K and 12 MPa [87].

For dimensioning purposes, knowledge of the flooding point is required since flooding is the principal factor limiting the maximal capacity of the column. In normal applications, a column is designed to work at roughly 70 to 80% of its flooding capacity in order to be able to deal with fluctuations on the process flow rates [144].

Flooding is a complex phenomenon and several flooding mechanisms have been proposed. At high solvent-to-feed ratios, droplet entrainment is expected to be the cause of flooding while frictional momentum transfer is responsible for flooding at lower solvent-to-feed ratios [13,26,145].

Only a few studies have modeled the hydrodynamic behavior under high pressure conditions. Woerlee proposed a general theoretical model for prediction of pressure losses (based on the model of Brauer [146] for vertical tubes) and flooding (based on entrainment) with a good qualitative agreement with experimental data, though quantitative prediction of the flooding point was less successful [26]. Stockfleth and Brunner [87] tested different empirical gas-liquid correlations including Stichlmair model [147] for pressure losses and Wallis-type equations [148] for flooding, with good agreement once parameter adjustments have been performed. Their results have been used for scale-up procedures by other authors [104,149]. Fernandes et al. (2007) applied the Rocha-Bravo-Fair model [150], originally developed for high pressure distillation with gauze packings and reported good agreement with experimental data after some parameter adjustments [72]. Authors have also used liquid-liquid flooding correlations, with variable results [76,145]. Catchpole et al. compared the Seibert and Fair model [151] (developed for liquid-liquid systems) and Billet and Schultes' model [152] (developed for gas-liquid systems) predictions to flooding data and reported important deviations, though the Seibert and Fair model gave generally conservative values and lower deviations, as opposed to the Billet and Schultes model [76].

At standard and vacuum pressure conditions, and for a given packing and system, graphical interpolation of the flooding factor (c_G ; defined according to equation (1.1)) as a function of the flow parameter (ψ , defined according to Equation (1.2)) is still the best available method for flooding point prediction [144].

$$c_G^* = u_G \left(\frac{\rho_G F_P}{\Delta \rho g} \right)^{0.5} \quad (1.1)$$

$$\psi = \frac{u_L}{u_G} \left(\frac{\rho_L}{\rho_G} \right)^{0.5} \quad (1.2)$$

As an example, a flooding diagram constructed from the experimental values given by Meyer and Brunner [153] for the flooding point of the corn seed oil/carbon

dioxide system at 20 MPa and different temperatures using Sulzer EX packings is presented in Figure 2.8. It shows very good correlation between experiences at different temperatures.

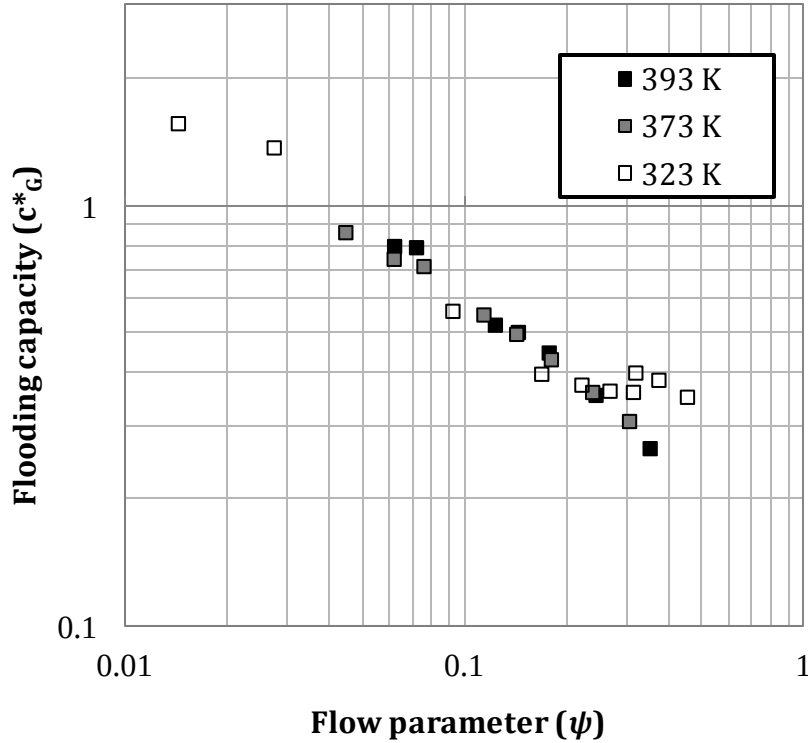


Figure 2.8: Flooding diagram for corn seed oil at 20 MPa and different temperatures using Sulzer EX packing, constructed from experimental data by Meyer and Brunner [153].

Flooding diagrams of this type have been used by Stockfleth and Brunner [13,87] and Budich and Brunner [46] to represent their experimental data under supercritical conditions for ethanol/water and olive oil deodorizer distillates fractionation using carbon dioxide with Raschig Rings, Berl Saddles and Sulzer EX and CY structured packings. These diagrams can be used to estimate the flooding capacity but caution should be exercised when extrapolating the results for other systems or packings.

Finally, for dimensioning purposes, care has to be taken since little is known about the effect of scale on high pressure column hydraulics. Siebert et al. [131]

reported that a 2.5 cm diameter column had a liquid holdup 40% higher than a 9 cm diameter column. Studies on a pilot scale automated fractionation column reported a 60% increase in the solvent cross section capacity compared to a non-automated column [38].

2.5.3.2. The column height

As stated, the column height is determined by the separation difficulty and by the column transfer capacity. In order to model the column capacity, two approaches exist, namely equilibrium models and non-equilibrium models. Equilibrium models consider the column to be conceptually equivalent to a series of perfectly mixed stages atop of each other (see Figure 2.5). This conceptualization is not necessarily representative of the real concentration profiles along the column. Empirical data on the extract and raffinate composition can be used to determine the column Height Equivalent to a Theoretical Stage (HETS value) for extrapolation purposes. On the other hand, the NTU approach uses a differential material balance along the column and takes into account the continuous variation on compositions and the deviation of those compositions from equilibrium.

HETS or HTU (Height of a Transfer Unit) values are easier to obtain applying equilibrium models to experimental data, but care has to be made on the hydraulic conditions. For example, Hurtado-Benavides et al., [94] reported experimental HETS values under conditions at which the density difference between carbon dioxide and their olive oil feed is very low (under 150 kg.m^{-3}). An inspection on the obtained HETS values shows an important sudden increase with feed flow, which may be due to a transition from a trickling column regime to a bubble column regime. Their data also presented high scattering and HETS values greater than their column height, which throw some doubts into the data quality. HETS values have been obtained on packed,

sieve-tray and spray columns [39,47,131,154]. Bernad et al. [155] compared a trickle bed and bubble column transfer capacity for the extraction of ethanol from water with supercritical carbon dioxide and found their HETS values to be similar and to vary from 0.5 to 1.5 m. Bernad [155] obtained HETS values by use of the Kremser equation and the Ponchon-Savarit method. Transfer coefficient through the HTU-NTU method were also obtained, but no correlation was attempted though all models seem to be able to fit data well.

Non-equilibrium models can be used for the optimization of packed columns. Usual simplifications include to neglect radial concentration profiles along the column and to assume equilibrium conditions at the interphase. Axial mixing effects are generally neglected. It is a common simplification to assume that the rate in which one of the components is transferred is far greater than that of the others, basically reducing the problem to the diffusion of a single component on a stagnant double layer. A further simplification is to consider the overall transfer coefficients to be independent on the composition of the corresponding phases. This hypothesis leads to the HTU-NTU method, which can be used to assess the volumetric transport coefficients by considering the driving force and transfer resistance independently [156]. Furthermore, if equilibrium compositions at the interface may be modeled by means of a constant partition coefficient (which is a common assumption for binary mixtures with low solubility), an analytical solution for the model exists. This is the most widely used method for transfer coefficient determination under supercritical conditions [44,71,94,157]. However, since mass transfer rates can be non-negligible for all components, multicomponent transport phenomena may take place and have an impact on the process. In this case, non-equilibrium models can become quite complex even for binary feeds. The implications of the non-ideality of the system and the effects of

convective transport are not discussed in fractionation literature, but the problem has been addressed in distillation and liquid-liquid processes [158–160].

Finally, an isothermal steady-state non-equilibrium model has been applied to the fractionation of edible oils by Martín and Cocero [123]. A non-isothermal dynamic one has also been presented by the same team [72]. These models are the most complex ones developed for this kind of applications but the hydrodynamic equation used for holdup could be improved by taking into account factors such as buoyancy. Furthermore, some data used for parameter fitting were obtained on conditions in which flooding is likely [94] or liquid distribution may have been poor [106], which hampers the predictive capabilities of the model. Since net convective mass transfer is not considered in their model, overall liquid and solvent mass flow rates are constant along the column. Such model is adequate only for low solubility feeds.

An interesting perspective is the application of computational fluid dynamics in this field. CFD modeling has been applied in many fields to optimize flow patterns, reduce pressure losses or increase mixing. This tool is useful for the optimization of equipment internals, pushing process intensification to its limits. To the knowledge of the author only the two-part CFD modeling article by Fernandes et al. [161,162] has addressed supercritical fractionation. This two-part study explored the hydrodynamic regime in a gauze packing under supercritical conditions. These results remained only explorative in nature, as they were used to fit some model parameters and validate the numerical method used.

2.6. Conclusions and future research

The conception of a supercritical fractionation unit is a difficult problem to approach. The straightforward conception following classical rules from literature data is, at best, unreliable. The applicability of the existing data to a specific system is also hard to assess. No generic rules have been developed and no widely-implemented industrial applications exist. Published data should be treated with caution.

To overcome these difficulties, three key aspects have to be developed:

- *Experimental data and modeling of the flooding phenomena:* The hydraulic limits must be further studied in order to have a reliable estimation procedure since some studies present great deviations from the expected values. Further discussion will be presented in Section 4.
- *Experimental data and correlation of the transfer rates at high pressure:* Transfer rates have been reported to be higher than in liquid-liquid processes; however, a general quantitative correlation is needed.
- *Economic feasibility and scale-up studies:* SFPs will remain as a marginal industrial application as long as no robust design tools exist. It is important to have simple and reliable tools for the conception and implementation of the process at large scale. Also, demonstration-scale units need to be put in place to attract industrial interest.

Some of these points will be addressed in the following chapters, notably the reliability of the equilibrium-stage models for scale-up; the prediction of the flooding point based on literature data and the use of a simplified calculation method for the rapid optimization of the process based on experimental data.

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3. Ethanol-Water fractionation

3.1. Introduction

In this chapter, in order to explore the reliability of laboratory-scale experiences for the conception of a large-scale fractionation unit, small-scale experimental data and model predictions have been compared to experiences with higher-scale units. Moreover, experiments carried on larger fractionation units have provided more information on the influence of the solvent apparent velocity and nature of the packing on the efficacy of the operation.

In order to focus the effort into the engineering aspects of the operation rather than the thermodynamic modeling of the equilibrium concentrations, a widely studied system was chosen to determine the limits and working range of the column and validate the experimental procedure for further studies. The ethanol-water fractionation by supercritical carbon dioxide was selected, being the most studied operation of this kind. This process drew the attention of the scientific community as a mean to overcome the thermodynamic restraints on distillation processes to obtain pure ethanol in a single step imposed by the existence of the ethanol-water azeotrope [1–4]. The same reasoning imposed the working temperature and pressure to be chosen at 333 K and 10.1 MPa, respectively, in order to take advantage of the vapor-liquid equilibrium data (VLE data) of Budich and Brunner [4], Lim et al. [5], and Furuta et al. [6].

Supercritical fractionation of ethanol-water mixtures by carbon dioxide has been previously modeled by the Ponchon-Savarit method [4], however, little experimental fractionation data was available and no comparison was drawn between experimental and simulated data. The McCabe-Thiele method was also portrayed by Brunner and

Machado [7] for the fractionation of edible oils, and in this case a good agreement between experimental and simulated data was found.

In this chapter, the result of a series of experimental fractionation runs conducted on three fractionation units at different scales using the ethanol/water/CO₂ system are presented, interpreted and modeled following using an equilibrium-stage approach. These experiences will be used to assess the operative range of the columns employed and ultimately, to validate the use of laboratory units for scale-up procedures.

3.2. Material and methods

3.2.1. Materials

Double-distilled water and technical-grade anhydrous ethanol (>99.8%) was used. Technical grade carbon dioxide (>99.8%) used was provided by Air Liquide Méditerranée (France).

3.2.2. Fractionation unit

Three countercurrent fractionation set-ups were used for this study, each one corresponding to different scales, ranging from a laboratory-scale fractionation column with an 19 mm ID to a semi-industrial-size 126 mm ID column. Their internal diameter, height and packings are detailed in Table 3.1.

Table 3.1: Column characteristics

Scale	ID [mm]	Height [m]	Packing
Laboratory	19	2	VFF Interpack (10 mm)
Pilot	58	4	VFF Interpack (10+15 mm)
Industrial	126	8	Sulzer CY

3.2.3. Experimental conditions

Through all experiments, the fractionation column temperature was kept at 333 K and pressure was regulated at 10.1 MPa. These conditions were chosen based on available experimental vapor-liquid equilibrium (VLE) data [4-6].

3.2.4. Analytical methods

All ethanol-water compositions were determined by density measurements. Samples were treated by ultrasounds in order to remove excess carbon dioxide. Compositions were obtained from literature density tables [8]. All reported values were obtained with an Anton Paar DMA 4500 unit (Austria).

3.2.5. Laboratory-scale unit

3.2.5.1. Description

A picture of the laboratory-scale fractionation set-up is presented in Figure 3.1 and a simplified schematic diagram of the laboratory-scale fractionation set-up is shown in Figure 3.2. This fractionation unit supplied by Separex (France) includes a packed column with an internal diameter of 19 mm and 2 m height with a viewing cell located at the bottom of the column, below the solvent injection nozzle. The column is able to withstand pressures up to 35 MPa, and its temperature is controlled by means of two independent heating jackets.

During operation, carbon dioxide under roughly 4.5 MPa is cooled to 275 K in a double tube heat exchanger (C1) before being pumped and then heated to the working temperature in an electrical heater (H2). A high pressure piston pump (P2) from Separex (France) with a top capacity of 15 L h⁻¹ (~14 kg h⁻¹) of liquid carbon dioxide and a maximum attainable pressure of 35 MPa delivers the supercritical solvent at the suitable flow rate. Once the supercritical solvent leaves the column, an electrical heater (H1) can be used to reduce the solvent power of the solvent by heating, but was not used for the

fractionation of ethanol-water mixtures. The overhead current is depressurized through a backpressure regulator (PV) to recover the extract in a pressurized cyclonic separator (S1). The recovered solvent may be recycled and condensed into the cooler (C1) to reduce carbon dioxide consumption. Solvent was recycled in all experiences conducted at this scale. The liquid mixture is fed by a Gilson 307 HPLC piston pump (P1) (France), with a 20 mL min^{-1} ($\sim 1.2 \text{ kg h}^{-1}$) maximum capacity. The carbon dioxide flow rate is controlled by a Rheonik RHE 14 mass flowmeter (Germany), while the liquid feed flow rate is directly controlled by the pump speed.



Figure 3.1: Laboratory-scale unit. M2P2 laboratory (Aix-en-Provence, France)

The extract and raffinate are collected from the bottom of the cyclonic separator and column, respectively, by manual regulation of the corresponding valves (V2 and V7). Under high feed rates, the liquid is continuously withdrawn, while an accumulation and purge method is preferred for small liquid rates. In the case of continuous withdrawal of raffinate, the liquid level in the column is kept constant by adjustment of the corresponding valve and observation through the windows at the bottom of the column. The corresponding dead volume is estimated to be 40 mL, while the total column volume is around 600 mL.

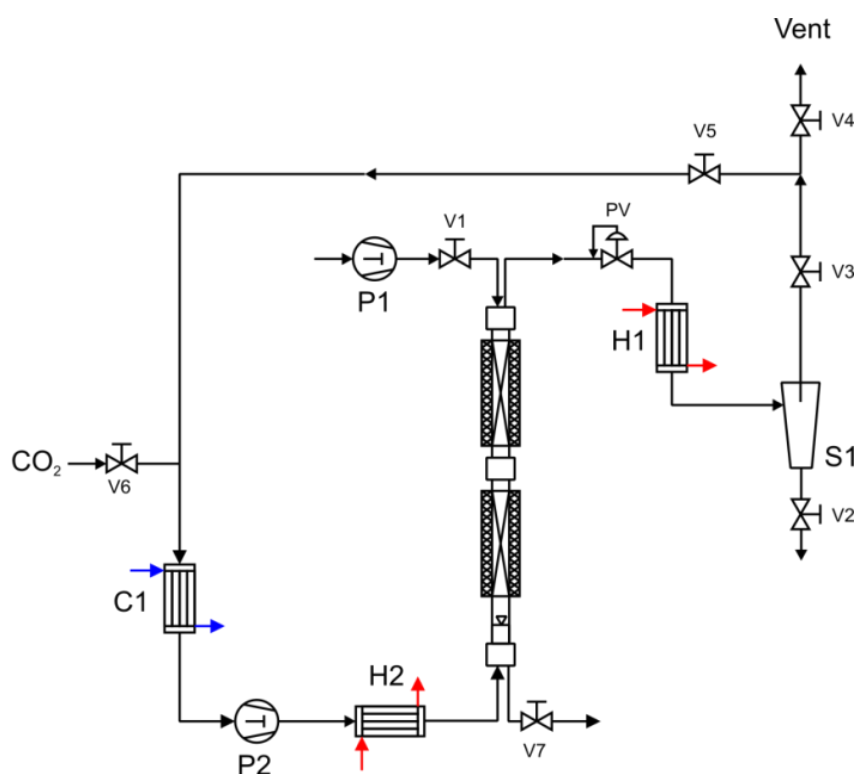


Figure 3.2: Schematic diagram of the laboratory-scale fractionation column

3.2.5.2. The packing characteristics

The column is filled with 10 mm Interpack random packings from VFF (Germany), with a measured apparent density of 588 kg m^{-3} , a specific surface area of $580 \text{ m}^2 \text{ m}^{-3}$ and a void fraction of 0.917 in order to improve mass transfer efficiency. A picture of the packing elements is presented in Figure 3.3.

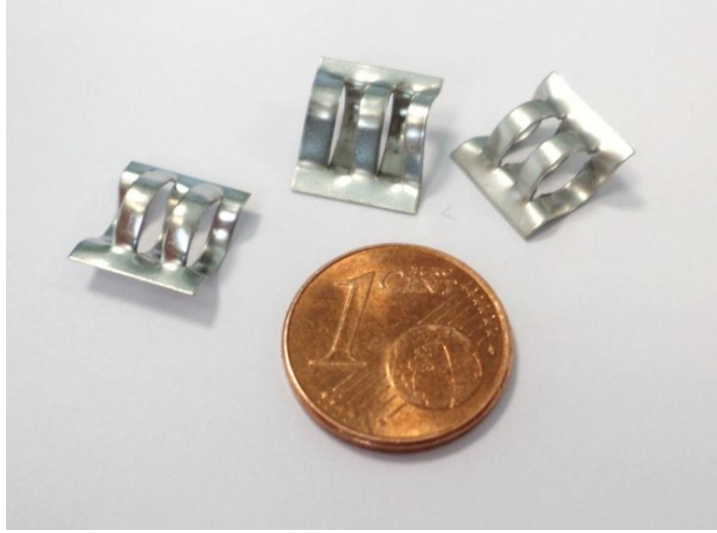


Figure 3.3: 10 mm Interpack packings from VFF.
1 cent euro coin for reference (diam. = 16.25 mm)

The packing characteristics were determined in the following manner. The void fraction was determined by measuring the apparent density of a bed of packing elements and the density of the packing elements themselves. In order to take into account the wall effect on the porosity of the bed, a 25 mL graduated cylinder with an internal diameter of 20 mm was used (the internal diameter of the column is 19 mm). The apparent density was found by double weighting of the cylinder. The density of the packing elements themselves was determined by volume displacement using a 10 mL volumetric flask. Finally, the void fraction was obtained using Equation (3.1).

$$\varepsilon_b = 1 - \frac{\rho_{\text{apparent}}}{\rho_{\text{packing}}} \quad (3.1)$$

The surface of a single packing element was determined from its measures, as presented in Figure 3.4.

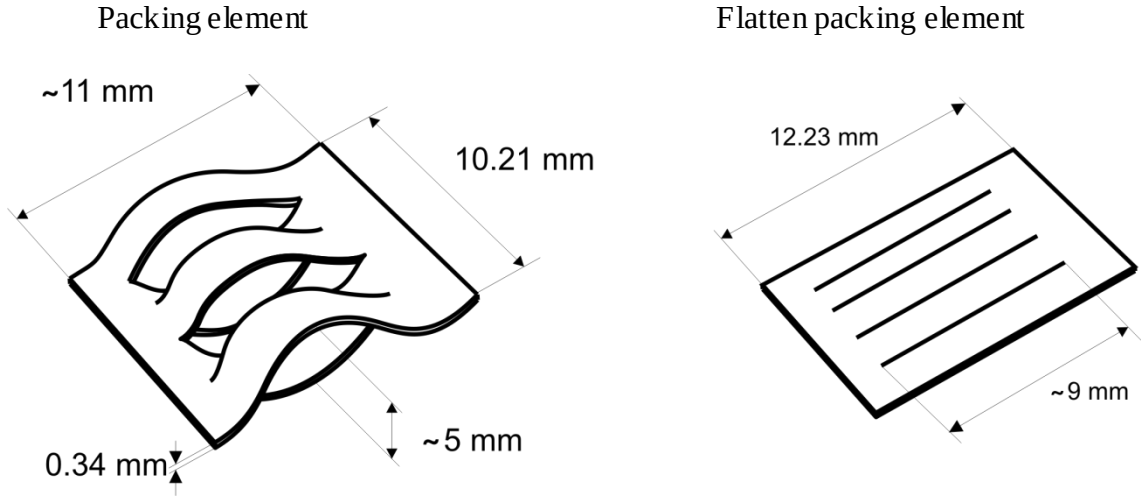


Figure 3.4: Packing element dimensions.

Then, the specific surface area was obtained using the following equation:

$$a = \frac{A_p}{m_{packing}} \rho_{apparent} \quad (3.2)$$

The equivalent particle diameter is defined as the diameter of a sphere with the same volume (V_p) than the particle.

$$D_p = \left(\frac{6 V_p}{\pi} \right)^{\frac{1}{3}} \quad (3.3)$$

Finally, the sphericity was determined from packing dimensions according to the following relation:

$$\phi_s = \left(36 \pi \frac{V_p^2}{A_p^3} \right)^{\frac{1}{3}} \quad (3.4)$$

where A_p stands for the surface area of a packing element.

Table 3.2: Packing characteristics

Characteristic	Symbol	Value	Units
Void fraction	ε	0.917	—
Specific surface area	a	580	m-1
Equivalent diameter	D_p	4.324	mm
Sphericity	ϕ_s	0.2035	—

3.2.5.3. Fractionation methodology

For all runs, the pressure on the column was regulated at 10.1 MPa while the temperature was set at 333K. The cyclonic separator pressure was kept about 4.5 MPa

and at a temperature of 293 K to avoid ethanol entrainment by the recycled solvent. Ethanol entrainment was easily detected since the condensation of liquid drops in the solvent cooler caused the solvent pump input check-valves to jam.

During all fractionation experiments, extract and raffinate samples were taken regularly and steady-state conditions were assumed to be reached when the standard deviation among three successive samples was less than 0.5 wt. % of ethanol.

Before each run, carbon dioxide was pumped for roughly 45 minutes in order to ensure a steady temperature regime. Once the feed injection started, a typical run lasted for 2 hours.

For all experimental runs, the liquid phase was chosen as the dispersed phase according to the relatively high solvent-to-feed ratios.

3.2.6. Pilot-scale unit

3.2.6.1. Description

The pilot-scale column and the industrial-scale column used in this part of the study are located at the Atelier Fluides Supercritiques (AFS) plant (Nyons, France) and are automated. The pilot-scale unit possesses a 58 mm internal diameter and 4 m height column, packed with a mixture of 10 mm and 25 mm VFF's Interpack packings. A picture and a schematic representation are presented in Figure 3.5 and Figure 3.6 respectively.

The liquid feed mixture may be pumped by two Milton Roy (U.S.A.) membrane pumps (P1 and P2) with a 5 and 25 L min⁻¹ maximum capacity, respectively. The carbon dioxide flow is provided by a Lewa (Germany) high pressure diaphragm pump (P3) with a top capacity of 80 kg h⁻¹ at 30 MPa. Separator and column temperatures are regulated by circulating a water-glycerol mixture into their respective external jackets.



Figure 3.5: Pilot-scale unit. Atelier Fluides Supercritique (Nyons, France)

3.2.6.2. Methodology

In a typical run, the column temperature was set at 333 K and the column was left to stabilize overnight. Then, the solvent pump was activated and the unit was left to achieve thermal steady-state for an hour before starting the feed pump. Both the feed and solvent flow rates were manually set by adjustment of the piston displacement length.

In order to recover the extract, a timer was set to open the valves V8, V9, V11 and V12 alternatively in cycles between 20 and 30 seconds in duration. V7 was set to be totally open while V6 remained closed at all times. To confirm that no extract was being retained at the S1 or S3 separators, the valves V10 and V13 were purged every 15 minutes. The extract samples collected from the V9, V10, V12 and V13 were mixed and weighted over time intervals of 15 to 30 minutes. Raffinate samples were collected by manual purge using the V19 valve, following the same time intervals than the extract samples. The solvent was recycled to reduce carbon dioxide consumption.

A typical run was carried out for 6 hours. At the end of the run, the column was isolated and the accumulated liquid holdup was left to drain for 1 h. The liquid holdup was then purged and weighted.

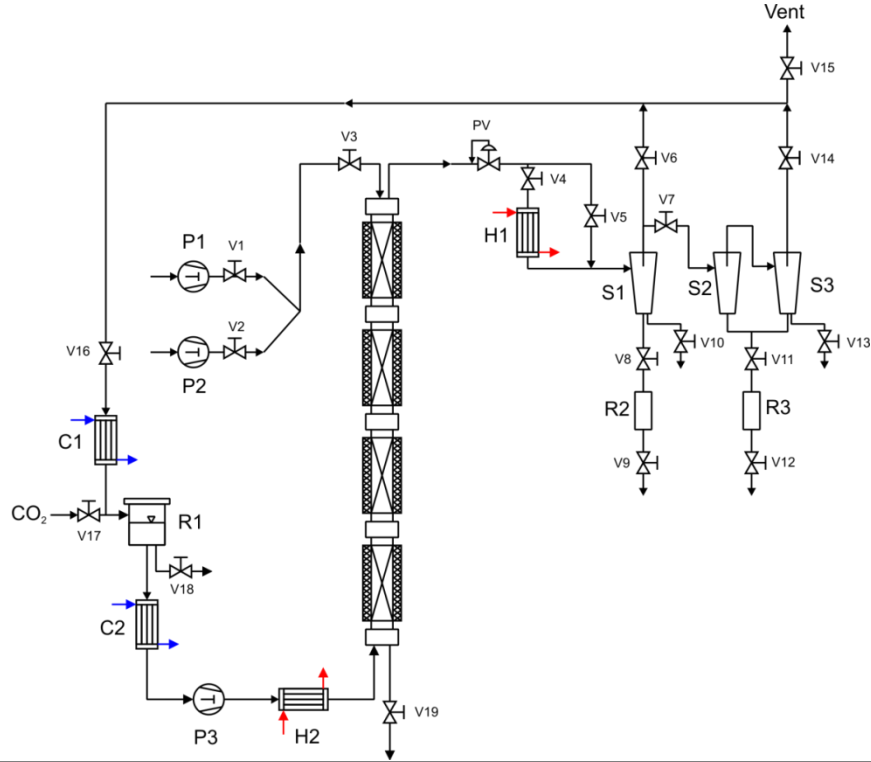


Figure 3.6: Schematic diagram of the pilot-scale fractionation column.

3.2.7. Industrial-scale unit

3.2.7.1. Description

The industrial-scale unit's column has an internal diameter of 126 mm and a 8 m height. A picture is presented in Figure 3.7 and a schematic representation is presented in Figure 3.8. The column contains four sections of Sulzer CY structured packing (Figure 3.9).

Carbon dioxide is fed by a 600 kg h^{-1} Speck (U.S.A.) prototype piston pump (P2). The liquid feed is provided by a 50 L h^{-1} Lewa diaphragm pump (P1). The carbon dioxide reservoir (R1) has a 200 L volume. Separators S1 (1.13 m height, 15 cm ID) and S2 (0.8 m height, 12.5 cm ID) were filled with mesh wire packings to increase thermal transfer and favor drop coalescence in order to avoid entrainment of small

droplets into the solvent recycle loop. Raffinate was purged from the column at regular intervals and accumulated into the R2 reservoir until it was collected for sampling and weighting. An optic level detector below the injection nozzle was used to prevent excessive raffinate accumulation at the bottom of the column.



Figure 3.7: Industrial-scale unit. Atelier Fluides Supercritiques (Nyons, France)

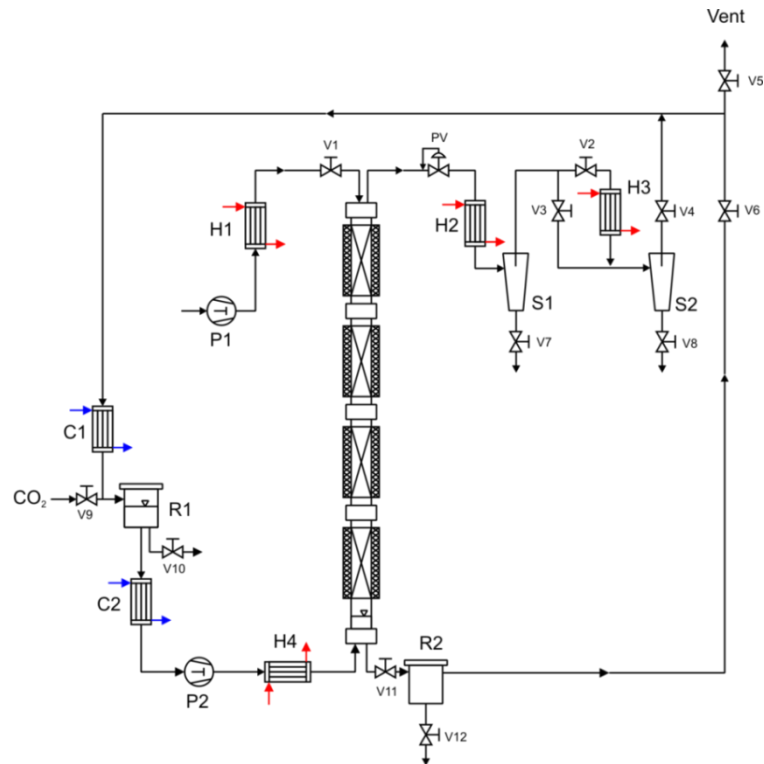


Figure 3.8: Schematic diagram of the industrial-scale fractionation unit.



Figure 3.9: An element of a Sulzer CY structured packing.
1 Euro coin for size comparison (diam. = 23.25 mm)

3.2.7.2. Methodology

As in the case of the pilot-scale unit, working temperatures were set on the controller and the column was left to stabilize overnight. The liquid feed pump was started 45 min after carbon dioxide injection. Extract samples were collected by purge of the S1 and S2 separators, mixed, sampled and weighted every 15 or 30 min. Raffinate was purged from the R2 reservoir, sampled and weighted at 15 or 30 min intervals. The solvent was recycled after recovery of the extract. A typical run was carried out for 8 hours. At the end of the run, the column was isolated and the accumulated liquid holdup was left to drain for 1 h. The liquid holdup was then purged and weighted.

3.3. Theoretical considerations

3.3.1. An equilibrium stage model

3.3.1.1. Introduction

The extract and raffinate compositions obtained in steady state are major parameters to evaluate the fractionation process performances, and to analyze and compare experimental results at different scales. In the same way, for the sake of understanding, it is also of interest to compare experimental results to process simulation results. For the process simulation, equilibrium stage models were chosen as a compromise between easiness of implementation, availability of input data and scientific meaning.

In the following discussion, carbon dioxide is considered the solvent while ethanol is the solute to be transferred given the high selectivity of carbon dioxide towards ethanol. In this system, water is considered the diluent.

A predictive simulation based on the Ponchon-Savarit and McCabe-Thiele models as well as on available VLE data was implemented. Equilibrium stage models

were historically developed for distillation processes upon plate towers. These models can be used for supercritical fractionation by a simple change of variables [4,7–11]. Although the principle of clearly differentiated equilibrium stages does not stand in the case of packed towers, experience has shown that equilibrium stage model predictions do agree with experimental results and hence are widely used for packed column design applications [9].

A schematic representation of the conceptual stage model is presented in Figure 3.10. For both McCabe-Thiele and Ponchon-Savarit models, the liquid and vapor exiting a stage are considered in equilibrium with each other, *i.e.* L_i is in equilibrium with V_i . Both models were first developed for distillation processes and considered that the distillation column was perfectly isolated and in steady-state conditions. These models can be used for liquid-liquid extraction process and supercritical fractionation if one replaces the energy balance with the mass balance of solvent and expressing all concentrations in solvent-free bases.

The difference between both methods is that in the McCabe-Thiele method applied to distillation, the latent heat of vaporization of both compounds is considered equal. Hence, for every kilogram of one component condensed from the vapor there must be an equal quantity of the other component that evaporates in order to satisfy the energy balance along the column. In the case of supercritical fractionation, the corresponding assumption is that the vapor load (*i.e.* the mass fraction of non-solvent – water and ethanol in our case - in the vapor phase) is constant and independent on the composition. In that case, for every kilogram of one component that condenses from the solvent-rich vapor, there must be an equal quantity of another component that dissolves from the liquid into the vapor.

In applications with very limited mutual solubility between both phases, both liquid and vapor flow rates can be considered constant along the column, which

simplifies the resolution of the model equations for both cases, since the operating line becomes straight and the solvent-to-feed ratio can be used as an acceptable approximation of the vapor-to-liquid ratio. These hypotheses are not suitable for the ethanol-water-carbon dioxide system given the high solubility of carbon dioxide in the liquid phase and the variable vapor load as a function of its composition; hence a different approach had to be considered.

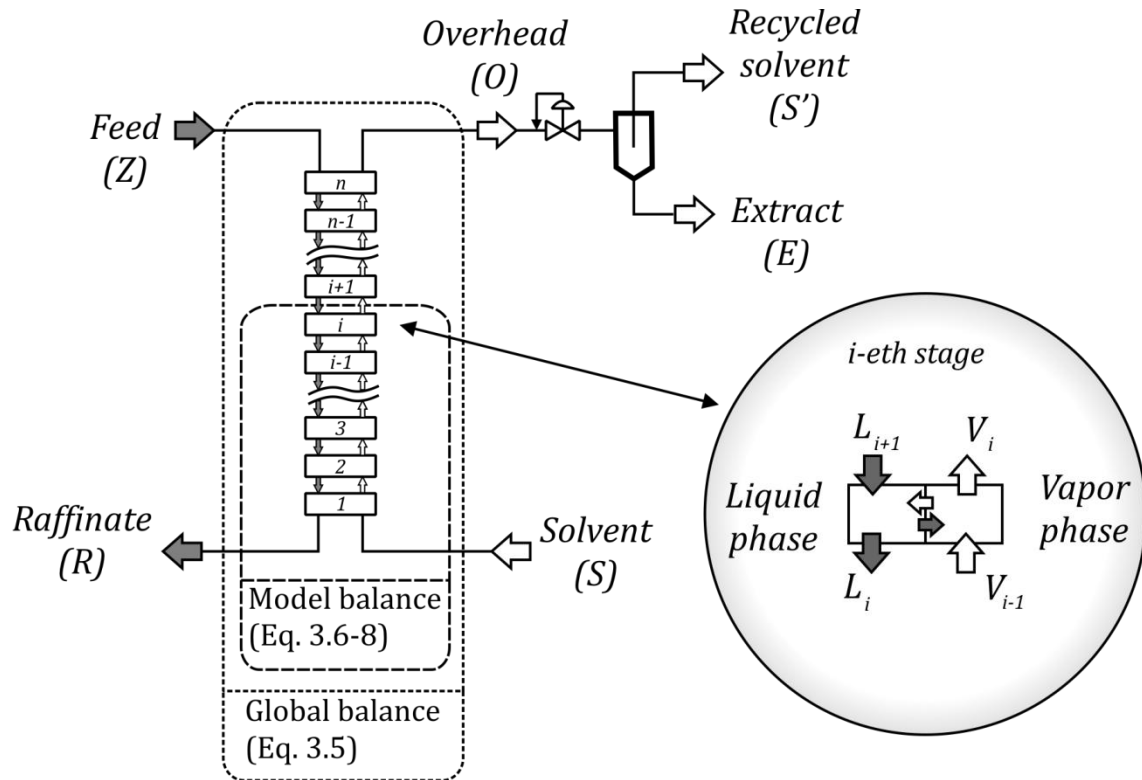


Figure 3.10: Equilibrium stage conceptual representation of a countercurrent column for supercritical fractionation

In these simulations, the pressure and temperature were fixed and the feed composition and the solvent-to-feed ratio were varied according to the range covered by the experimental studies. The number of theoretical plates (N) was also varied to assert its influence in the model output. The model equations, given in Table 3.3, corresponding to a system of non-linear algebraic equations, were numerically solved using a secant algorithm, leading to the composition profile along the column, and in particular to the extract and raffinate compositions. In all cases, a pure solvent and a

solvent-free feed were assumed. For both models, the solute from the overhead is supposed to be totally recovered in the separation vessels, thus becoming the extract. Hence, the overhead solvent-free ethanol mass fraction is equal to the extract ethanol mass fraction ($Y_O = X_E$). For the McCabe-Thiele method, the fluid loading used was computed at the overhead composition. This method is different from the classical McCabe-Thiele approach, since the operating line slope cannot be known in advance and is greatly affected by the overhead composition.

Table 3.3: Model equations

Global component balance	
$\frac{N_O - \Omega}{\Omega - M_R} = \frac{Y_O - X_Z}{X_Z - X_R}$	(3.5)
Ponchon-Savarit model	
$X_{i+1} = \frac{M_{i+1} - M'}{N_i - M'} (Y_i - X_R) + X_R$	(3.6)
$M' = -N_O \frac{\Omega - M_R}{N_O - \Omega}$	(3.7)
McCabe-Thiele model	
$X_{i+1} = \frac{\Omega}{N} (Y_i - X_R) + X_R$	(3.8)
Ω is the solvent-to-feed ratio; X_Z, X_R, X_i represent the solvent-free ethanol mass fraction of the feed, raffinate and liquid exiting the i-eth stage respectively; Y_O and Y_i stand for the solvent-free ethanol mass fraction of the overhead and solvent leaving the i-eth stage; M_R, N_O, N_i and M_i are the solvent-to-non-solvent ratios of the raffinate, overhead and of the liquid and solvent leaving the i-eth stage respectively.	

According to VLE data [4-6], the ratio between carbon dioxide and the other species in the liquid and vapor phases is affected by the ethanol solvent-free mass fraction. The selectivity of carbon dioxide towards ethanol is also a function of the liquid composition. A correct representation of these parameters is crucial for an accurate description of the fractionation process.

3.3.1.2. The solvent selectivity (α)

The selectivity of the solvent towards ethanol (α) is defined as

$$\alpha = \frac{Y/(1-Y)}{X/(1-X)} \quad (3.9)$$

where X and Y stand for the solvent-free ethanol mass fraction in the liquid and vapor phase, respectively. The selectivity is used in order to compute the composition of the vapor in equilibrium with a given liquid phase.

Experimentally determined selectivity values present some scattering produced by technical difficulties. Hence, a correlation with two sets of parameters fitted to different data sources were used to verify the impact of data deviations on the simulated output compositions. The following equation proposed by Budich and Brunner [4] was used to model for the solvent selectivity.

$$\alpha_i = A_i \exp(-B_i X) + C_i \quad (3.10)$$

where X represents the solvent-free ethanol mass fraction in the liquid phase and A, B and C are empirical coefficients. The first parameter set was based on VLE data provided by Budich and Brunner [4] (α_B) while a second set was fitted from data from Lim et al. [5] (α_L). Both sets of values are presented in Table 3.4 and the experimental data and fitted curves are depicted in Figure 3.11. Although all experimental points show the same tendency and both fitted models are similar, these deviations have a non-negligible impact in the model output, as will be discussed further in Section 3.3.1.5.

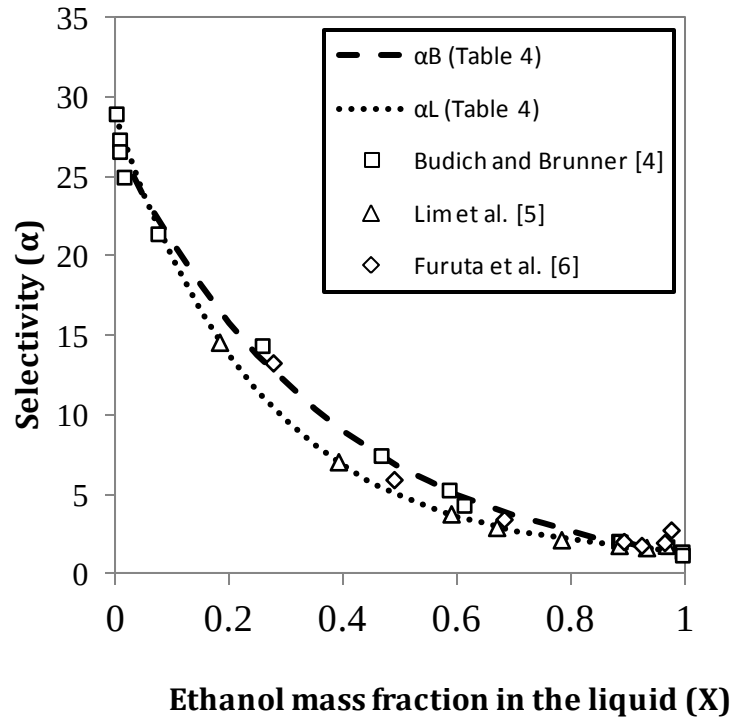


Figure 3.11: Carbon dioxide selectivity towards ethanol at 333 K and 10.1 MPa as a function of the liquid phase ethanol mass fraction. Lines represent a simple model (Eq. (3.10)) fitted from different data sets

Table 3.4: Empirical correlations for selectivity calculation

Correlation	Fitting data set	Parameter		
		A	B	C
α_B	Budich and Brunner [4]	28.1	-2.65	-0.73
α_L	Lim et al. [5]	28.0	-3.91	0.92

3.3.1.3. The solvent-to-non-solvent ratio in the liquid (M)

The solvent-to-non-solvent ratio is the least important parameter since the high solvent-to-feed ratio makes the solvent losses by dissolution through the raffinate negligible. The following correlation proposed by Budich and Brunner [4] is sufficient for the needs of the equilibrium stage model:

$$M_B = \frac{1}{23.6 - 36.7X + 13.7X^{2.5}} \quad (3.11)$$

A comparison with experimental data is drawn in Figure 3.12. The correlation fits the experimental data well.

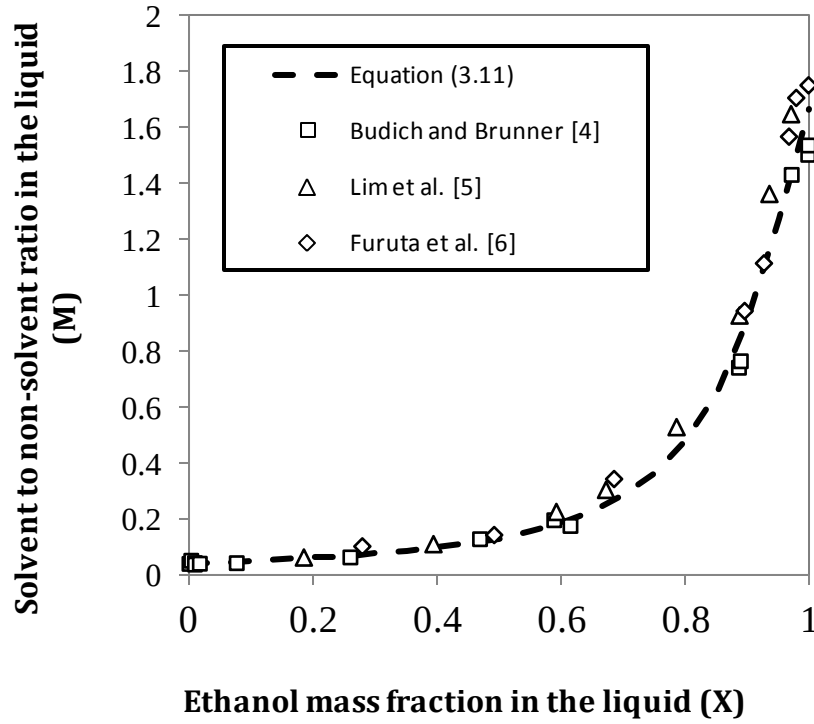


Figure 3.12: Comparison between experimental solvent-to-non-solvent ratios in the liquid and the correlation proposed by Budich and Brunner.

3.3.1.4. The solvent-to-non-solvent ratio in the vapor (N)

The extract yield is a crucial operating parameter and is imposed by the overhead load (ℓ_o) and the solvent-to-feed ratio (Ω). The overhead load (ℓ_o) is defined as the amount of non-solvent, i.e. water and ethanol, in the overhead stream (stream O in Figure 3.10). The solvent-to-non-solvent ratio in the vapor (N) is related to the overhead load by the following relation:

$$N = \frac{1 - \ell_o}{\ell_o} \Leftrightarrow \ell_o = \frac{1}{1 + N} \quad (3.12)$$

Using a correlation from Budich and Brunner for the N parameter, the vapor load (ℓ) can be calculated as a function of the solvent-free ethanol mass fraction in the vapor (Y):

$$\ell = \frac{1}{427 - 1290Y^{1.5} + 884Y^2} \quad (3.13)$$

Figure 3.13 shows the good correlation between the experimental VLE data of Budich and Brunner [4] and Equation (3.13). Data from Lim et al. [5] and Furuta et al.

[6] deviate from the experimental values of Budich and Brunner but follow the same tendency reasonably.

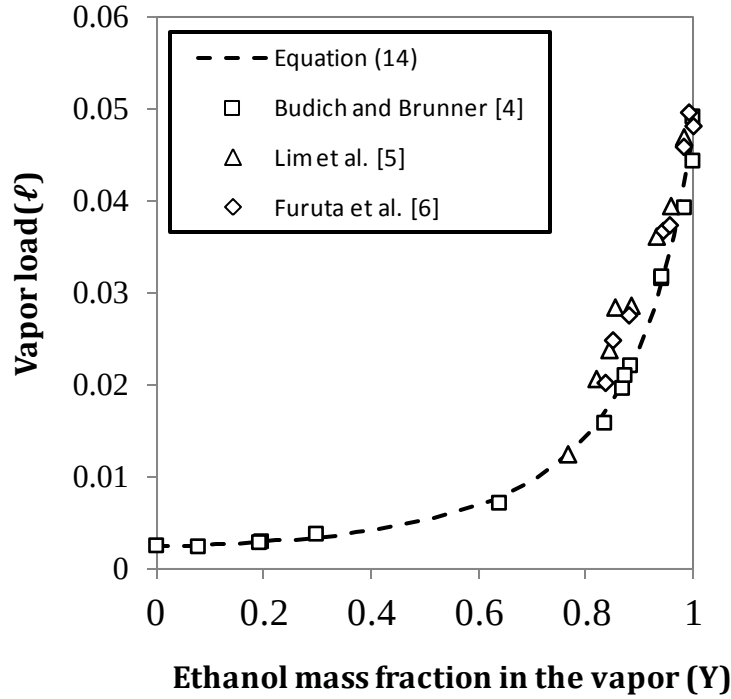


Figure 3.13: Comparison between experimental and vapor load values and the correlations used in this study.

3.3.1.5. The number of theoretical stages

The number of theoretical stages required for a given separation provides a measure of its difficulty and it is only a function of the imposed extract and raffinate compositions and the thermodynamic relations between the mass fractions of all components (i.e. α , ℓ and M). Equilibrium stage models are required to compute it.

On the other hand, the Height Equivalent to a Theoretical Stage (HETS) is a measure of the transfer capacity of a column. The lesser the HETS, the more intense are mass transfer phenomena between the contacting phases. The factors affecting the HETS are numerous, including packing characteristics, the physical properties of the phases in contact and the hydrodynamic state of the column. Therefore, the HETS is usually experimentally determined for the working conditions and later used for scale-up. For the determination of the HETS, the height of the column used is divided

by the number of theoretical stages required for the obtained separation. To do so, the number of stages has to be obtained from experimental extract and raffinate compositions.

Since all thermodynamic parameters correlated in the previous sections from experimental data present some scattering (*cf.* Figure 3.11, Figure 3.12 and Figure 3.13), a question worth asking is how much error will these deviations introduce in the determination of the number of theoretical stages. Moreover, there are several external factors that may introduce further errors. For example, it is worth noting that the regulation of the pressure and temperature of a column operated in a continuous manner is much more difficult than in the case of an equilibrium vessel.

As an example, Figure 3.14 presents the predicted extract and raffinate compositions for a solvent-to-feed ratio of 20 and a feed with a 0.4 ethanol mass fraction as a function of the number of theoretical stages calculated according to Equation (3.10) and using both parameter sets given in Table 3.4. The predicted extract and raffinate compositions are mostly unaffected by the change in the number of stages. The predicted values converge fast towards those of a pinched column, i.e. a column where the operating line intercepts the equilibrium line. It can also be seen, that the choice of the selectivity factor has a bigger influence than the number of theoretical plates, since the difference between curves of different selectivity factors is greater than between consecutive stage counts. This result is caused by the column operating near pinching conditions at the top, as shown by the McCabe-Thiele construction for this example (Figure 3.15). Under these circumstances, the gain from adding extra stages is marginal. This condition is correlated to the high selectivity and high solvent-to-feed ratio used in this kind of applications.

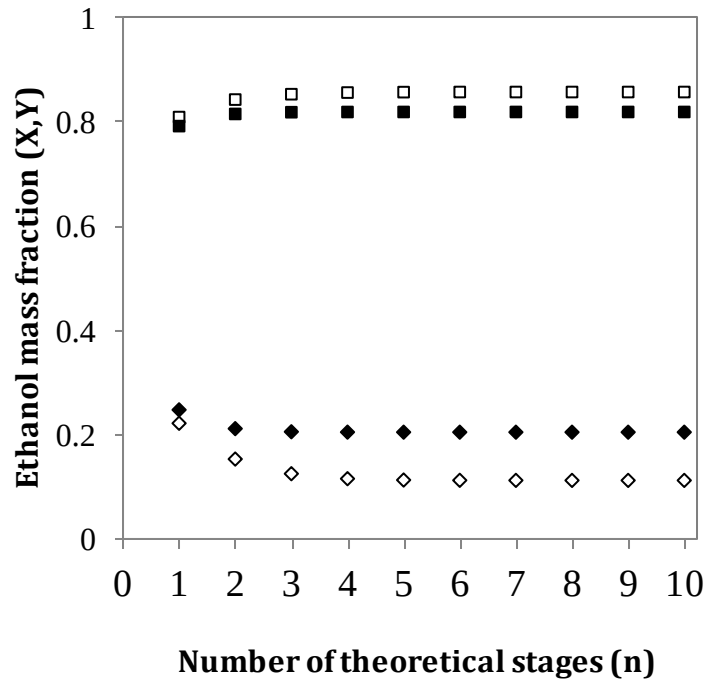


Figure 3.14: Predicted extract (□, ■) and raffinate (◇, ◆) ethanol mass fraction as a function of the number of theoretical stages using the selectivity correlation based on the data from Budich and Brunner (□, ◇) and Lim et al. (■, ◆).
Solvent-to-feed ratio: 20. Feed ethanol mass fraction: 0.4.

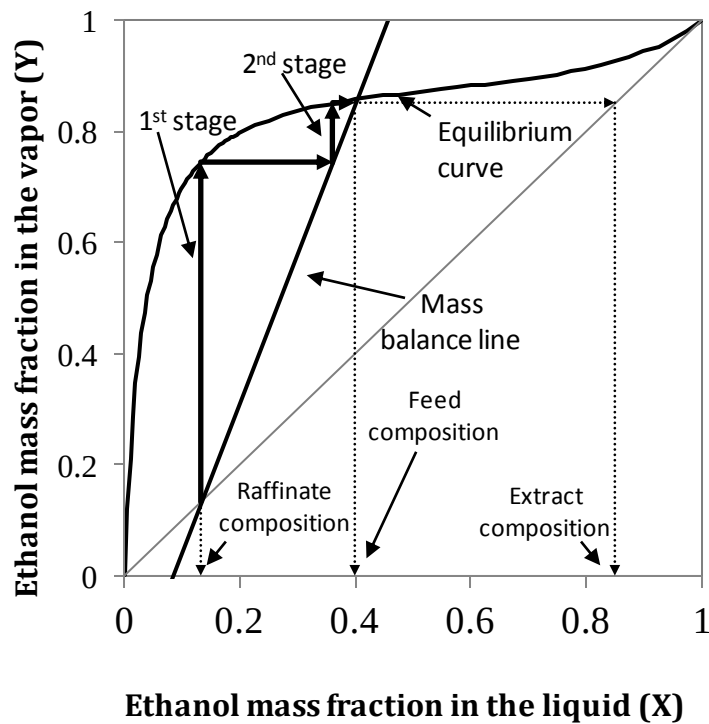


Figure 3.15: McCabe-Thiele construction. Solvent-to-feed ratio: 20. Number of stages: 2. Feed ethanol mass fraction: 0.4. Parameter set used for the selectivity calculation: α_B .

Moreover, the feasibility region of the model, i.e. the range of possible extract and raffinate compositions is very narrow, and if experimental extract and raffinate compositions are found beyond this region the determination of the number of theoretical stages is impossible.

As a corollary, extract and raffinate compositions could not be used to accurately assert the number of theoretical stages. Hence the height of a theoretical stage cannot be computed from the data presented.

Finally, since the number of stages could not be determined by this method, and given the relatively low influence of this parameter on the output compositions, an arbitrary number of theoretical stages was chosen to represent the column, as will be discussed further in the next section.

3.3.1.6. Ponchon-Savarit, McCabe-Thiele and flash calculations

Given model behavior, there is little difference between the outputs given using the Ponchon-Savarit or McCabe-Thiele methods. If only one stage is considered, the flash calculation is the only possibility. For a great number of stages, both models converge towards the same limits. However, since the solvent selectivity is high both models converge fast towards the same value and hence the difference between them becomes negligible. In our tests using solvent-to-feed ratios from 20 to 60 and feed ethanol mass fractions from 0.1 to 0.9 the relative difference between both models predicted composition was always less than 2%.

For the sake of simplicity, it was decided to initially model the process as a single flash using the equilibrium correlations proposed by Budich and Brunner (parameter set α_B of Table 3.4).

3.3.2. Column hydrodynamics

3.3.2.1. Flooding

Flooding occurs when the solvent or feed flow rates are increased beyond the maximum hydraulic capacity of the column. Flooding can present itself in several ways, either by an excessive increase in the solvent pressure drop, an excessive accumulation of liquid on the packing, the entrainment of liquid droplets by the solvent, an excessive liquid build-up above the packing, etc. Under these conditions, mass transfer rates drop and the separation efficiency of the system falls rapidly (Figure 2.6, page 45).

For dimensioning purposes, knowledge of the flooding point is required since it is the principal factor limiting the maximal capacity of the column. In normal applications, a column is design to work at roughly 70 to 80% of its flooding capacity in order to be able to deal with fluctuations on the process flow rates [12].

3.3.2.2. The overhead load

An experimental overhead load can be obtained assuming the following hypothesis: all the solute is recovered from the overhead as the extract; the solvent loss by dissolution in the raffinate is negligible; no accumulation occurs in the column (steady-state operation). The overhead load can be estimated from experimental data using the following equation

$$\ell_o (Y_o) = \frac{\varepsilon}{\Omega} = \frac{1}{\Omega} \left(\frac{X_Z - X_R}{X_E - X_R} \right) \quad (3.14)$$

where X_Z , X_R and X_E are the solvent-free ethanol mass fraction of the feed, raffinate and extract respectively, Ω is the solvent-to-feed ratio and ε is the extract yield (the mass ratio between the extract and feed).

The comparison between the experimental overhead loading and the maximum theoretical vapor loading is of interest seeing that deviations may be related to poor mass transfer, accumulation of liquid in the column and/or liquid entrainment.

3.4. Results and discussion

3.4.1. Laboratory-scale unit experiments

3.4.1.1. Extract and raffinate compositions

Firstly, the reproducibility and transient state evolution of the extract and raffinate compositions were studied. A comparison of the extract and raffinate composition as function of time between two independent runs under the same conditions is presented in Figure 3.16. Standard deviation for the raffinate and extract ethanol fractions, once steady-state operation is achieved, is lower than 0.5%. In steady state, deviations, for the mean ethanol mass fractions, between the two runs were lower than 0.01.

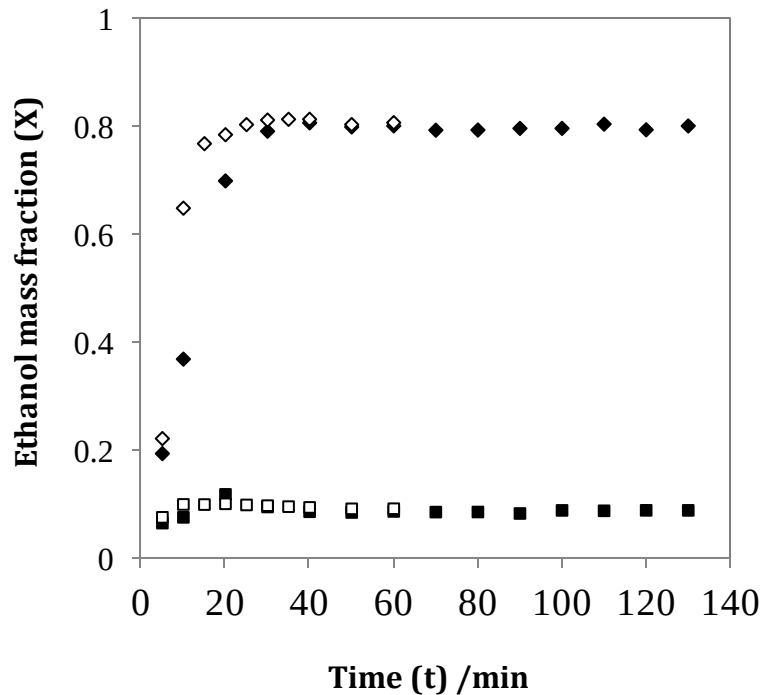


Figure 3.16: Composition of the extract (◆,◇) and raffinate (□,■) as a function of time for two independent runs. Feed ethanol mass fraction: 0.267 (.....); Feed flow rate: 0.578 kg h⁻¹; Solvent flow rate: 10 kg h⁻¹; Solvent-to-feed ratio: 17.4. Full and hollow symbols represent different runs.

It was also found that the time required to achieve steady-state operation was somewhat affected by the ethanol mass fraction of the feed. For ethanol contents lower than 0.4, the time required for steady-state operation was around 40 min while for

higher ethanol concentrations in the feed, the stabilization time was around 20 min. Since the stabilization time was found to be variable, extract and raffinate samples were collected at regular time intervals in all the runs in order to verify operation under steady-state for each run. As a corollary, it can be concluded that neglecting the dynamic transition towards steady-state conditions can introduce severe deviations on short fractionation runs.

A series of 34 experiments with solvent-to-feed ratios ranging from 5.2 to 78.8 and feed ethanol mass fractions from 0.05 to 0.9 were conducted on the laboratory-scale unit. The conditions used and results obtained are presented in Table 3.5. Predicted extract and raffinate compositions were in good agreement with experimental values, as shown in Figure 3.17. The actual separation efficiency is consistently higher than predicted, implying that the column is superior to a single flash, while following closely the same tendencies. The actual number of stages was not computed for the reasons stated in Section 3.3.1.5.

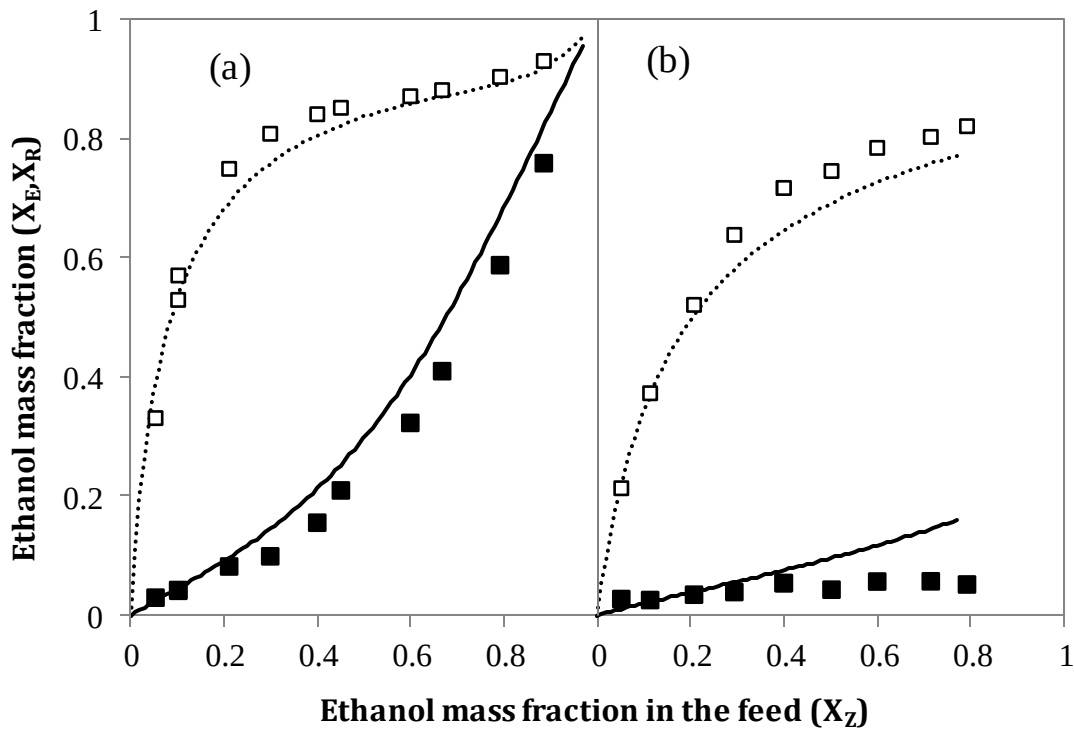


Figure 3.17: Comparison between the experimental raffinate ($\square$) and extract ($\blacksquare$) composition and the prediction of a single-stage model for the laboratory-scale unit. Solvent rate = 12 kg h^{-1} (a) Solvent-to-feed ratio = 20 (b) Solvent-to-feed ratio = 70.

Table 3.5: Summary of experimental results

Scale	$S / \text{kg h}^{-1}$	$Z / \text{kg h}^{-1}$	X_Z	X_E	X_R	Ω
Laboratory	6.0	0.237	0.1010	0.5301	0.0437	25.3
	“	0.295	0.1004	0.5294	0.0430	20.4
	“	0.947	0.1960	0.7673	0.1443	6.3
	“	0.947	0.4980	0.8644	0.4467	6.3
	“	0.947	0.6952	0.8852	0.6061	6.3
	“	1.097	0.4979	0.8640	0.4464	5.5
	“	1.163	0.1950	0.7665	0.1438	5.2
	9.6	0.576	0.2662	0.8075	0.0934	16.7
	“	0.576	0.2665	0.7966	0.0859	16.7
	12.0	0.152	0.7903	0.8207	0.0523	78.8
	“	0.156	0.7127	0.8027	0.0577	77.1
	“	0.161	0.5979	0.7843	0.0573	74.8
	“	0.164	0.5000	0.7455	0.0436	73.0
	“	0.168	0.3981	0.7171	0.0546	71.3
	“	0.168	0.3972	0.7171	0.0546	71.2
	“	0.172	0.2918	0.6385	0.0396	69.8
	“	0.174	0.2056	0.5211	0.0352	68.9
	“	0.176	0.1115	0.3730	0.0263	68.0
	“	0.178	0.0497	0.2137	0.0279	67.4
	“	0.238	0.3870	0.7503	0.0543	50.4
	“	0.381	0.3870	0.8161	0.1045	31.5
	“	0.493	0.8837	0.9300	0.7587	24.3
	“	0.508	0.7899	0.9033	0.5877	23.6
	“	0.526	0.6659	0.8812	0.4100	22.8
	“	0.535	0.5977	0.8709	0.3232	22.4
	“	0.555	0.4490	0.8515	0.2100	21.6
	“	0.561	0.3984	0.8408	0.1559	21.4
	“	0.573	0.2976	0.8080	0.0996	21.0
	“	0.580	0.2097	0.7492	0.0825	20.7
	“	0.589	0.1008	0.5704	0.0417	20.4
	“	0.594	0.0520	0.3313	0.0302	20.2
	“	1.043	0.6940	0.8842	0.6054	11.5
	“	1.191	0.3890	0.8499	0.2890	10.1
	“	1.437	0.3106	0.8446	0.2703	8.4
Pilot	25	0.528	0.3700	0.7953	0.0725	47.3
	25	1.268	0.3900	0.8486	0.2108	19.7
	23.9	2.028	0.3900	0.8423	0.2896	11.8
	51.2	1.032	0.3911	0.7571	0.0740	49.6
	51.5	2.373	0.3911	0.8338	0.1456	21.7
	52.6	5.065	0.3750	0.8399	0.3129	10.4
Industrial	398	9.627	0.3980	0.8180	0.1350	41.3
	142	11.710	0.3941	0.8518	0.2699	26.0

3.4.1.2. The overhead solvent-loading

As shown in Figure 3.18, the overhead loading values obtained from experimental runs with solvent apparent velocities between 20 and 40 mm s⁻¹ (corresponding to solvent flow rates between 6 and 12 kg h⁻¹) presented very good agreement with the theoretical maximum values calculated from the VLE data from Budich and Brunner [4]. Good agreement is also found with loadings computed from Lim et al. [5] and Furuta et al. [6] VLE data, though deviations are larger. From this comparison, it was concluded that the solvent overhead was saturated (i.e., that the amount of ethanol and water dissolved was the maximum thermodynamically stable) at the exit of the column for solvent apparent velocities between 20 and 40 mm s⁻¹, implying good mass transfer between the liquid and fluid phase.

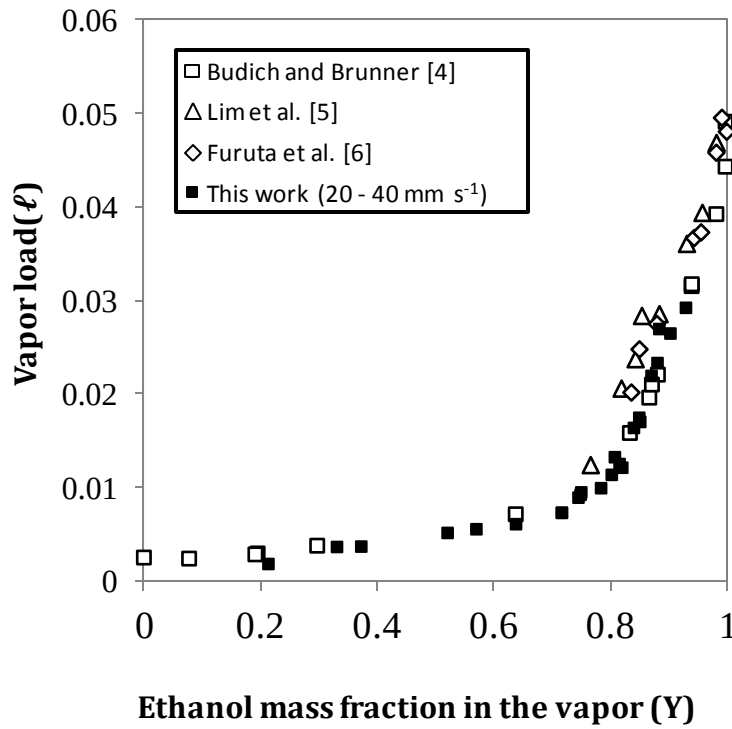


Figure 3.18: Comparison between vapor loads obtained from experimental runs with a solvent velocity between 20 and 40 mm s⁻¹ as a function of the overhead solvent-free ethanol mass fraction and VLE data.

3.4.1.3. Droplet entrainment and flooding

Droplet entrainment problems were found at the minimum apparent solvent velocities of 12 mm s^{-1} (3.6 kg h^{-1}). Steady-state operation could not be achieved under these conditions, as shown in Figure 3.19 for two independent runs at a feed rate of 0.173 kg h^{-1} ; a solvent flow rate of 3.6 kg h^{-1} , a feed ethanol mass fraction of 0.112 and a solvent-to-feed ratio of 20.8. A threefold increase in both the solvent and feed flow rates allows the column to achieve steady-state operation in less than 40 min.

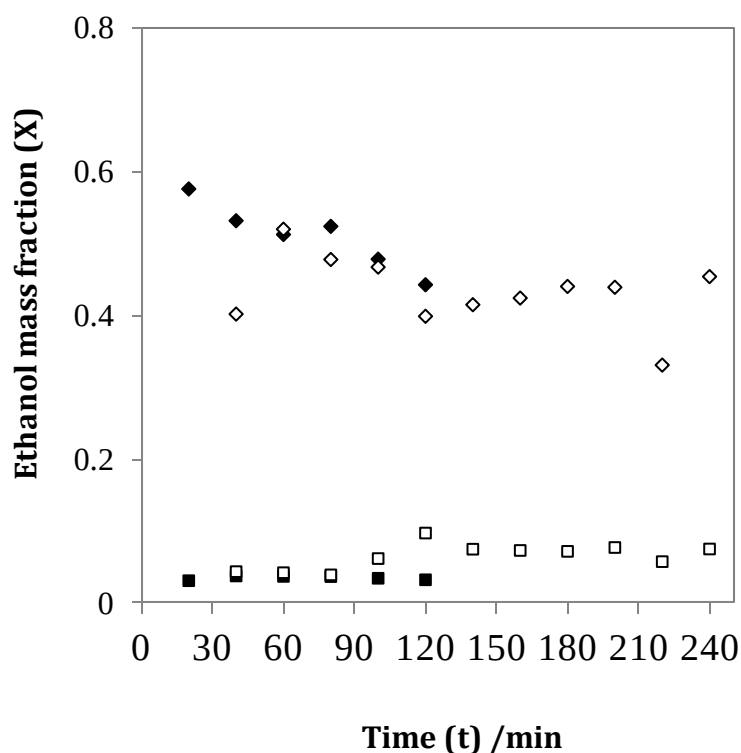


Figure 3.19: Evolution of the raffinate (■, □) and extract (◆, ◇) composition for two runs under the same conditions. Full and hollow symbols represent different runs. Feed flow rate = 0.173 kg h^{-1} ; Solvent rate = 3.6 kg h^{-1} ; Solvent velocity = 12 mm s^{-1} ; Feed ethanol fraction = 0.112

Droplet entrainment was confirmed by the effective overhead load as shown in Figure 3.20. Given the way in which the overhead loading is computed, deviations can be caused by liquid accumulation inside the column. In some cases, perturbations were encountered after steady-state conditions while in the rest of the cases it was impossible to achieve steady-state operation. Typically, after a while the extract ethanol fraction

was found to decrease while the overhead loading increased. This behavior would normally be attributed to entrainment flooding. Such unexpected behavior at low solvent flow rates could be caused by the larger flow fluctuations produced by the solvent double-piston feed pump at lower flow rates. Pulsing is known to reduce liquid droplet diameter in liquid-liquid extraction columns, favoring droplet entrainment [13,14]. No entrainment was found when increasing the solvent flow rate either at constant liquid flow or solvent-to-feed ratio.

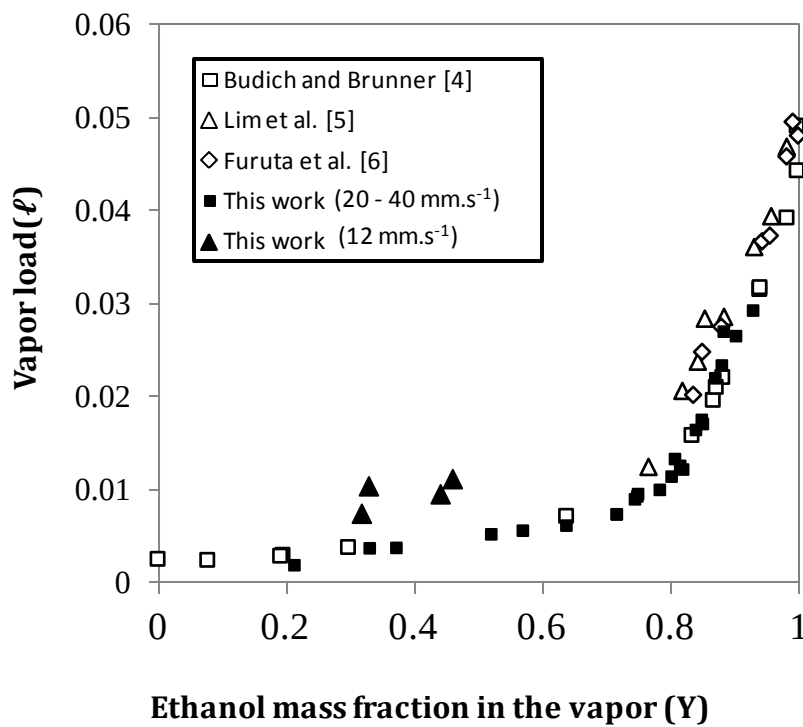


Figure 3.20: Overhead load as a function of the extract composition showing entrainment flooding at low solvent apparent velocities.

Macroscopic flooding was found at a solvent-to-feed ratio of 5 (the lowest used) and a 0.112 feed ethanol mass fraction and a solvent apparent velocity of 20 mm s⁻¹ (12 kg h⁻¹). Flooding was detected by the lack of raffinate flow. After an hour of operation, one third of the packed volume was found to be filled with liquid. Product composition analysis showed a progressive drop on both the extract and raffinate ethanol mass fraction. Under the same conditions but with a 0.498 feed ethanol mass

fraction, no flooding was observed. This observation is in agreement with data from Budich and Brunner [4] who reported a diminution of the flooding capacity at lower liquid ethanol mass fractions for structured Sulzer EX packings. These results will be discussed further in the following chapter.

3.4.2. Pilot-scale fractionation runs

Experimental runs on the pilot-scale fractionation unit were conducted to study the reliability of laboratory-scale studies for column scale-up. The scale factor (i.e. the cross-section ratio) between both columns is 8.7 while the height ratio is 2.

For this part of the study, a feed with a 0.40 ethanol mass fraction was used. Six runs were conducted with a solvent-to-feed ratio set at 10, 20 or 50 while 9.3 and 18.6 mm s⁻¹ solvent velocities were used (i.e. solvent flow rates of 25 and 50 kg h⁻¹). Experimental extract and raffinate compositions are presented in Table 3.5 (page 89).

The operation was controlled by weighting the raffinate and extract at regular time intervals. Once steady-state operation was attained, the global mass balance closed within 5% while ethanol mass balances closed within 10% for all runs.

3.4.2.1. Extract and raffinate compositions

A good agreement between laboratory-scale and pilot-scale results was found, as summarized in Figure 3.21. Deviations between simulated and experimental extract and raffinate compositions at high solvent-to-feed ratios will be discussed later. The separation efficiency for a solvent-to-feed ratio of 10 was found to be lower in the case of the pilot-scale unit which could be attributed to the lower solvent velocities attainable on the pilot-scale set-up.

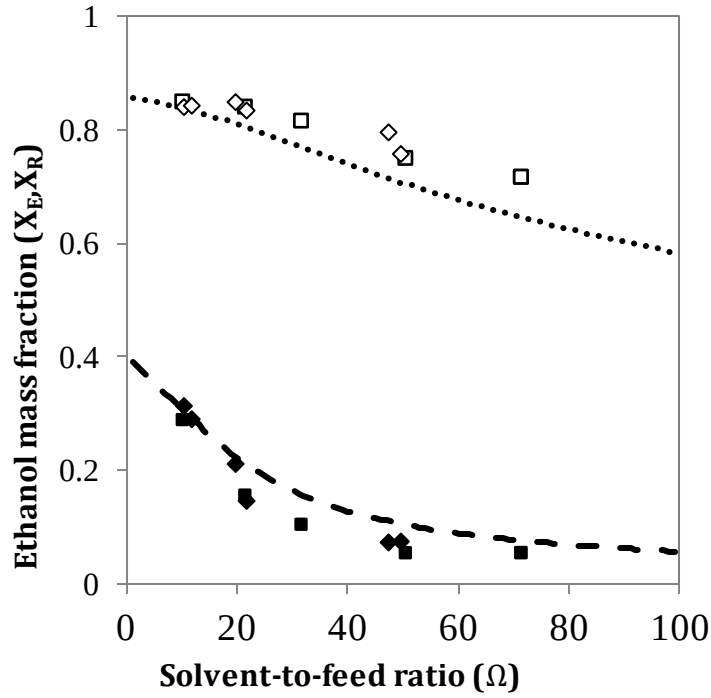


Figure 3.21: Comparison between the experimental extract (hollow symbols) and raffinate compositions (full symbols) obtained on a laboratory-scale (■, □) and a pilot-scale unit (◆, ◇) as a function of the solvent-to-feed ratio. Lines represent the single-flash model.

3.4.2.2. The overhead solvent-loading

As can be seen in Figure 3.22, for a solvent velocity of 18.6 mm s^{-1} , the overhead loadings were found to be in very good agreement with the experimental values obtained at the laboratory-scale column. Under these conditions, the overhead can be considered to be saturated, implying a good mass transfer capacity. For the lower solvent velocity, however, overhead loads were found to be lower. It can be concluded that mass transfer capacity was hence reduced.

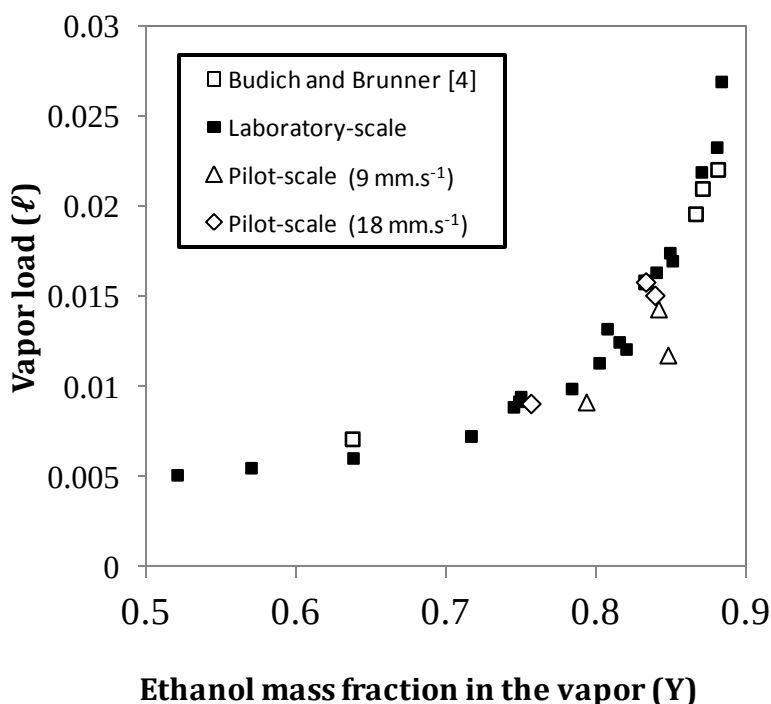


Figure 3.22: Comparison between the overhead load in the pilot-scale unit at different solvent flow rates with laboratory-scale results and VLE data.

3.4.2.3. Column hydrodynamics

At pilot-scale operations, flooding was not detected under any condition. Although there the packings used were bigger than in the laboratory column, the type of packing used was the same; hence, the flooding capacity is expected to be similar. However, since the bigger packing elements provide a lower specific surface area, the solvent velocity required to achieve flooding conditions will be higher than those in the pilot-scale unit. In this set of experiments solvent velocities were smaller than those used in the pilot-scale column and therefore flooding was not expected. No droplet entrainment was found either, supporting the hypothesis that pump pulsations are the cause of this problem, since flow rate fluctuations were greatly reduced.

A short experience was conducted at solvent velocities around 20 mm s^{-1} (a solvent flow rate around 80 kg h^{-1}). The cyclonic separators were unable to cope with those high solvent flow rates and the experience was concluded after 30 min with no

evidence of droplet entrainment. The experience was stopped due to the raising pressure at the separators and column.

In addition, dynamic liquid holdup measurements were conducted for 5 runs at different conditions, as shown in Figure 3.23. The values reported here correspond to the mass of liquid recovered since density values at working conditions were unavailable. As expected, the liquid holdup increases when the feed flow rate increases. However, the effect of the solvent flow rate seems to be less important, indicating that the column is operating below or near the loading point.

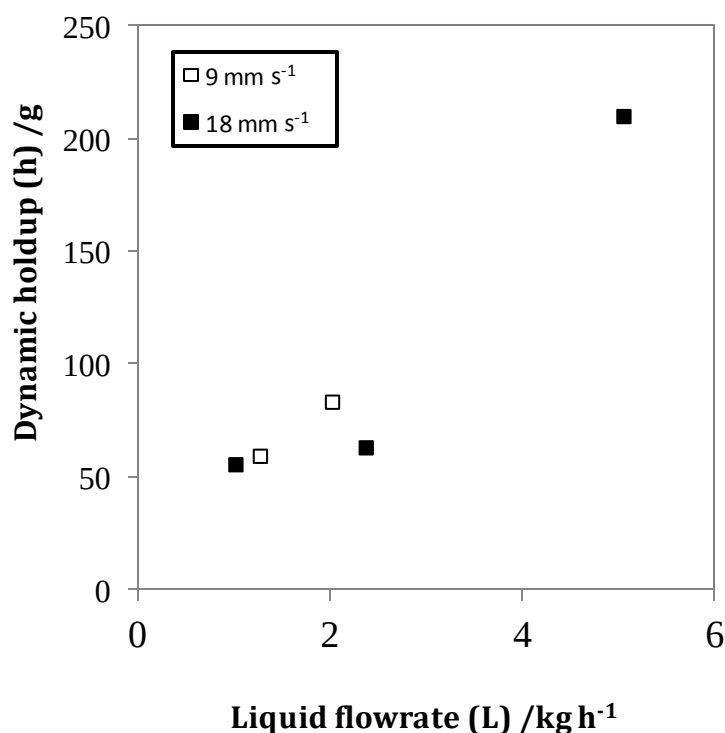


Figure 3.23: Dynamic holdup expressed as the mass of recovered liquid as a function of the feed flow rate for the pilot-scale column.

3.4.3. Industrial-scale fractionation runs

Fractionation runs performed on the industrial-scale column presented stronger hydrodynamic effects. First, entrainment flooding was detected. Secondly, in the absence of flooding the extract and raffinate compositions were found to deviate from the expected values, indicating strong solvent by-pass. An experimental determination

of the flooding point for a solvent-to-feed ratio of 12 was also carried. Experimental extract and raffinate composition are presented in Table 3.5 (page 89). The scale-up factor (i.e. the cross-section ratio) between the industrial-scale and laboratory-scale column is 44.

3.4.3.1. Extract and raffinate compositions

As shown in Figure 3.24, the experimental extract and raffinate compositions are not in very good agreement with the tendency presented by the laboratory or pilot-scale units. The extract and raffinate compositions from the flooding-point experiments (in which mass transfer rates are especially high) are however in better agreement with the laboratory and pilot-scale results. In order to better comprehend the reasons for this deviations, the overhead loading should be taken into account.

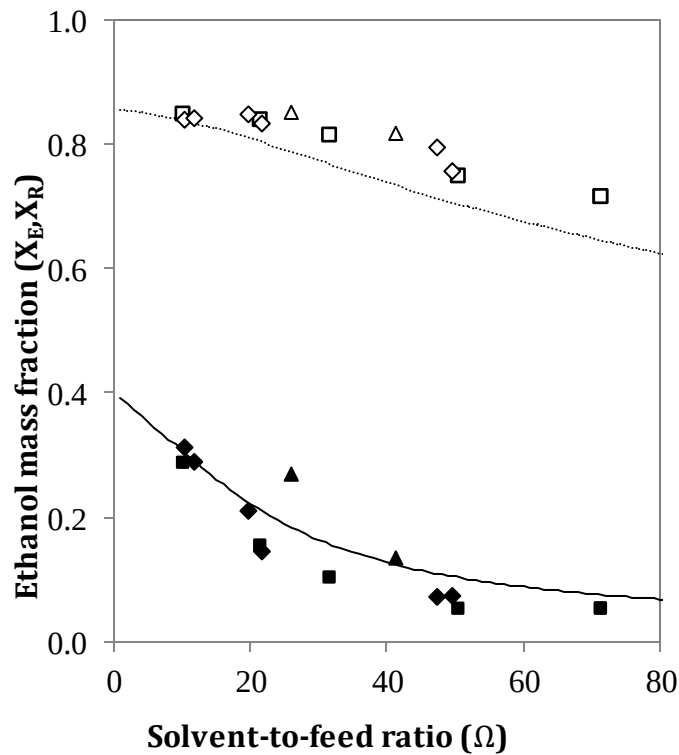


Figure 3.24: Comparison between the extract (hollow symbols) and raffinate (full symbols) compositions at laboratory-scale (■, □), pilot-scale unit (◆, ◇) and industrial scale (▲, △) as a function of the solvent-to-feed ratio. Lines represent the single-flash model.

3.4.3.2. Overhead loading

For the run with the higher solvent-to-feed ratio, the overhead loadings are at least 20% lower than expected, as shown in Figure 3.25.

The deviations of the industrial-scale results in Figure 3.24 and Figure 3.25 could be related. From Equation (3.11), the overhead load is computed using the solvent-to-feed ratio, hence inaccuracies in the solvent mass flow or solvent bypass in the column could affect both plots.

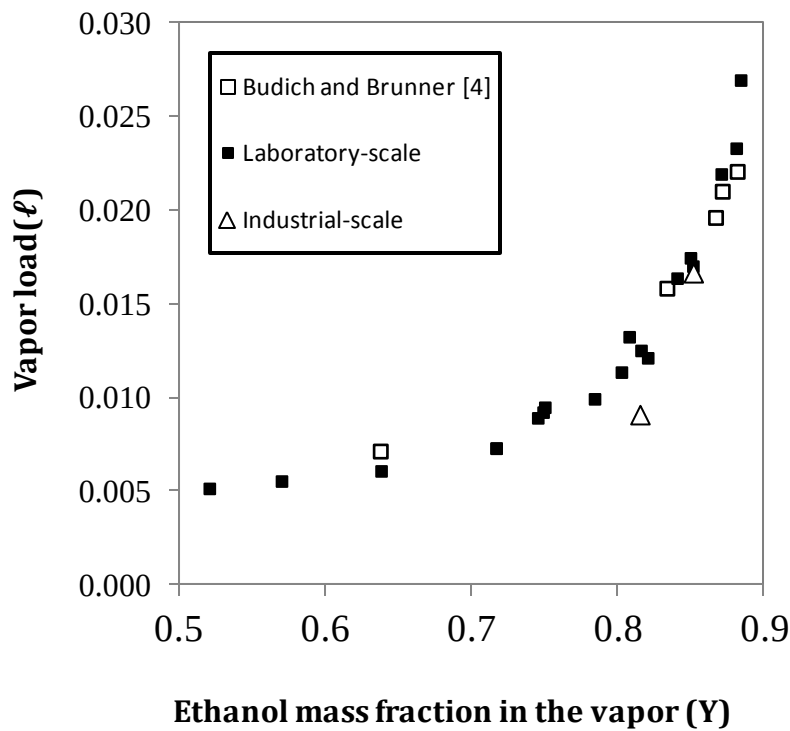


Figure 3.25: Comparison between industrial-scale and laboratory-scale overhead loadings

From Equation (3.11), the extract yield can be interpreted as an indirect measure of the effective solvent-to-feed ratio. In the case of the pilot- and industrial-scale columns, the extract yield is obtained directly by weighting of the extract and feed and is hence independent of the solvent mass-flow. If the composition of the extract and raffinate is plotted as a function of the extract yield instead of the solvent-to-feed ratio

there is a much better correlation between all experimental results, as shown in Figure 3.26.

These results can be interpreted either as a strong solvent bypass or inaccurate determination of the solvent mass flow rate. Solvent bypass may be caused by poor initial liquid distribution and by the lack of redistributors between the packing elements.

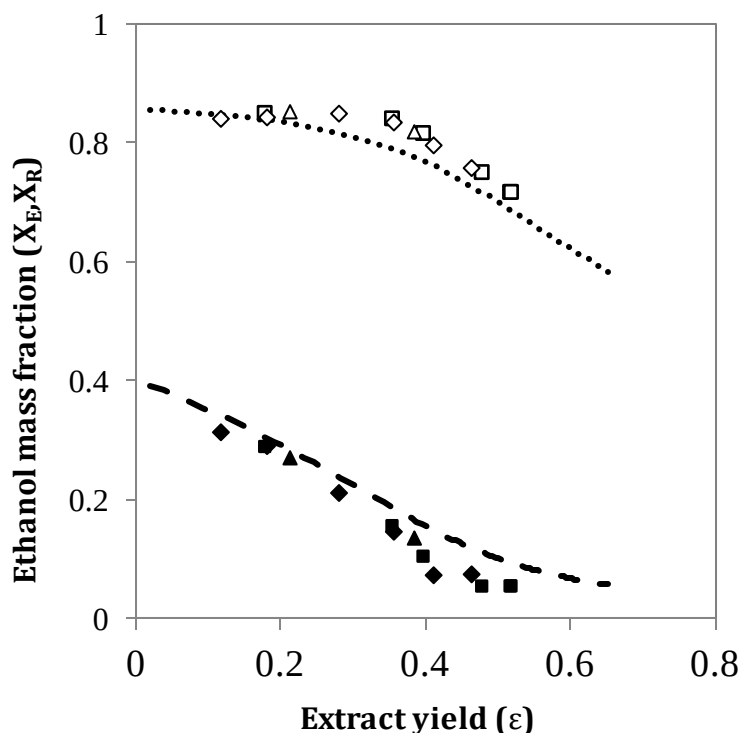


Figure 3.26: Comparison between the extract (hollow symbols) and raffinate (full symbols) compositions at laboratory-scale ($\blacksquare, \square$), pilot-scale unit ($\blacklozenge, \diamond$) and industrial scale ($\blacktriangle, \triangle$) as a function of the extract yield. Lines represent the single-flash model.

3.4.3.3. Column hydrodynamics

Contrary to the other two columns used in this study, the industrial-scale column was packed with a structured Sulzer CY packing. A run conducted with a 19 kg h^{-1} feed flow rate and a 305 kg h^{-1} solvent flow rate (i.e., a solvent velocity of 23 mm s^{-1} and a solvent-to-feed ratio of 16), was found to suffer from severe droplet entrainment. A plot of the accumulated raffinate, output (extract + raffinate) and feed mass shows liquid accumulation in the column until a sudden increase in the extract flow rate, at approximately 60 min from the start (Figure 3.27). At the same time, the extract ethanol

mass fraction was found to drop from 0.8 to 0.6. At this point, the extract recovered was more than five times over the maximum vapor loading.

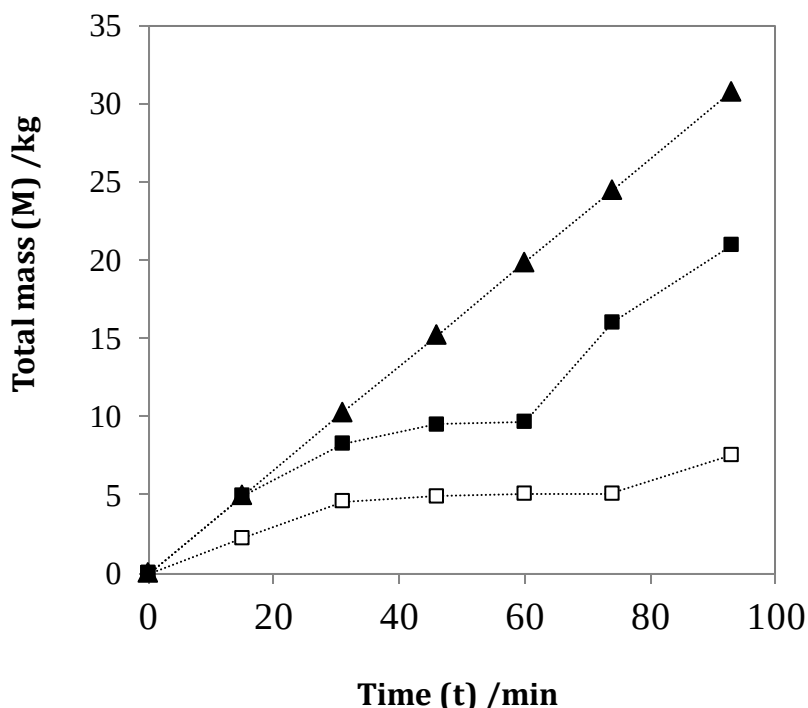


Figure 3.27: Accumulated mass of the feed (▲), raffinate (□) and total output (■) during flooding. Industrial-scale unit. Solvent flow rate = 305 kg h^{-1} . Feed flow rate = 11.7 kg h^{-1} .

It is important to note that droplet entrainment was detected only after an hour of operation. Also, a quasi-steady state was reached by reducing the feed and solvent flow rate to 15.6 kg h^{-1} and 254 kg h^{-1} , which permitted stable operation for 4 hours while liquid slowly accumulated in the column.

An experimental determination of the flooding point for a constant solvent-to-feed ratio of 12 was then performed. Operation was found to be stable at a 11.7 kg h^{-1} feed and 142 kg h^{-1} solvent flow rate (10.9 mm s^{-1} vapor velocity), with an estimated liquid holdup of 4 kg while severe droplet entrainment was detected at a feed flow rate of 13.6 kg h^{-1} and 158 kg h^{-1} of solvent (12.1 mm s^{-1}).

According to these results, flooding and vapor bypass define a narrow area of operation which is a sign of poor packing performance. In view of these findings, a

closer inspection of the packing elements was performed and it was found that some packing elements had suffered from severe compression. This could explain the observed deviations from the predicted behavior. A column revamping is under way and further studies are planned once it is operational.

3.5. Revisiting the equilibrium-stage model

Numerous experimental overhead load values were obtained in this work and found to present less scattering than those obtained from VLE data. The correlation proposed by Budich and Brunner fits the VLE data well, but the vapor loads found in this work show a steeper curvature change for an ethanol mass fraction around 0.8.

In order to improve the correlation, the following expression was fitted to the vapor loading values of Budich and Brunner and to those obtained in the laboratory-scale column using the maximum solvent flow rate:

$$\ell_o = \sum_{i=0}^6 a_i Y^i \quad (3.15)$$

The values of the coefficients a_i are given in Table 3.6 and depend of the value of Y . A comparison between both correlations and experimental values is presented in Figure 3.28.

Table 3.6: Coefficients to calculate the overhead load

i	a_i		
	$Y \leq 0.46$	$0.46 < Y < 0.85$	$0.85 \leq Y$
0	0.00233	0.0683491	0.2389
1	0.00111	-0.912368	-0.6612
2	0.00744	5.0967	0.4710
3	0	-14.6475	0
4	0	23.0503	0
5	0	-18.8833	0
6	0	6.32066	0

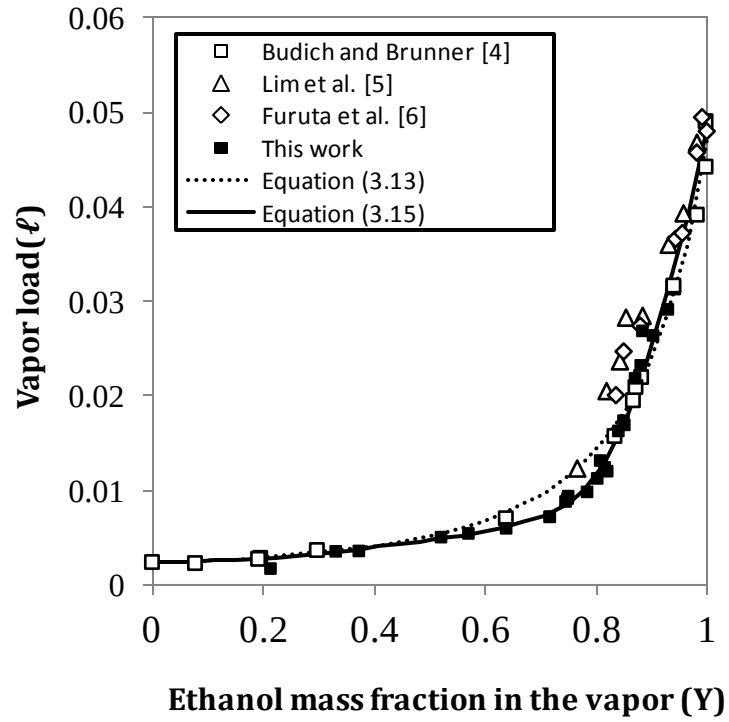


Figure 3.28: Comparison between experimental VLE data and the results of this work and the correlations from Equations (3.13) and (3.15).

The vapor load has a greater impact in the model output for high solvent-to-feed ratios. In this case, the column tends to be pinched at the bottom, i.e. the raffinate ethanol mass fraction tends to zero and the extract composition is only determined by the amount of feed dissolved by the solvent.

Using this new correlation for the vapor load, the predicted extract and raffinate compositions were found to be in much better agreement particularly in the case of high solvent-to-feed ratios as can be seen in Figure 3.29.

As expected, the change is unnoticeable for lower solvent-to-feed ratios, as shown in Figure 3.30.

From both figures it can also be seen that, as already discussed, the number of theoretical stages has little impact in the model output.

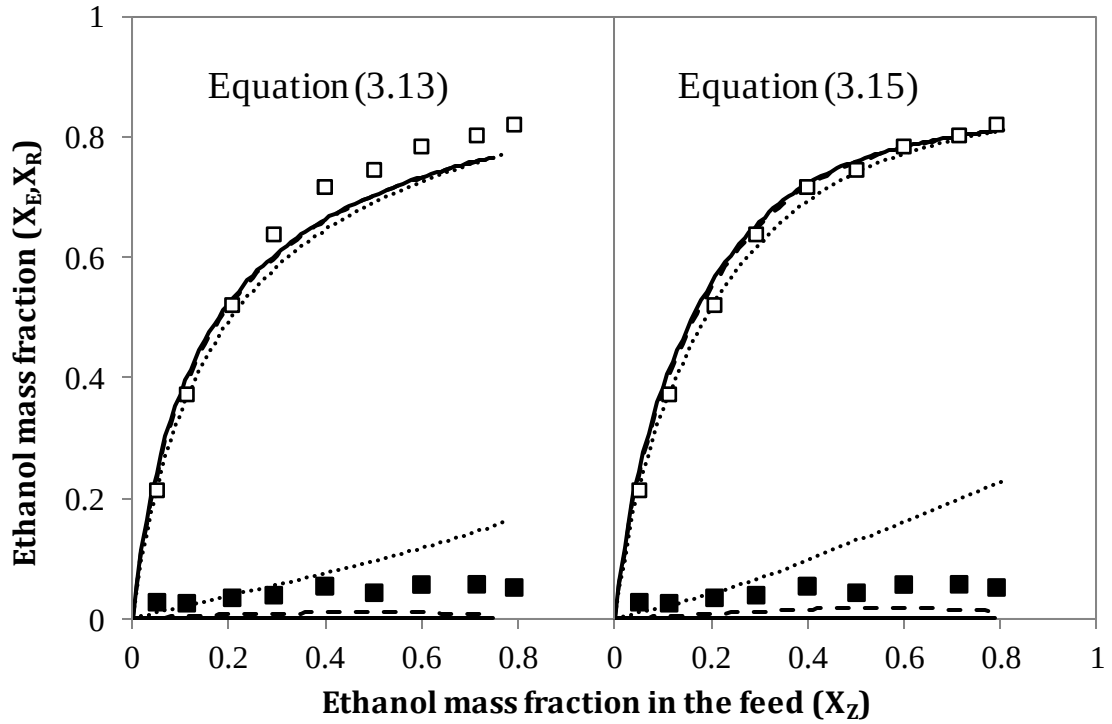


Figure 3.29: Comparison between experimental and predicted extract and raffinate ethanol mass fractions as a function the feed ethanol mass fraction for a solvent-to-feed ratio around 70. Hollow and full symbols represent the extract and raffinate, respectively. 1 stage model; ---- 2 stage model; — 10 stage model.

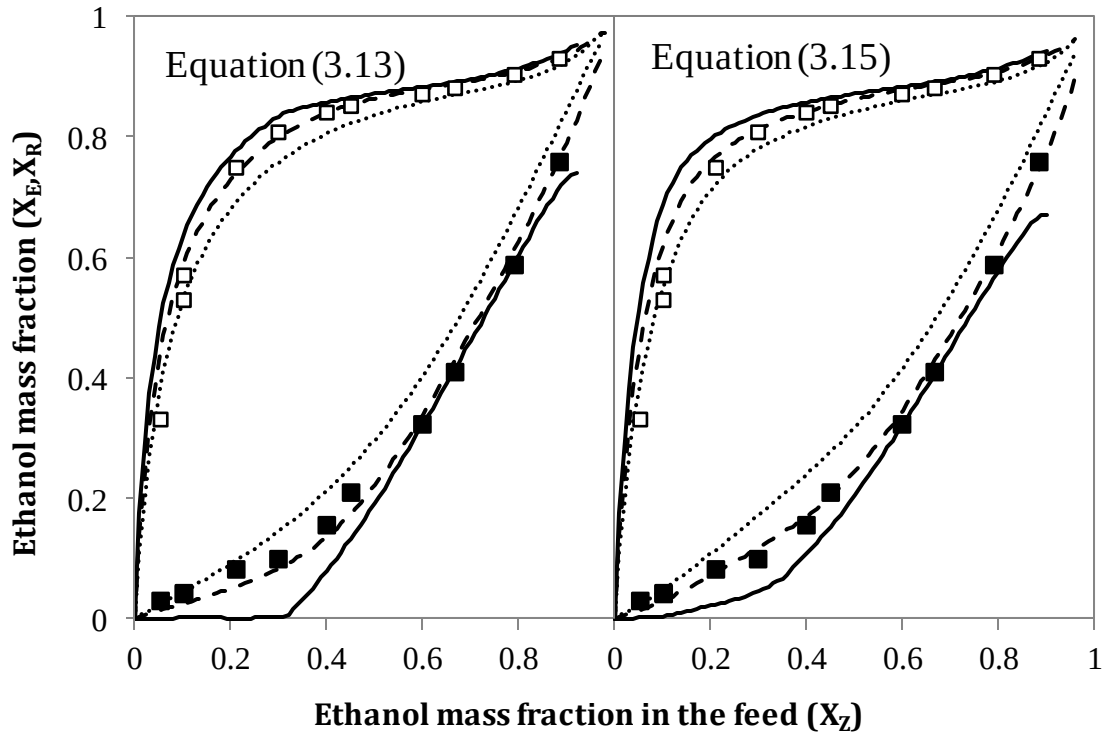


Figure 3.30: Comparison between experimental and predicted extract and raffinate ethanol mass fractions as a function the feed ethanol mass fraction for a solvent-to-feed ratio around 20. Hollow and full symbols represent the extract and raffinate, respectively. 1 stage model; ---- 2 stage model; — 10 stage model.

3.6. Conclusions

A multiple scale study of the supercritical fractionation process was conducted.

First, the dynamic stabilization time was found to be dependent on the feed composition. Repeated sampling proved to be an adequate and reproducible method to ensure steady-state operation.

Steady-state extract and raffinate compositions were found to be in agreement with a single-flash equilibrium model. Although the Ponchon-Savarit and McCabe-Thiele models could also be used, it was found that the influence of the number of theoretical stages in the model output was negligible compared to the influence of the equilibrium relation chosen to describe the thermodynamic behavior of the system. This modeling problem is a consequence of the high solvent selectivity and lack of external reflux and puts forward the importance of the quality of the VLE data for process modeling purposes. Hence, the height of the column is expected to have a low influence in the extract and raffinate compositions, and deviations between different columns imply large differences in the hydrodynamic state.

Experiences with low solvent flow rates were found to be affected by several problems. In the laboratory-scale unit, droplet entrainment was detected in all runs with solvent velocities below 12 mm s^{-1} . At pilot-scale, mass transfer was found to be less efficient at solvent velocities of 9 mm s^{-1} , though entrainment was not detected. Mass transfer rates were found to be important at solvent velocities between 20 and 40 mm s^{-1} since, according to our own data, the overhead can be considered saturated under these circumstances.

In the laboratory-scale unit, macroscopic flooding was found to be dependent on the ethanol content of the feed mixture and entrainment flooding was detected at low solvent apparent velocities. A more profound analysis of these phenomena will be presented in the following chapter.

Entrainment flooding and vapor bypass problems were found in the industrial-scale unit. Strong vapor bypass at conditions close to the flooding point was detected. This unexpected behavior was found to be caused by damaged packing elements.

Finally, a new correlation for the vapor load was developed from experimental data and used to reduce the deviations observed between experimental and predicted output using the Ponchon-Savarit model, especially at high solvent-to-feed ratios.

The results presented here show that the fractionation of ethanol-water mixtures using supercritical carbon dioxide can be a useful tool for studying or troubleshooting a fractionation unit. In one hand, the small influence of the number of theoretical stages in the column output can be interpreted as a problem as it prevents obtaining the height of theoretical stage from fractionation run results. However, it allows assessing the existence of solvent by-pass, flooding or very poor mass transfer, since deviations from the expected operating range can only be due to important hydrodynamic problems. These results have been recently submitted and published in a peer-reviewed journal [15].

3.7. References

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4. The prediction of the flooding point

4.1. Introduction

An estimation of the flooding capacity of a countercurrent column is vital for its conception since its diameter is adopted based on hydrodynamic restrictions. Taking into account that the wall width of a high pressure vessel is proportional to its diameter, its weight and cost will be proportional to its size. Hence, underestimating the flooding capacity may have a major impact in the economic analysis of a process. On the other hand, overestimating the flooding capacity may render the column unfit for its separation duty, either reducing the throughput or separation efficiency.

In order to estimate the flooding capacity, a comparison is drawn with other known systems. Extrapolation from experimental data is still the most successful method. Nonetheless, there are several semi-empirical models that allow comparing different packing elements and also to evaluate the influence of the fluids properties in the flooding point.

In the previous experimental section, two interesting points were raised regarding the flooding behavior of the ethanol/water/CO₂ system. In one hand, the flooding point was confirmed to be dependent on the feed ethanol mass fraction and in the other hand entrainment flooding was detected at solvent velocities lower than expected because of damaged packing elements in the industrial-scale unit.

It is not surprising that the composition of the liquid affects the flooding behavior. The ethanol mass fraction in the liquid affects its density, viscosity and interfacial tension, which in turn have a non-negligible impact on the flooding capacities. The reduction of the overall flooding capacity due to local accumulation of liquid is also a known phenomenon and can be related to the hydrodynamic stability of

the countercurrent flow. The question that will be addressed in the following discussion is whether or not the magnitude of these effects can be quantified based on available literature data and under which conditions can these effects be neglected.

4.2. The liquid and vapor density

The density of the phases involved has a great impact in the flooding phenomena. The diminution of the flooding capacity at high pressure compared to normal pressure and vacuum systems can be justified by the influence of pressure on the density of the phases involved. Temperature also plays a significant role, as it has a strong influence on the density of the phases involved.

Meyer and Brunner [1] measured the flooding point of the corn seed oil/ CO_2 system with a Sulzer EX structured packing at 20 MPa and for temperatures of 323, 373 and 393 K. Their results are presented in Figure 4.1.

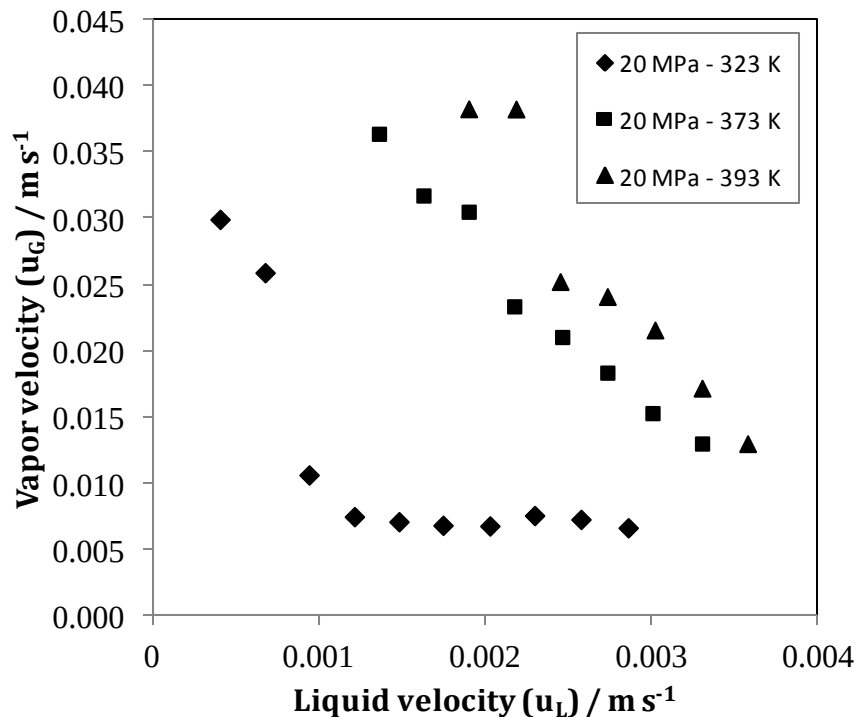


Figure 4.1: Flooding capacity diagram of the corn seed oil/ CO_2 system with a Sulzer EX structured packing at 20 MPa and for temperatures of 323, 373 and 393 K [1].

The effect of the density of the phases is taken into account by use of the vapor capacity factor (F_V) proposed by Stockfleth and Brunner [2] as a function of the flow parameter (ψ), as defined in equations (4.1) and (4.2). The resulting plot is presented in Figure 4.2. Except for some point at high flow parameter values, all experimental points lie in a single curve and the plot may be used to estimate the maximum solvent velocity.

$$F_V = u_G \sqrt{\frac{\rho_G}{\Delta\rho}} \quad (4.1)$$

$$\psi = \frac{u_L}{u_G} \sqrt{\frac{\rho_L}{\rho_G}} \quad (4.2)$$

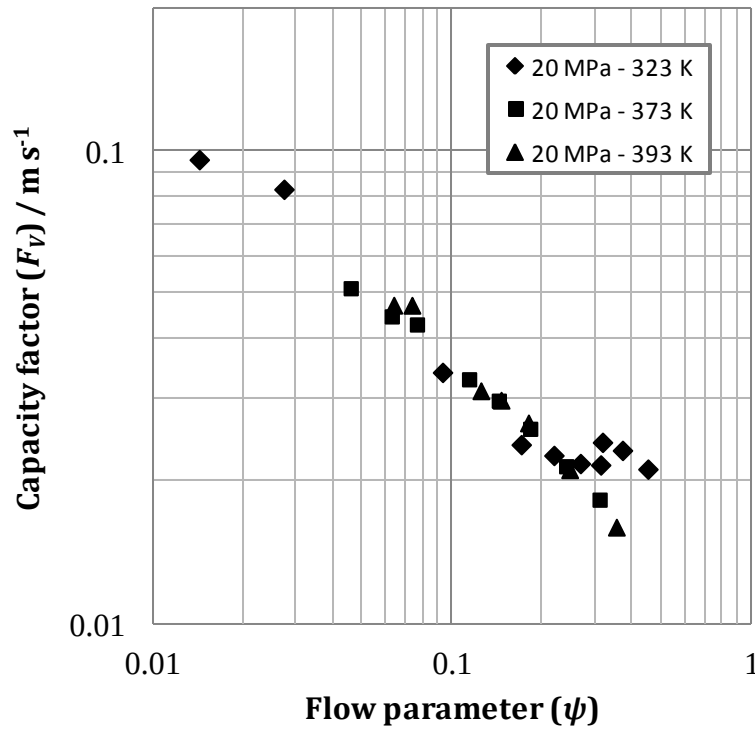


Figure 4.2: Capacity factor (F_V) as a function of the flow parameter (ψ) for the corn seed oil/ CO_2 system with a Sulzer EX structured packing.

4.3. The packing

In order to compare flooding capacities for different packings, Sherwood et al. [3] used a variable known as the packing factor (F_P), as defined in Equation (4.3).

$$F_P = \frac{a}{\varepsilon_b^3} \quad (4.3)$$

Later, Lobo et al. [4] proposed to use the packing factor as a fitting parameter in order to provide a better fitting between different packings. The use of a fitting parameter is nonetheless undesirable for this discussion since it may compensate for deviations due to other hydrodynamic effects. In the following discussion, all packing factors used are calculated using equation (4.3).

The capacity factor (c_G) and the dimensionless capacity factor (c_G^*) can be used to compare the performance of different packings and are defined according to equations (4.4) and (4.5), respectively.

$$c_G = u_G \sqrt{\frac{\rho_G}{\Delta \rho} F_P} \quad (4.4)$$

$$c_G^* = u_G \sqrt{\frac{\rho_G}{\Delta \rho} \frac{F_P}{g}} \quad (4.5)$$

Figure 4.3 presents the dimensionless capacity factor as a function of the flow parameter for the experimental flooding points obtained by Stockfleth and Brunner [5] for the water/CO₂ system between 313 and 373 K at 20 MPa using a structured Sulzer CY packing ($a = 860 \text{ m}^{-1}$; $\varepsilon_b = 0.86$) and Berl saddles ($a = 1520 \text{ m}^{-1}$; $\varepsilon_b = 0.61$). Even though structured and random packings are very different, their capacity factors are in good agreement with each other.

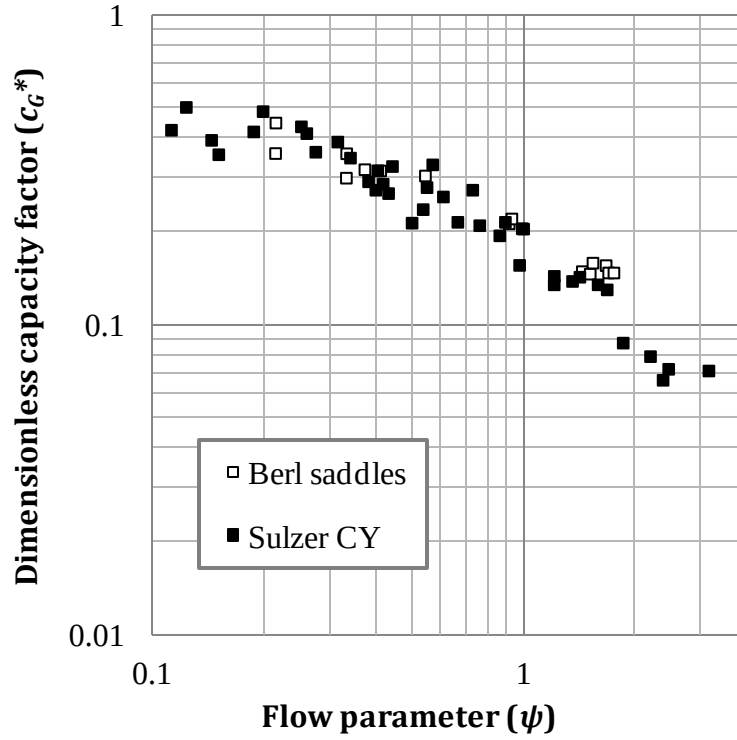


Figure 4.3: Dimensionless capacity factor (c_G^*) as a function of the flow parameter (ψ) for the water/ CO_2 system between 313 and 373 K at 20 MPa.

A database of 394 experimental flooding point values was compiled from the literature on supercritical fractionation. The corresponding flooding diagram is presented in Figure 4.4. The following correlation represents the general tendency:

$$c_G^* = 0.196 \psi^{-0.49} \quad (4.6)$$

The Average Absolute Relative Error (AARE) over the whole data set is 40.2%.

It should be noted that the original Sherwood correlation [3] presents an AARE of 43.8% over a dataset of 1104 flooding point values [6]. More recent models such as those of Billet and Schultes [7] and Maćkowiak [8] present AAREs of 11.1% (over 164 flooding points) and 10.8% (over 226 flooding points) respectively, but both models include specific packing constants than need to be determined experimentally. Moreover, these models have been developed for vacuum and atmospheric processes and predict a diminution of the flooding capacity as the pressure is increased, contrary to the tendency shown in Figure 4.4. These researchers have take into account the influence of pressure according the tendencies noted in high pressure distillation

services such as ethylene, propylene or methane purification and recovery. In those processes, the column capacity is generally severely affected by entrainment of the liquid, although the pressure rarely exceeds 3 MPa [9].

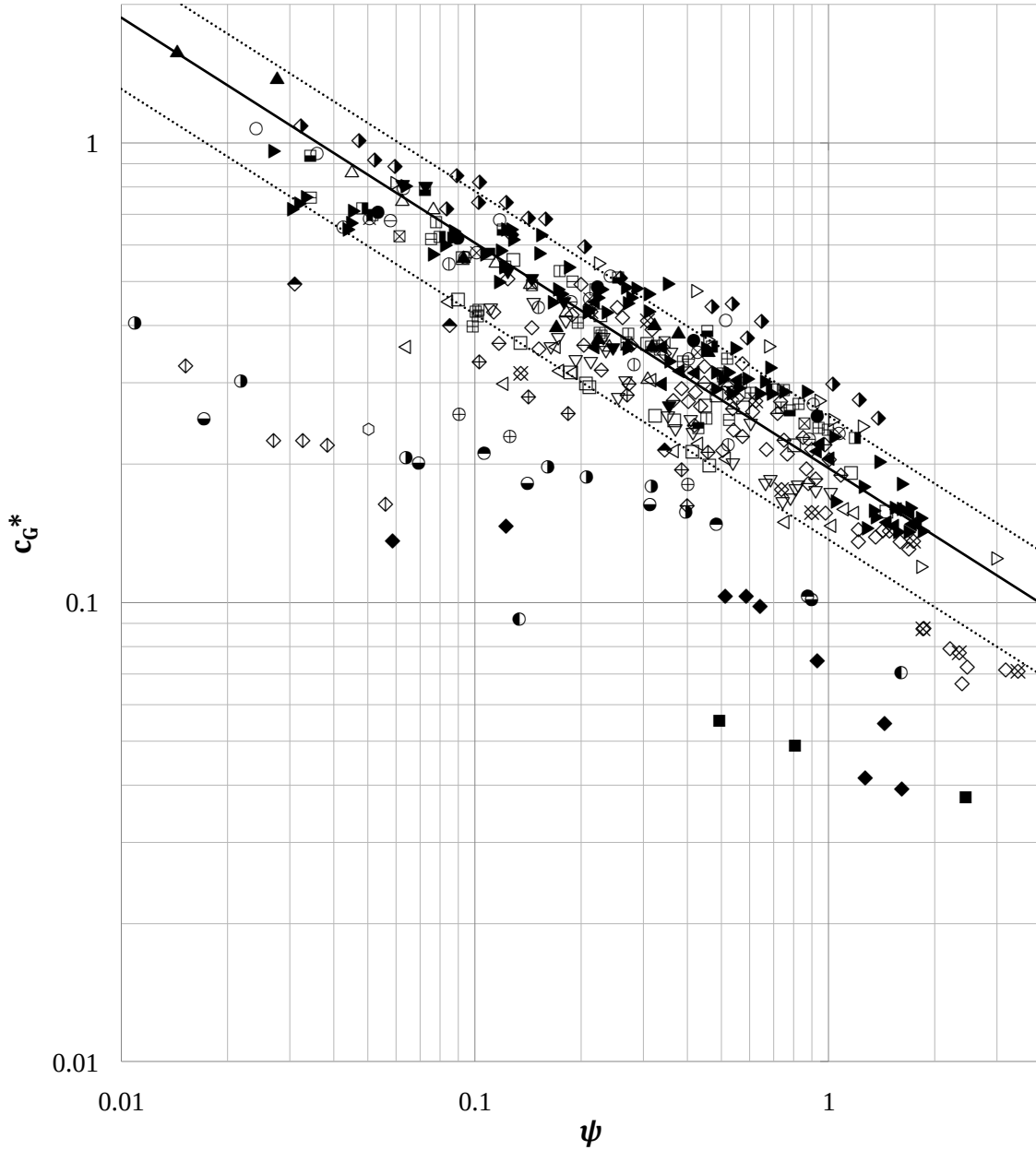


Figure 4.4: Flooding diagram for countercurrent columns using supercritical carbon dioxide. The straight line represents the correlation given by Equation (4.6). Dashed lines represent a 30% deviation. Symbol references can be found in Table 4.1.

Two interesting points can be raised from an analysis of the plot in Figure 4.4. Although an estimate within 30% of the flooding capacity might be sufficient for the conception of a fractionation column, there are some points that present a flooding capacity that is 6 times lower than the value expected using equation (4.6). Furthermore, the shape of the flooding diagram is not in agreement with experimental results at lower pressures, as can be seen in Figure 4.5. Since most models were developed from data at low pressures, their predictions are also not in agreement with the tendency presented in this flooding diagram. In order to shed some light into the source of these discrepancies it may prove useful to analyze the influence of some other physical properties on the flooding capacity. In the following sections, the influence of the viscosity, interfacial tension, wettability and holdup will be discussed to better understand the source of these discrepancies.

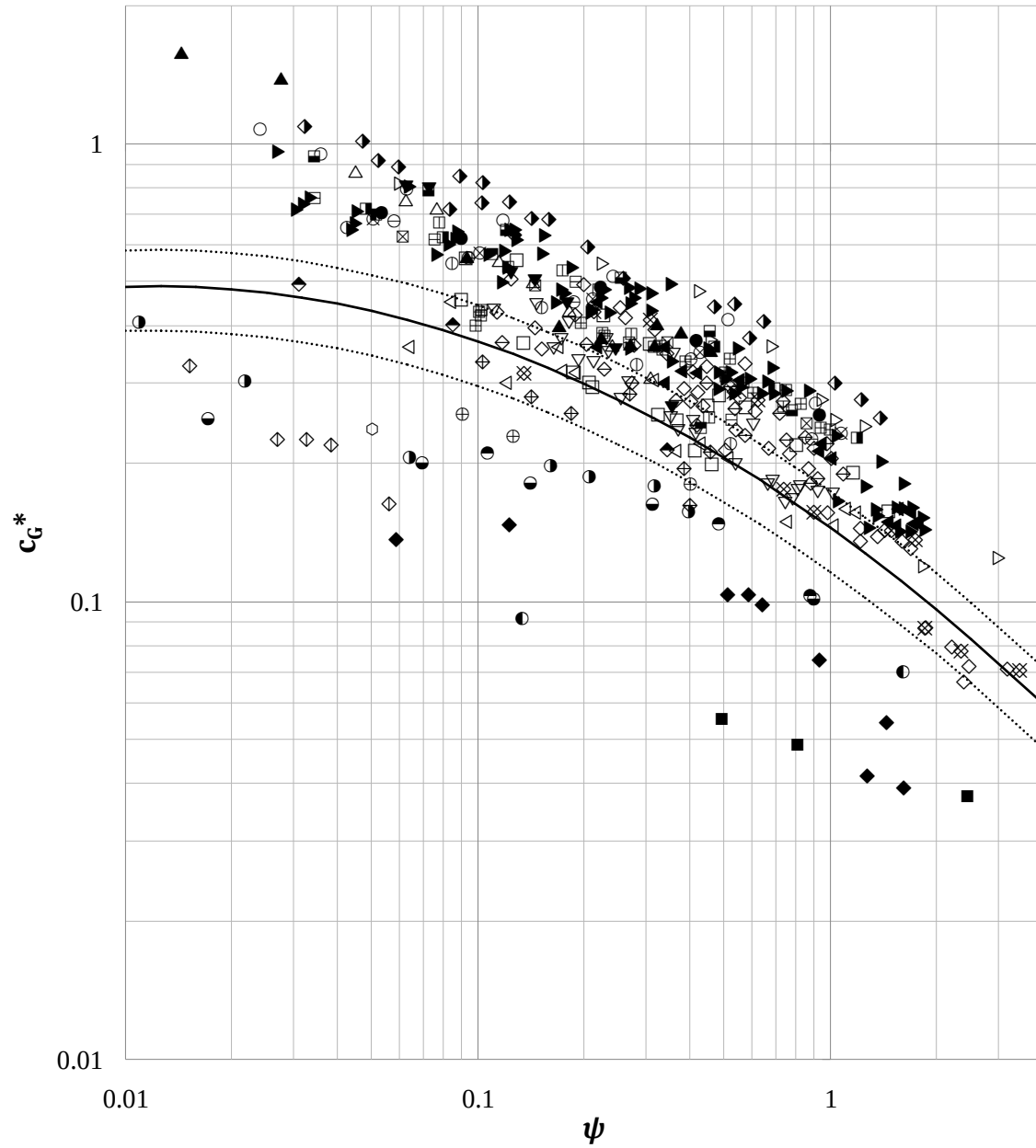


Figure 4.5: Comparison between the flooding correlation of Sherwood (according to the equations given by Piché *et al.* [6]) and the experimental flooding points under supercritical conditions. Dashed lines represent a 30% interval. The viscosity used for the Sherwood correlation is 1 mPa.s.

Table 4.1: Experimental conditions, packings, systems and symbol reference for Figure 4.4.

Reference	Feed	Packing	Temperature / K	Pressure / MPa	Number of points	Symbol
[10]	Orange peel oil	Sulzer EX	323	8.3	4	☒
				9	5	☐
				9.3	4	☐
				9.5	2	■
			333	10	5	■
				10.9	6	■
				11.2	3	■
			343	10.7	5	●
				12.4	7	○
				13	3	⊕
[11]	90.4% Ethanol / 9.6% Water	Sulzer EX	333	10	5	⊗
	80.1% Ethanol / 19.9% Water				5	⊖
	69.6% Ethanol / 30.4% Water				5	⊕
	56% Ethanol / 44% Water				3	●
	50% Ethanol / 50% Water				7	◐
	44.6% Ethanol / 55.% Water				5	◑
	19.5% Ethanol / 80.5% Water				2	◑
[1]	Corn seed oil	Sulzer EX	323	20	10	▲
			373		8	△
			393		7	▼

Table 4.1 (continuation) Experimental conditions, packings, systems and symbol reference for Figure 4.4.

Reference	Feed	Packing	Temperature / K	Pressure / MPa	Number of points	Symbol
[5]	Olive oil deodorizer distillates	Berl Saddles	313 - 343	8.2 - 18	26	▽
	Water		313 - 373	20	16	◀
	Olive oil deodorizer distillates	Raschig rings	313 - 343	8.2 - 18	14	◁
	Water		313 - 373	20	69	▶
	Olive oil deodorizer distillates	Sulzer EX	313 - 343	8.2 - 18	10	▷
	Water		313 - 373	20	9	◆
	Sulzer CY	40			◇	
[12]	Water	Gauze packing	323	11.4 - 17.1	7	⊞
				22.9	3	■
	Hexadecane		313 - 333	8 - 17.3	19	□
[2]	“Toco”	Sulzer CY	333 - 353	16 - 28.5	21	⊞
	Water - Triton-X-100		313 - 373	8 - 30	12	⊞
[13]	Squalene-Tocopherols-Sterols	Sulzer CY	323 - 393	20 - 30	17	◇
[14]	Crude Palm Oil	Sulzer EX	-	-	5	◇
[15]	Terpenes	Sulzer EX	333	11.3	3	◆
				10.1 - 11.1	21	◀
This work	11.2% Ethanol / 88.8% Water	Interpack VFF	333	10.1	1	⬡

4.4. The liquid viscosity

In order to compensate for the effect of the liquid viscosity, Sherwood et al. [3] introduced an empirical correction factor. Based on his work, let us introduce a corrected dimensionless capacity factor (c'_G):

$$c'_G = u_{GF} \sqrt{\frac{\rho_G}{\Delta \rho} \frac{F_p}{g}} \left(\frac{\mu_L}{\mu^\circ} \right)^{0.1} \quad (4.7)$$

where μ° is a reference viscosity of 1 mPa s (1 cP).

Unfortunately, liquid viscosity values for most of the systems studied are not available. Minimum and maximum liquid viscosity values are given by Stockfleth and Brunner regarding their experiments using water and Olive Oil Deodorizer Distillates (OODD) [5]. Even if only a mean value was used in the construction of Figure 4.6, it is clear that the viscosity correction improves the correlation between water and OODD flooding capacities.

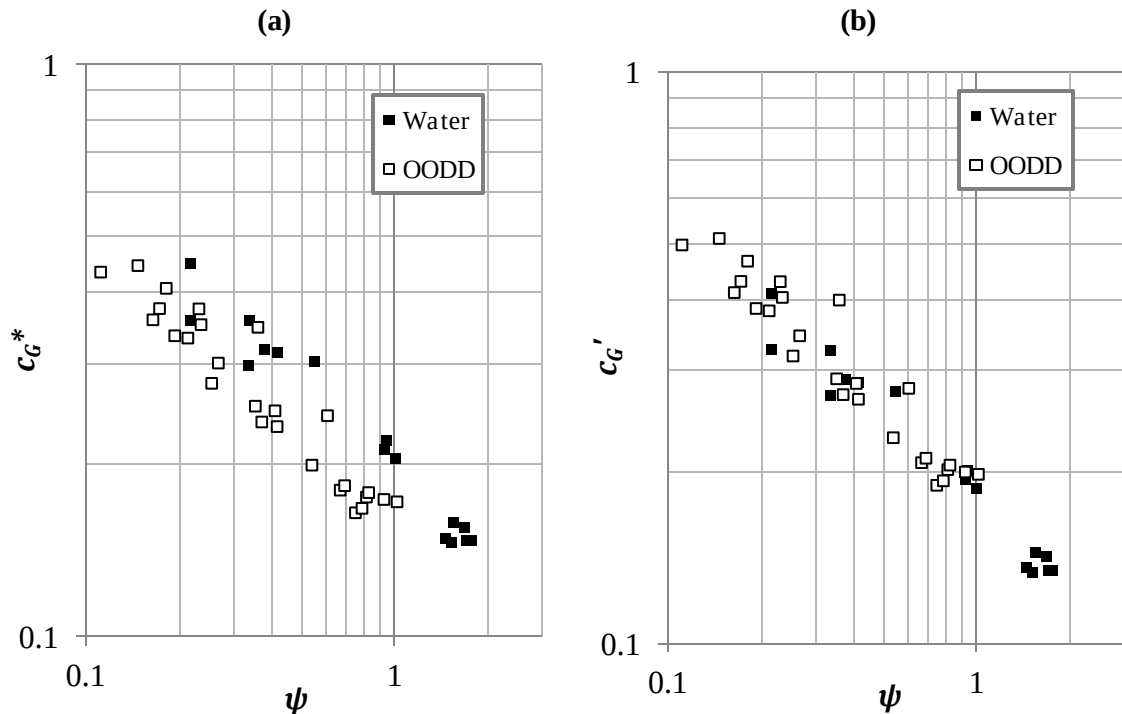


Figure 4.6: Dimensionless flooding capacity (a) and corrected flooding capacity (b) for Berl saddles using water and Olive Oil Deodorizer Distillates.

Nonetheless, the small exponent in the correction factor implies that using the corrected capacity values is only a marginal improvement for most systems. For this parameter to be able to compensate for the most extreme point deviations, the viscosity of the liquid should be in the order of 60 million times larger than water.

4.5. The interfacial tension

The effect of the interfacial tension in the flooding capacity at supercritical conditions is hard to assess. The interfacial tension values in supercritical fractionation are generally much lower than at normal pressure and vacuum processes. There are several different effects that need to be addressed in order to fully appreciate the possible influences of these lower values.

The effect of interfacial tension in gas-liquid contactors is somewhat debatable. Sherwood [3] found no influence of the interfacial tension in non-foaming systems. Later work by Leva et al. [16,17], Lobo et al. [4], Takahashi et al. [18] and Billet and Schultes [7] did not take the interfacial tension into account. Particularly, Billet and Schultes had access to mass transfer experiences from distillation studies up to 3 MPa and they state that a minimum value of 30 mN m^{-1} should be used for all calculations. According to them, for lower interfacial tension values the packing is fully wet and further reducing the interfacial tension has no effect on mass transfer rates.

On the other hand, a reduced flooding capacity is predicted for low interfacial tension systems according to the model of Maćkowiak [8], based on the suspended-droplet-bed. Since the mean droplet size is estimated to be proportional to the square root of the interfacial tension, lower interfacial tension values give place to smaller drops which are more easily entrained. In this case, the flooding capacity is expected to be proportional to the eighth root of interfacial tension.

In the case of liquid-liquid systems, the opposite tendency appears. The Dell and Pratt correlation (as presented by Raja Rao and Ventaka Rao [19]) predicts an increase in the flooding capacity for low interfacial tension systems. Rearranging the equation, one can find the following expression:

$$c_G^* = \frac{C \sigma^{-0.125}}{\left(1 + m \psi^{\frac{1}{2}}\right)} \quad (4.8)$$

where C and m are system-dependent constants. In this case, it is clear that lowering the interfacial tension increases the flooding capacity of the system. Furthermore, the Crawford and Wilke correlation modified according to Watson et al. (as reported by Koncsag and Barbulescu [20]) can be rearranged in the following manner:

$$c_G^* = \frac{C \sigma^{-n}}{\left(1 + m' \sigma^{-0.25} \psi^{\frac{1}{2}}\right)^2} \quad (4.9)$$

where n varies between 0.4 and 0.6 depending on the properties of the liquids. From equation (4.9), it can be deduced that low interfacial tensions have a clear positive effect for low flow parameter values while their effect is negligible at high flow parameter values.

At this point, supercritical fractionation appears to be more in line with the tendencies presented in liquid-liquid systems. Having a much lower interfacial tension than conventional gas-liquid systems their capacity is somewhat higher, notably at low flow parameter values. This effect could explain the deviations from the tendency predicted by the Sherwood equation (Figure 4.5). Nonetheless, the extremely low flooding values remain unexplained.

An interesting study case is the dependence of the flooding capacity of a Sulzer EX packing for the fractionation of ethanol/water mixtures with carbon dioxide as reported by Budich and Brunner [11]. The corresponding flooding diagram is presented in Figure 4.7. The flooding capacity of the Sulzer EX packing diminishes rapidly as the

water content in the liquid phase increases. The same tendency can also be found in the results presented in the previous chapter (Section 3.4.1.3, page 91). As already stated, viscosity variations are not sufficient to explain this result. On the other hand, the interfacial tension varies hugely from ethanol/CO₂ to water/CO₂. According to Sun and Shekunov [21], the interfacial tension of pure ethanol in contact with CO₂ equilibrated with ethanol is around 1 mN m⁻¹ at 333 K and 10 MPa. Sutjiadi-Sia [22] gives a value of 32 mN m⁻¹ for pure water at the same conditions. If the influence of the interfacial tension is well represented by equation (4.9) the flooding capacity of ethanol/CO₂ should be 4 to 8 times greater than that of the water/CO₂ system at low flow parameter values.

Another factor to take into account is the fact that ethanol wets stainless steel perfectly at these conditions (the contact angle fades to zero) while water does not wet stainless steel (the contact angle is around 120°) [22]. The effect of the wettability is discussed in the following section.

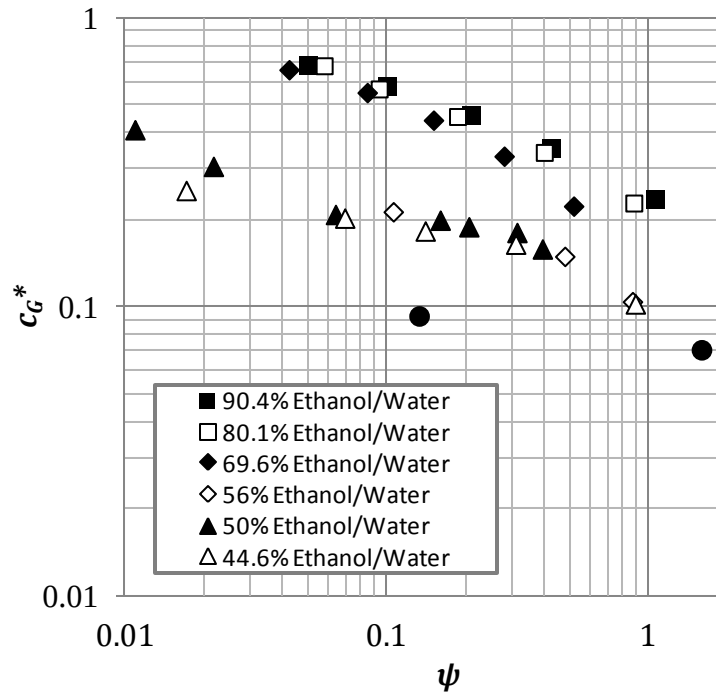


Figure 4.7: Flooding capacity of a Sulzer EX structured packing at 333K and 10 MPa as a function of the flow parameter and the ethanol mass fraction in the liquid.

This is an interesting lead, but not a definitive conclusion. For instance, the flooding capacity values for the water/CO₂ system using a Sulzer CY packing are in good agreement with those obtained with corn seed oil even though the interfacial tension values are greatly different [23]. Sulzer CY packings have a lower surface area, higher void fraction and greater clearance between sheets than EX packings. This result could shed some light into the mechanism that reduces the flooding capacity.

4.6. The liquid holdup

A rapid analysis of the points that shown important deviations in Figure 4.4 would indicate that they all correspond to studies performed on a Sulzer EX and gauze packing, except for the one presented in this work; which could imply that the phenomenon behind this deviations is only present in structured packings.

However, if the flooding capacity values for Raschig Rings would have been calculated using their geometrical surface area, all values would have been reduced by half, placing those points below the general tendency. Instead, for the calculation of the flooding capacity the surface area values were taken from Stockfleth and Brunner [5]. In their work, they calculate a corrected surface area value of 3365 m² instead of 900 m² in order to take into account the restrictions imposed on the gas flow by gussets and dead volumes filled with liquid. In other words, this higher surface area value compensates for the reduced void fraction and increased static liquid holdup introduced by the particular geometry of the Raschig Rings.

In their hydrodynamic study of a countercurrent column for supercritical fractionation, Stockfleth and Brunner [5] assumed the static holdup to be negligible due to the low interfacial tension values. They present a correlation developed by Blas and Kurtz for Raschig Rings (equation (4.10)). It should be pointed that the correlation predicts a holdup around 0.032 while their measured dynamic holdup values for

Raschig Rings are in a range between 0.04 and 0.2. In this correlation, the static holdup is linked to the Bond number, as defined in equation (4.11).

$$\frac{h_{stat}}{\varepsilon_b} = \frac{0.037}{Bo^n} \quad (4.10)$$

$$n = \begin{cases} 0.07 & \Leftrightarrow Bo < 1 \\ 0.65 & \Leftrightarrow Bo \geq 1 \end{cases}$$

$$Bo = \frac{\rho_L g}{\sigma a^2} \quad (4.11)$$

If the same correlation is valid at high pressure, the static holdup in the water/CO₂ system will be much higher than for the ethanol/CO₂ system, as shown in Table 4.2.

Table 4.2: Estimation of the liquid holdup for Raschig Rings using different systems at 10 MPa and 333 K.

		Water/CO ₂	Ethanol/CO ₂
Specific surface area	a	900 m ⁻¹	
Void fraction	ε_b	0.82	
Liquid density	ρ_L	1247 kg m ⁻³	830 kg m ⁻³
Interfacial tension	σ	32 mN m ⁻¹	1 mN m ⁻¹
Bond number	Bo	0.472	10.05
Static holdup	h_{stat}	0.032	0.0068

On the other hand, the dynamic holdup values of Stockfleth and Brunner [5] appear to be lower for water than OODD for the Sulzer EX packing. The wetting capacity of the liquid might play a substantial role in this behavior, since water might not wet stainless steel at the studied conditions [22].

For vacuum and atmospheric pressure applications, it is generally recommended to choose a packing well wetted by the liquid feed since the spread of the liquid is supposed to increase the contact area between the gas and liquid [24]. Hence, the flooding capacity of non-wetting systems has received little attention. Some studies have found the flooding capacity of non-wetting systems to increase due to the lower liquid holdup [25]. The opposite tendency is depicted by the ethanol/water/CO₂ system

in Figure 4.7, although, as already mentioned, the loss of capacity at low ethanol contents might be related to the increase in interfacial tension.

Also, although the dynamic holdup might be lower for the water/CO₂ system, it increases much more rapidly as a function of the pressure drop. In general, the holdup increases much faster for water/CO₂ system than for OODD/CO₂. This effect is even more pronounced for the Sulzer CY than EX packing. Although the former presents a higher holdup it appears to be able to better cope with this increase and thus presents a higher flooding capacity.

4.7. The hydrodynamic stability

Dankworth and Sundaresan [26] presented a stability analysis of a countercurrent packed column based on models developed for a concurrent flow regime. They found that the flooding capacity could be reduced by an excessive accumulation of liquid in the bottom of the column. Under such condition, a rapid accumulation of liquid would propagate from the bottom of the column towards the top.

This description is in line with the observations of Stockfleth and Brunner [2] who reported that flooding originated at the bottom of the packing for flow parameters lower than 0.4. It also agrees with the observation of Budich and Brunner [11] who found that flooding occurred well under the maximum capacity of the column if the raffinate was projected towards the packing. Furthermore, it explains our own results in which a couple of damaged packing elements could drastically reduce the overall capacity of the industrial-scale column used.

Fourati et al. [27], using tomographic measurements, detected an increased liquid holdup at the juncture between elements of a Mellapak 250.X structured packing. In conjunction with an overall increased holdup for the reasons stated in the previous

section, this holdup might be high enough to reach the unstable holdup limit, thus initiating an early flooding.

This early flooding condition might be stimulated by non-wetting of the packing and a lesser dispersive effect of the liquid interfacial tension, but also from pulsed liquid or solvent flow. This hydrodynamic instability might be the cause for the superior flooding capacity of an automated column compared to a non-automated one, as reported by Fleck et al. [28].

4.8. Conclusions

A flooding correlation between the flooding and capacity factor has been proposed based on literature data. The differences between this correlation and normal pressure correlations such as the correlation by Sherwood et al. may be explained by the extremely low interfacial tension values found in supercritical fractionation. This new correlation should be accurate enough for dimensioning purposes. Nonetheless, at present, it is recommended to carry out some flooding capacity measurements at least to exclude the possibility of early flooding and reduce incertitude on the flooding point determination.

Finally, the phenomenon originating early flooding problems has been discussed and a more profound study of the early flooding phenomena should be addressed. Further studies should address the effect of the wetting capacity of the liquid, but also of the interfacial tension, especially from a holdup and stability point of view. The use of a single packing type with different surface treatments should help understanding the effect of wetting. The use of foaming agents to study the effect of the interfacial tension should be avoided, since the surface agent could be affected by the supercritical phase. Instead, it is proposed to study the flooding point of different mixtures of water and alcohols in order to assess the effect of the fluids wettability, density, viscosity and interfacial tension. Finally, a larger number of packing elements should be studied. Structured packings represent more than two thirds of our database and may not be well suited for low interfacial tension systems. Also, most of the data for random packings comes from Raschig rings and Berl saddles, which are first generation packings with lower performance than more recent packings.

4.9. References

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5. Fractionation of fish oil FAEEs

5.1. Introduction

The regular consumption of ω -3 fatty acids has been correlated to a reduced risk of cardiovascular diseases [1,2]. According to the World Health Organization, convincing evidence exists linking the consumption of EicosanoPentaenoic Acid (EPA) and DocosanoHexaenoic Acid (DHA) with reduced risk of cardiovascular diseases. In the light of these facts, there is interest in the purification of EPA and DHA as dietary supplements.

The principal source of these fatty acids is fish and particularly fish oil in which EPA and DHA are found as triglycerides. The enrichment of EPA and DHA in the form of triglycerides is unviable, mostly because of the quasi-random distribution of fatty acids in triglyceride molecules [3]. Hence, the oil has to be transesterified with methanol or ethanol to separate the different fatty acids as fatty acid methyl or ethyl esters (FAME and FAEEs, respectively).

Eisenbach [4] and Nilsson and Hudson [5] found that purification of EPA up to a mass fraction higher than 90% could be achieved in a semi-batch configuration, using supercritical carbon dioxide as a solvent and temperature gradients and pressure programming to extract the lighter components from a fish oil FAEE mixture. Nilsson and Hudson achieved EPA and DHA purities higher than 90 wt.% with yields over 70%, but the semi-batch nature of the procedure and the high solvent consumption (between 275 and 600 kg of CO₂ per kg of product) render the industrial application of the product too cumbersome and costly.

Fleck et al. [6] studied the continuous countercurrent fractionation of fish oil FAEEs at temperatures between 333 and 353 K and pressures between 14.5 and 19.5

MPa. They studied the flooding phenomena at an industrial-scale column (13.6 m high; 36 mm ID) and found the higher maximum capacity at 333 K and 14.5 MPa.

Riha and Brunner [7] studied the continuous supercritical fractionation process applied to the concentration of EPA and DHA ethyl esters at temperatures between 333 and 353 K and pressures between 6.5 and 19.5 MPa, and they found that the optimal conditions were 333 K and 14.5 MPa. They classified the different FAEEs present in the mixture into 5 pseudo-components as a function of the fatty acid chain length and used distribution coefficients obtained from phase equilibrium measurements. To represent the operation, they used an equilibrium-stage model that was solved using ASPEN+ software in conjunction with user-made modules. They found good agreement between their experimental and modeled concentration profiles along the column. They were also able to estimate a Height Equivalent to a Theoretical Stage (*HETS*) around 0.3 m for a Sulzer CY structured packing.

In this work, a series of experiences were conducted to determine the influence of the solvent-to-feed ratio in the fractionation of a mixture of fish oil FAEEs with supercritical carbon dioxide. The conditions were set at 333 K and 14.5 MPa and the solvent-to-feed ratio was varied from 24.1 to 105. The extract and raffinate flow rates were determined by weighting and their compositions were obtained by gas chromatography. In order to exploit these results, a simple approximation of the equilibrium stage model was developed. This approach reduces the workload and allows obtaining the characteristic parameters directly from the results of a series of experimental fractionation runs. The model is able to correlate satisfactorily the influence of the solvent-to-feed ratio on the yield and composition of the extract and raffinate, which are the most important variables for an economic analysis.

5.2. Material and methods

5.2.1. Materials

A mixture of fatty acid ethyl esters from fish oil was kindly supplied by Atelier Fluides Supercritiques (AFS, France). It was produced by transesterification of fish oil with ethanol using potassium hydroxide as a catalyst. This mixture is very complex, having been derived from a natural source. It mainly contains FAEEs, principally derived from EPA (26.24 wt.%), DHA (12.26 wt. %) and palmitic acid (12.27 wt.%).

5.2.2. Fractionation methodology

The laboratory-scale unit used for the fractionation of water-ethanol mixtures was modified in order to reduce the fluctuations of solvent inlet temperature and pressure detected while conducting other studies. A supplementary 1 L reservoir was placed after the solvent heater and an additional 4 m double tube exchanger was added before the column. Also, a 1.5 m tube coil inserted in a controlled temperature bath was used to regulate the temperature of the liquid feed.

All fractionation runs were carried out at a temperature of 333 K and at 14.5 MPa. For all experiments, the carbon dioxide mass flow was set at 12 kg h⁻¹ and solvent was recycled after extract recovery. The solvent-to-feed ratio was varied from 24.1 up to 105 by changing the feed flow rate between 0.084 and 0.551 kg h⁻¹.

At the time the fractionation runs were carried, the chromatographic analysis of the FAEE mixtures could not be performed. Hence, it was not possible to study the dynamic evolution of the composition of the extract and raffinate in order to assure steady-state conditions. As an alternative criterion, steady-state operation was assumed when the extract and raffinate flow rates were stable and their sum was in agreement with the feed flow rate. In order to do so, a Kern PCB 3500-2 balance (Germany) with an automatic acquisition system with a precision of 0.01 g was used. First, the feed flow

rate was measured at the beginning of the fractionation run using the automatic acquisition system to measure the feed weight every 30 seconds. Then, during normal operation, the masses of the extract and recovered raffinate were measured regularly by double weighting of the corresponding collector vessel. The typical runtime was 1.5 hours. At the end of the run, extract and raffinate samples were recovered in tinted glass bottles and blanketed with carbon dioxide. Samples were kept at -15°C to avoid degradation. All flow rates were obtained as the slope of the accumulated weight as a function of time, obtained by linear regression. Figure 5.1 shows this procedure applied to Experience 1 (Solvent-to-feed ratio = 24.1).

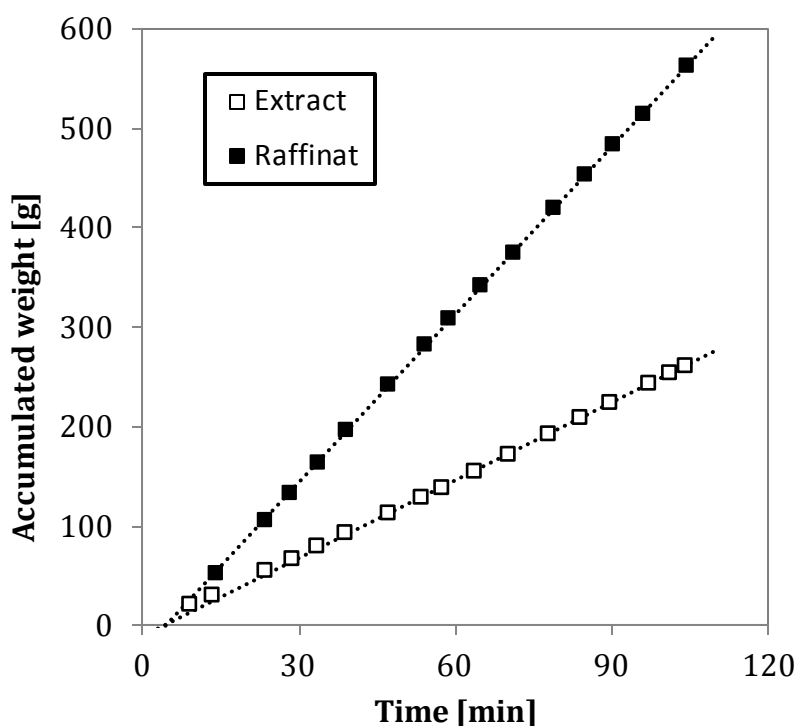


Figure 5.1: Accumulated weight of the extract and raffinate as a function of time and the linear regression used to determine its mass flow rate. Experience 1.

5.2.3. Chromatographic analysis

The determination of the composition of the samples collected was carried out by gas chromatography using a flame ionization detector (GC/FID) on a CP-3800 Varian Chrompack chromatograph (U.S.A.).

Helium supplied by Air Liquide (France) was used as the carrier gas with an inlet pressure of 20.5 psi, in order to provide a carrier velocity around 30 mm s^{-1} . A capillary fused silica OmegaWax 250 column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ film thickness) was used.

For each analysis, approximately 200 mg of the FAEE mixture to be analyzed were dissolved in 1 mL of hexane (HPLC grade, Fisher Chemical (United Kingdom)). For each run, 0.5 μL of this solution were injected with a split ratio of 50.

The injector temperature was set to 250°C , the oven temperature at 205°C and the detector temperature at 260°C . For the FID detector, the makeup flow was 25 mL min^{-1} , the hydrogen flow was 30 mL min^{-1} and the air flow was set at 300 mL min^{-1} .

5.3. Results and discussion

5.3.1. Overall mass balance

All experimental conditions and overall results are summarized in Table 5.1. It can be seen that overall mass balances were satisfactory since the biggest deviation is 4% with a 1.6% mean deviation. In Experiences 9 and 10, corresponding to the higher solvent-to-feed ratios, no raffinate was obtained.

Table 5.1: Summary of experimental conditions and results

Experience number	Mass flow rates /g min ⁻¹			(E+R)/Z	Ω	ε
	Z	E	R			
1	9.19	2.465	6.354	0.96	21.8	0.280
2	8.282	2.654	5.577	0.994	24.1	0.322
3	6.785	2.458	4.216	0.984	29.5	0.368
4	5.642	2.369	3.177	0.983	35.4	0.427
5	4.845	2.356	2.555	1.014	41.3	0.480
6	4.141	2.552	1.615	1.006	48.3	0.612
7	3.553	2.599	0.924	0.992	56.3	0.738
8	3.295	2.306	0.93	0.982	60.7	0.713
9	1.901	—	No raffinate	—	105	1
10	1.400	—		—	143	1

5.3.2. Solubility measurements

One of the major factors in determining the economic viability of a fractionation process is the solvent-to-feed ratio (Ω), as previously defined:

$$\Omega = \frac{S}{Z} \quad (5.1)$$

Both investment and operative costs will be strongly affected by this parameter.

The importance of the solubility comes from the fact that for a given solvent-to-feed ratio, the mutual solubility of the feed mixture and solvent will directly determine the extract yield (ε) and thus indirectly determine the fractionation efficiency. The extract yield is defined according to the following ratio:

$$\varepsilon = \frac{E}{Z} \quad (5.2)$$

In our fractionation runs the solvent-to-feed ratio was varied from 24.1 to 143. In the higher range, two runs (11 and 12) presented full feed entrainment by the solvent phase, i.e. no raffinate could be recovered and the extract flow rate matched the feed flow rate. For the rest of the runs, the extract yield varied linearly with the solvent-to-feed ratio, as shown in Figure 5.2. These results can be used in order to obtain the mutual solubilities of the FAEE mixture and carbon dioxide.

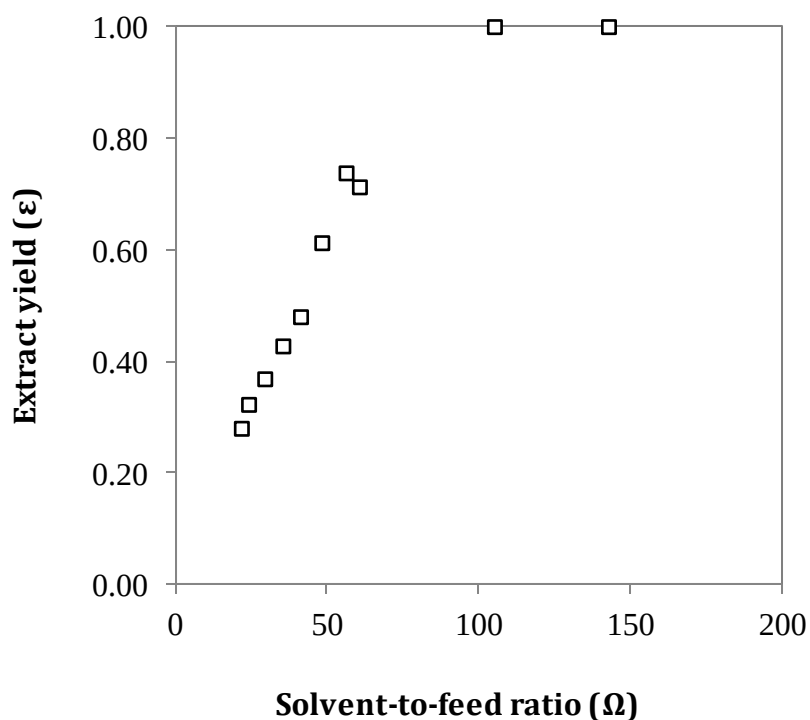


Figure 5.2: Extract yield as a function of the solvent-to-feed ratio for a fish oil FAEE mixture at 333 K and 14.5 MPa.

5.3.2.1. Ideal mixture assumption

A useful simplification is to consider that the FAEE mixture has an ideal mixture behavior. If this is the case, the overall FAEE solubility in the supercritical solvent will be constant and independent of the relative proportion of its components in the solvent.

Since the feed mixture is mostly composed of FAEEs, the primary interactions between the solute and carbon dioxide are van der Waals forces. Also, the quadrupole moment in carbon dioxide molecules will present some interaction with the polar ester groups and π -bond electrons in the case of unsaturated fatty acids. However, these interactions are weak and there is no reason to expect strong solute-solvent or solute-solute interactions in the lighter phase that could introduce a non-ideal mixture behavior.

It is possible to verify the consistency of this hypothesis with experimental results. First, let the mass balances for the FAEE mixture and the solvent be:

$$z = r_{FAEE} + o_{FAEE} \quad (5.3)$$

$$S = r_{CO_2} + o_{CO_2} \quad (5.4)$$

where z , r , o and S stand for the feed, raffinate, overhead and input solvent mass flows, respectively. Since a total recovery of FAEEs from the overhead is assumed, all the esters in the overhead will be recovered in the extract (e):

$$e = o_{FAEE} \quad (5.5)$$

If both the extract and raffinate are considered to be saturated then the solubility of the FAEEs in the solvent phase (s_{12}) and the solubility of the solvent in the FAEE mixture (s_{21}) it can be stated that:

$$s_{12} = \frac{e}{o} \quad (5.6)$$

$$s_{21} = \frac{r_{CO_2}}{r} \quad (5.7)$$

By combining these equations (Eq. (5.1) to (5.7)), the relation between the extract yield and the solvent-to-feed ratio becomes:

$$\varepsilon = \frac{s_{12}(1-s_{21})}{1-s_{12}-s_{21}}\Omega - \frac{s_{12}s_{21}}{1-s_{12}-s_{21}} \quad (5.8)$$

which is equivalent to:

$$\varepsilon = A\Omega - B \quad (5.9)$$

$$B = \frac{s_{12}s_{21}}{1-s_{12}-s_{21}} \quad (5.10)$$

$$A = \frac{s_{12}(1-s_{21})}{1-s_{12}-s_{21}} \quad (5.11)$$

This expression presents no further assumptions other than steady-state conditions and saturation of both raffinate and overhead currents. It is clear that the raffinate and overhead composition will vary as a function of the extraction rate (unless the solvent presents no selectivity, which is not the case as will be shown later). In the case of non-ideal mixtures, the coefficients A and B will vary as both solubilities are affected by the raffinate and overhead composition, describing a non-linear plot. Hence, the linearity of the extraction fraction as a function of the solvent-to-feed ratio implies that both A and B are constant. In that case the solubilities are constant, since:

$$s_{21} = \frac{B}{A+B} \quad (5.12)$$

$$s_{12} = \frac{A}{A+B+1} \quad (5.13)$$

To conclude, if the extract yield is a linear function of the solvent-to-feed ratio, then both the solvent solubility in the raffinate and the feed solubility in the solvent are independent of the composition, i.e. the feedmixture behavior is ideal.

Equations (5.12) and (5.13) allow computing the solubilities from Figure 5.2. In this case, the line with the best fit for the experimental points gives values of A and B of 0.01198 and -0.01726, respectively. This small and negative value of B has no physical significance, and will be discarded. When a zero value is imposed to B, the value of A giving the best fit for the data is 0.01237. The corresponding function is represented in

Figure 5.3. According to this value, 12.37 grams of FAEE per kg of carbon dioxide can be extracted. This corresponds to a negligible solubility of the solvent in the raffinate and to a FAEE solubility in the solvent of 0.01222.

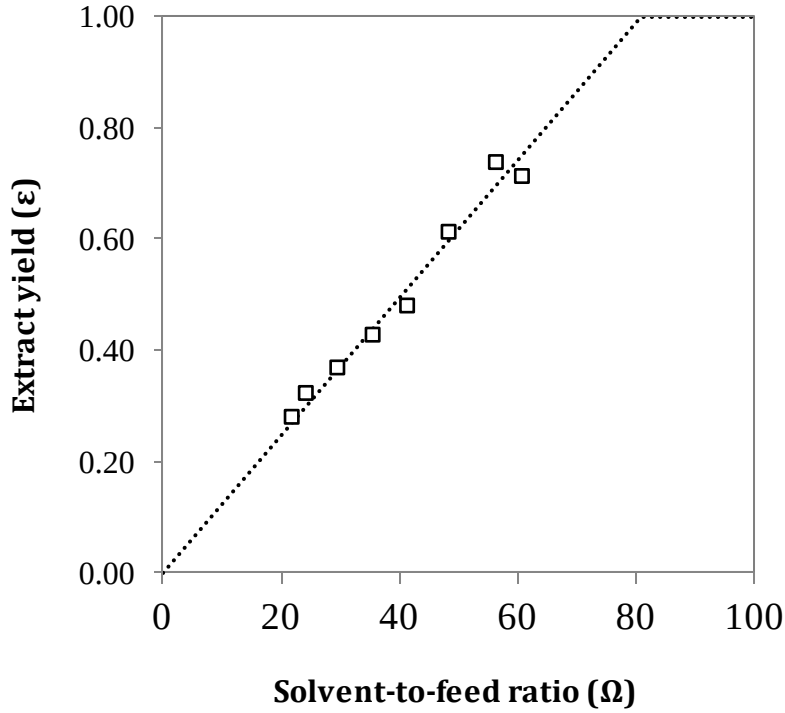


Figure 5.3: Extract yield as a function of the solvent-to-feed ratio for a fish oil FAEE mixture at 333 K and 14.5 MPa. The dotted line represents the line fitted line $\varepsilon = 0.01237 \Omega$. ($R^2 = 0.976$)

A useful corollary is that all the feed will be extracted for a solvent-to-feed ratio equal or higher than 80.86. The standard deviation between experimental points and the fitted curve is 0.027. Relative error values are given in Figure 5.4.

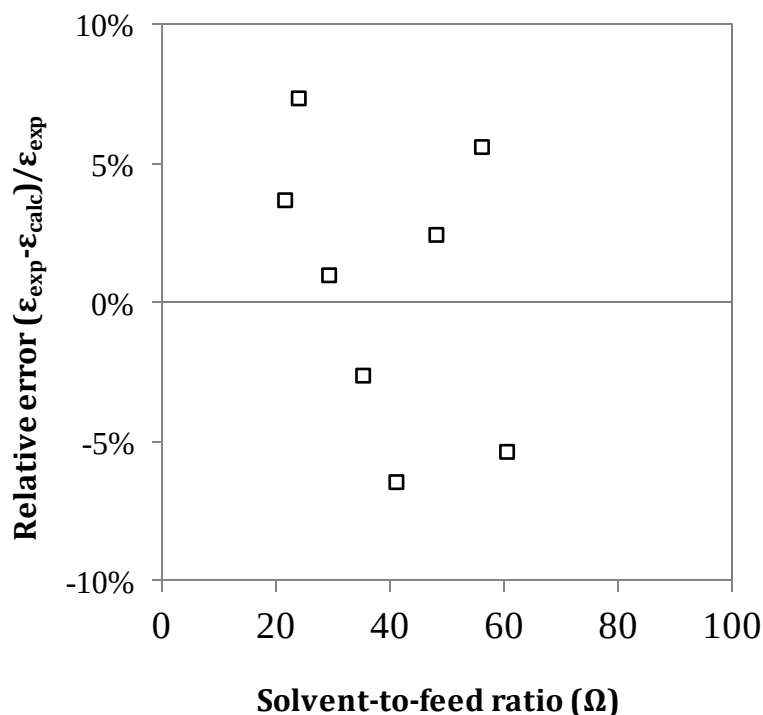


Figure 5.4: Relative error between experimental and calculated extract fraction values.

5.3.3. Product composition

5.3.3.1. Identification of the principal components

The use of a complex mixture with many unidentified products introduces many uncertainties in the interpretation of the obtained chromatograms. Although a handful of products with a known retention time were identified, a large quantity of peaks remains unknown. The eicosanopentaenoic ethyl ester (EPA-EE) was detected at 24.9 min with a carrier velocity around 30 mm.s⁻¹ and its retention time was taken as a reference. Eight components were identified according to their relative retention time, as presented in Table 5.2.

Table 5.2: Identified components of the FAEE feed mixture

Relative retention time (t_R)	Trivial name of the corresponding fatty acid	Lipid number	Surface area fraction in the feed
0.134	Myristic acid	14:0	2.91 %
0.206	Palmitic acid	16:0	12.27 %
0.340	Stearic acid	18:0	3.85 %
0.361	Oleic acid	18:1n9	9.45 %
0.590	Arachidic acid	20:0	0.76 %
1.000	Eicosanopentaenoic acid (EPA)	20:5n3	26.24 %
1.809	Docosapentaenoic acid (DPA)	22:5n3	1.88 %
1.952	Docosahexaenoic acid (DHA)	22:6n3	12.26 %

The identified components represent 69% of the total surface. The rest is distributed in lots of different components: up to 85 different compounds were found for the extract and raffinate. The fractionation process concentrates the components with a shorter aliphatic chain in the extract while the rest concentrates in the raffinate. Hence, it is easier to detect diluted components in the extract or raffinate than in the original feed mixture. For the following discussion, the surface area fraction of a component will be considered equal to its mass fraction. This assumption is justified in the Appendix A.

5.3.3.2. Verification of the steady-state assumption

Once steady-state operation has been established, the mass balance for each component i in the feed will be:

$$z_i = e_i + r_i \quad (5.14)$$

where z_i , e_i and r_i stand for the mass flow rate of component i in the feed, extract and raffinate respectively. Using solvent-free mass fractions, and the definition of the extract yield (Eq. (5.2)), this equation becomes:

$$X_i^Z = X_i^E \varepsilon + X_i^R (1 - \varepsilon) \quad (5.15)$$

The right hand term represents the overall composition of the product streams (X_i^*). Since the extract yield and all component concentrations are determined independently, a comparison between the feed and overall product composition can be

used to verify the steady-state assumption and quality of the chromatographic analysis. In order to focus the attention on the most important components, 24 compounds identified in the feed, extract and raffinate in all fractionation runs were selected. Such a plot is presented in Figure 5.5.

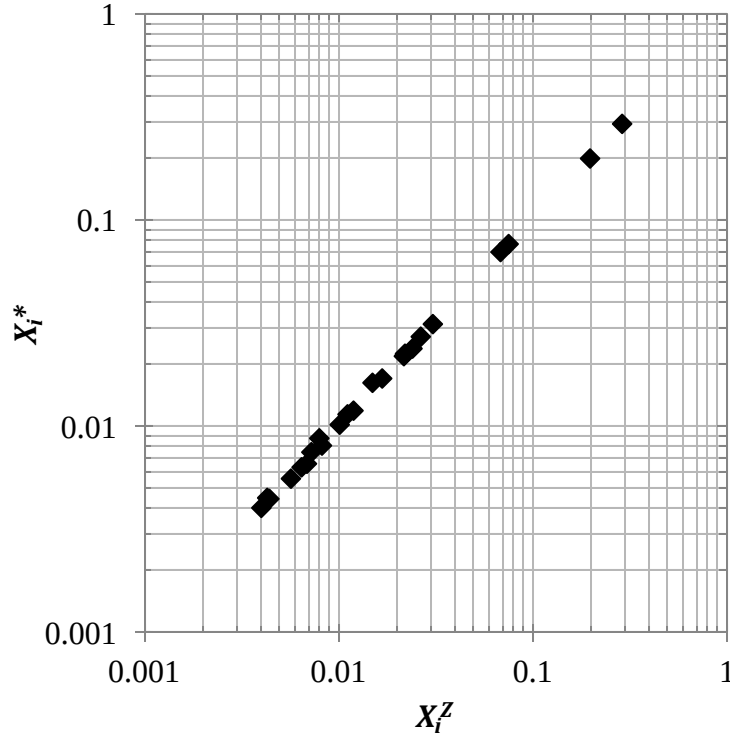


Figure 5.5: Comparison between the feed and overall mass fraction for 24 selected components in Experience 1 ($\Omega = 21.76$; $\varepsilon = 0.280$).

Figure 5.6 presents the relative error in the overall product composition against as a function of the product feed composition. As expected, the relative error is higher for the most diluted compounds.

Compared to the estimated analytical error obtained by comparison of duplicate analysis, the overall composition is equal to the feed composition within experimental uncertainty, thus validating the initial assumption of steady-state operation.

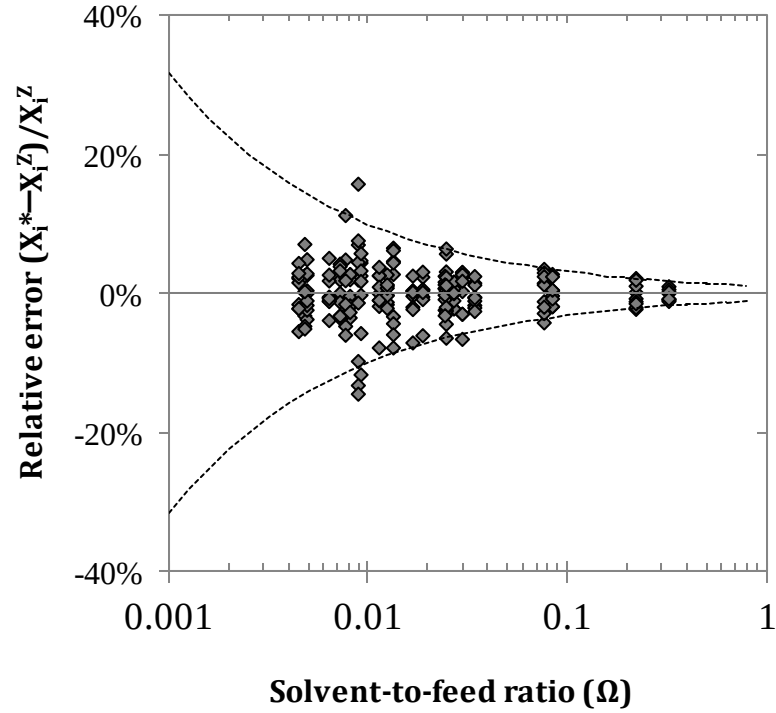


Figure 5.6: Relative deviation between the overall and feed mass fraction for 24 selected compounds and all experiences. The dashed line represents the uncertainty of the chromatographic analysis, determined between duplicate samples.

5.3.3.3. Modeling the extract and raffinate compositions

As already stated, the supercritical fractionation of FAEEs is of interest mainly for the concentration and purification of ω -3 FAEEs. However, as the proportion of ω -3 FAEEs increases in the raffinate, the selling price of the final product augments whereas the quantity decreases. Moreover, the quantity of solvent needed for the separation increases, which in turn will entrain higher running and investment costs. Under these conditions, an economic optimum will exist.

An equilibrium-stage model can be used to evaluate the evolution of the composition of the extract and raffinate as a function of the solvent-to-feed ratio in order to optimize the separation economic viability. In order to describe the operation, the distribution behavior of every component present in the feed is required. However, since several of the components in the feed are unidentified, a predictive approach based on literature data is not possible. Another parameter that cannot be asserted *a priori* for

this kind of separation is the number of theoretical stages of the column. Hence, a correlation approach is proposed, allowing us to determine these unknowns from experimental results.

5.3.3.3.1 Representing the equilibrium compositions

In this study, the relative selectivity between components was considered constant and independent of the overall liquid or vapor composition. Thus, the relation between the liquid mass fraction x and vapor mass fraction y of a component i can be expressed as:

$$Y_i = \frac{X_i}{\sum_j \left(\frac{X_j}{\alpha_{ij}} \right)} \quad (5.16)$$

where α_{ij} is defined as:

$$\alpha_{ij} = \left(\frac{Y_i}{X_i} \right) / \left(\frac{Y_j}{X_j} \right) \quad (5.17)$$

For a mixture of N components there are N^2 possible selectivity values but only $N-1$ are linearly independent since the others can be obtained from the following relations:

$$\alpha_{ii} = 1 \quad (5.18)$$

$$\alpha_{ik} = \alpha_{ij} \alpha_{jk} \quad (5.19)$$

$$\alpha_{ij} = 1/\alpha_{ji} \quad (5.20)$$

Equation (5.16) can also be written in terms of the distribution ratio K_i :

$$Y_i = \frac{K_i X_i}{\sum_j K_j X_j} \quad (5.21)$$

where

$$\frac{K_i}{K_j} = \alpha_{ij} \quad (5.22)$$

In this case, there are N distribution coefficients, but only the $N-1$ ratios between them are linearly independent. Hence, any single one can (and must) be chosen arbitrarily in order to determine the rest.

5.3.3.3.2 A simplified model based on the group method: advantages and drawbacks

The group method developed by Kremser and Edmister is a useful simplification over the rigorous stage-wise calculations on a countercurrent stripper or absorber [8].

First, an overall distribution ratio (K_i^*) is defined as the average of the distribution ratios in the column,

$$K_i^* = \bar{K}_i \neq f(X) \quad (5.23)$$

Then, the stripping factor (S_i) is defined as,

$$S_i = K_i^* \frac{V}{L} \quad (5.24)$$

where V and L represent the solvent-free vapor and liquid mass flow rates. By combining these definitions with the stage and overall mass balances it is possible to achieve an expression that relates the mass flow rate of a component i in the raffinate (r_i) with that in the feed (z_i) as a function of the stripping factor (S_i) and number of theoretical stages (n):

$$\frac{z_i}{r_i} = \frac{S_i^{n+1} - 1}{S_i - 1} \quad (5.25)$$

This equation should not be applied to a supercritical fractionation operation since it assumes that the solvent is already saturated when entering the column. In this work, a different expression was found (*cf.* Appendix B) by assuming that the injected solvent is pure (which is typically the case in supercritical fractionation):

$$\frac{z_i}{r_i} = \frac{S_i^{n+1} - 1}{S_i - 1} + \frac{\varepsilon}{1 - \varepsilon} S_i^n \quad (5.26)$$

where ε is the extract yield as defined in Eq. (5.2).

Also, since the vapor-to-liquid ratio (V/L) used is expressed in solvent-free basis, it becomes equal to the extract yield. Hence,

$$S_i = K_i^* \varepsilon \quad (5.27)$$

From these two expressions, the composition of the extract and raffinate can be readily computed for any given extract yield if the distribution coefficients and the number of theoretical stages are known. Reverse, these parameters can be obtained by fitting the model output to experimental data.

This approximate method is not perfect. Since the overall distribution ratios are taken as constant, the mass balance cannot close for all components. Let the stripping loss be defined as

$$\phi_{S,i} = \frac{r_i}{z_i} = \left(\frac{S_i^{n+1} - 1}{S_i - 1} + \frac{\varepsilon}{1 - \varepsilon} S_i^n \right)^{-1} \quad (5.28)$$

then,

$$\frac{r_i}{Z} = \frac{\phi_{S,i} z_i}{Z} = \phi_{S,i} X_i^Z \quad (5.29)$$

Taking the sum for all components,

$$\sum_i \frac{r_i}{Z} = \frac{R}{Z} = \sum_i \phi_{S,i} X_i^Z \quad (5.30)$$

Combining this equation with the overall FAEE mass balance (Eq. (5.3)):

$$1 - \varepsilon = \sum_i \phi_{S,i} X_i^Z \quad (5.31)$$

$$\sum_i \frac{\phi_{S,i}}{1 - \varepsilon} X_i^Z = 1 \quad (5.32)$$

Since the sum of all feed fractions is 1,

$$\sum_i \frac{\phi_{S,i}}{1 - \varepsilon} X_i^Z - \sum_i X_i^Z = 0 \quad (5.33)$$

Or alternatively,

$$\sum_i \left(\frac{\phi_{S,i}}{1 - \varepsilon} - 1 \right) X_i^Z = 0 \quad (5.34)$$

If the effective distribution coefficients are considered constant, the only way in which the equality would hold for every possible feed composition would imply that:

$$\frac{\phi_{S,i}}{1 - \varepsilon} - 1 = 0, \forall i \quad (5.35)$$

Hence,

$$\phi_{S,i} = 1 - \varepsilon \quad (5.36)$$

By definition of the stripping loss,

$$\frac{r_i}{z_i} = \frac{R}{Z} \quad (5.37)$$

Rearranging,

$$\frac{r_i}{R} = \frac{z_i}{Z} \Rightarrow X_i^R = X_i^Z \Leftrightarrow \begin{cases} X_i^R = X_i^E \\ \text{or} \\ \varepsilon = 0 \end{cases} \quad (5.38)$$

Hence, the model output can satisfy all mass balances for any feed composition if and only if there is no fractionation at all. Here lies the disadvantage of the group method: if the effective distribution coefficients are considered constant, the mass balance for each component cannot close. This does not mean that this simple model is without use, but care has to be taken in exploiting its results.

5.3.3.3.3 Calculating the extract and raffinate composition

If the stripping loss of the column is known, then by combining Eq. (5.15) and Eq. (5.29), the following result is achieved:

$$X_i^R = \frac{\phi_{S,i} X_i^Z}{1 - \varepsilon} \quad (5.39)$$

$$X_i^E = \frac{(1 - \phi_{S,i}) X_i^Z}{\varepsilon} \quad (5.40)$$

Given the discussion in Section 5.3.3.3.2, the sum of all mass fractions will not be equal to unity. Different expressions can be found by dividing Eq. (5.29) and Eq. (5.30):

$$X_i^R = \frac{\phi_{S,i} X_i^Z}{\sum_j \phi_{S,j} X_j^Z} \quad (5.41)$$

$$x_i^E = \frac{(1 - \phi_{S,i}) X_i^Z}{1 - \sum_j \phi_{S,j} X_j^Z} \quad (5.42)$$

These equations are better suited to model the interactions between multiple components, since the stripping loss of all components affect each component extract and raffinate composition.

5.3.3.3.4 Model application

The error distribution in the experimental data was assumed to be log-normal. Hence, the model parameters were obtained by minimizing the expression

$$f = \sum_{\forall i} (\ln(X_i^{exp}) - \ln(X_i^{mod}))^2$$

in which x_i represent both the extract and raffinate solvent-free mass fractions of 24 selected components and the rest of the compounds aggregated into a single pseudo-component.

The optimized distribution coefficients are given in Table 5.3. The best fitting number of theoretical stages is 3.5 (the best integer value is 4), which yields a Height Equivalent to a Theoretical Stage (*HETS*) of 0.57 m. This is somewhat greater than the value of 0.3 m obtained by Riha and Brunner [9], though they used a structured Sulzer CY packing and their experimental values varied between 0.15 and 0.6 m depending on the experience. A comparison between the experimental and modeled evolution of the mass fraction of the selected components in the extract and raffinate is presented in Figure 5.7.

As expected, the extract is enriched in the smaller chain compounds (from 14:0 up to 18:1n9) whereas the raffinate is mostly composed of longer chain (e.g. 22:5n3-EE and DHA-EE). Also, there is a certain fraction which is mostly unaffected unless at very high extract yields, which includes EPA-EE. The compromise between quantity and quality is evident. Concentrations of ω -3 FAEs in the raffinate as high as 71% could be achieved, but only with a raffinate yield lower than 0.25. The same can be told about

the extract, low extract yields produced an extract with high concentrations of miristic and palmitic acid ethyl esters. Although the conditions used were found to be satisfactory for the concentration and purification of DHA, EPA concentration was found to vary very little between the extract and raffinate.

Table 5.3: Distribution coefficients obtained by correlation of the experimental composition of the extract and raffinate as a function of the solvent-to-feed ratio

Relative retention time (t_R)	Reference Code	Corresponding lipid number	Feed mass fraction (X_i^Z)	Overall distribution coefficient (K_i^*)
0.134	C01	14:0	1.17%	3.423
0.206	C02	16:0	6.81%	2.328
0.221	C03		2.66%	2.412
0.256	C04		0.79%	2.261
0.262	C05		0.44%	1.819
0.279	C06		0.64%	1.989
0.361	C07	18:1n9	7.49%	1.526
0.368	C08		2.19%	1.488
0.410	C09		1.12%	1.528
0.446	C10		0.40%	1.299
0.492	C11		0.56%	1.455
0.534	C12		2.19%	1.540
0.591	C13	20:0	0.76%	0.852
0.627	C14		1.71%	0.901
0.644	C15		0.69%	0.897
0.721	C16		0.46%	0.932
0.823	C17		2.22%	1.019
0.940	C18		1.64%	0.926
1.000	C19	20:5n3	29.74%	0.980
1.102	C20		0.82%	0.535
1.364	C21		2.45%	0.783
1.601	C22		1.04%	0.659
1.809	C23	22:5n3	3.21%	0.633
1.954	C24	22:6n3	20.47%	0.643
Rest			8.32%	1.171

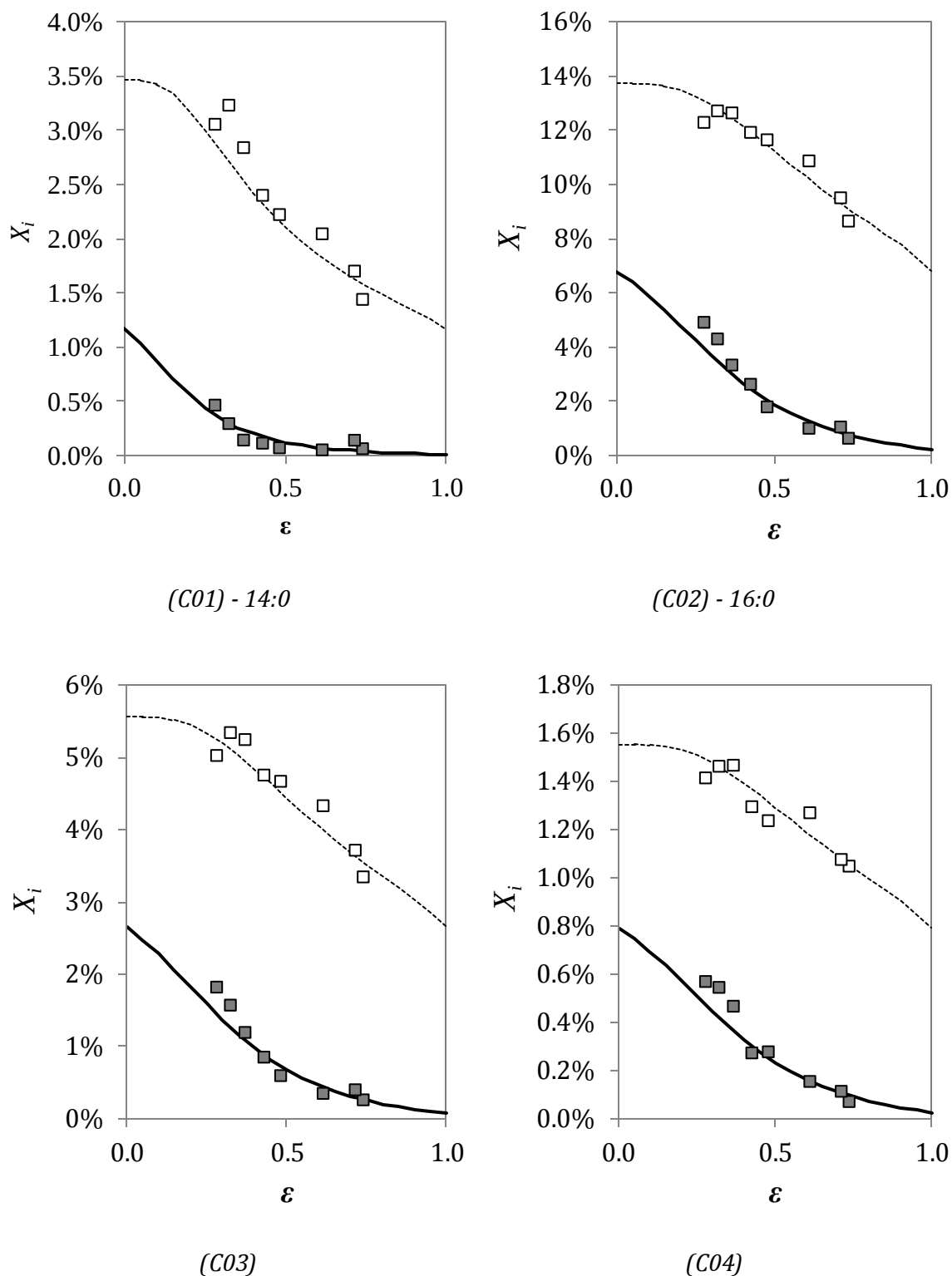


Figure 5.7: Evolution of the mass fraction of selected components in the extract and raffinate as a function of the extract yield. Model output is represented by a dashed (extract) and full (raffinate) lines. Squares represent the experimental extract (hollow symbol) and raffinate (full symbol).

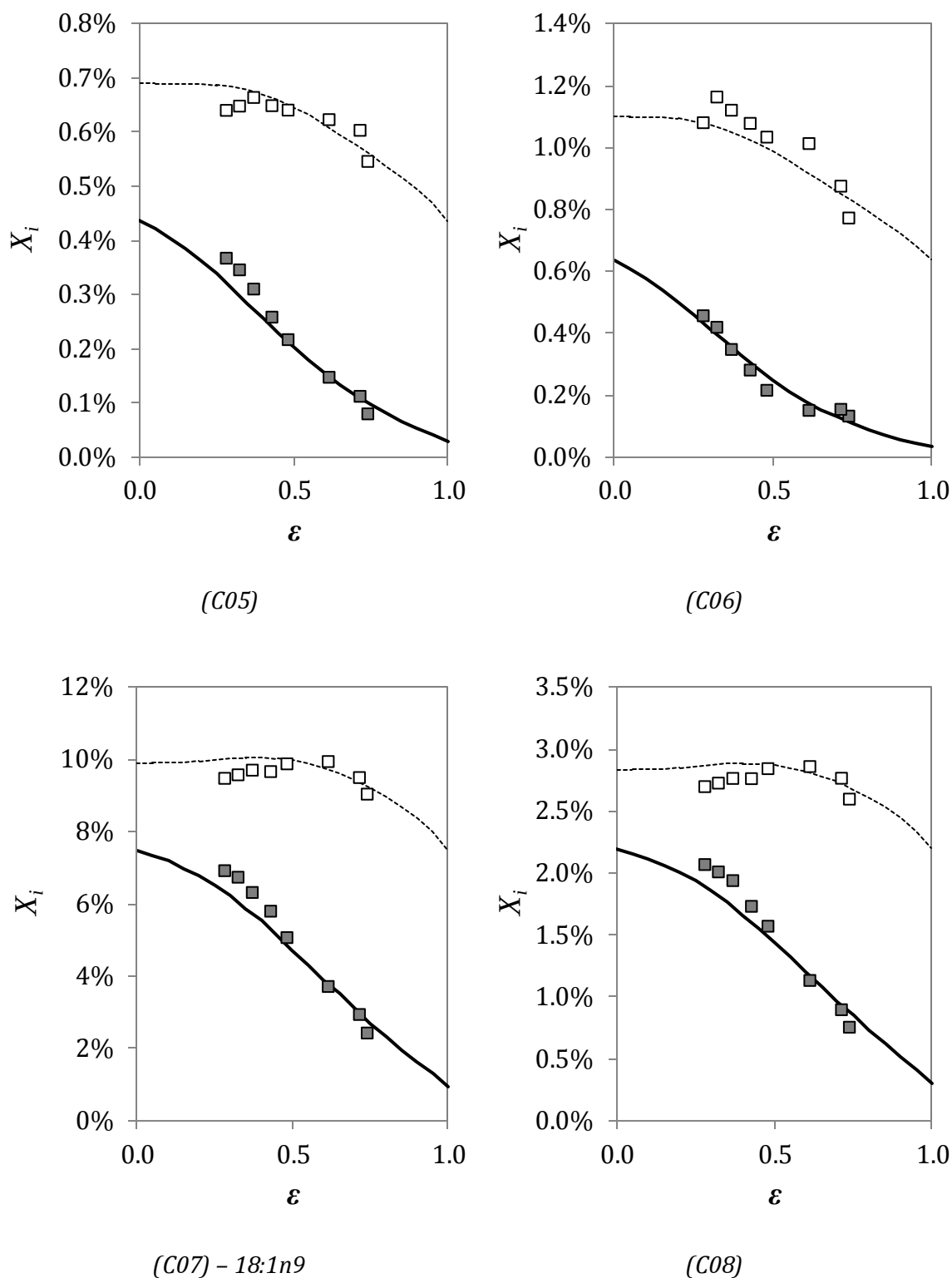


Figure 5.7 (continuation): Evolution of the mass fraction of selected components in the extract and raffinate as a function of the extract yield. Model output is represented by a dashed (extract) and full (raffinate) lines. Squares represent the experimental extract (hollow symbol) and raffinate (full symbol).

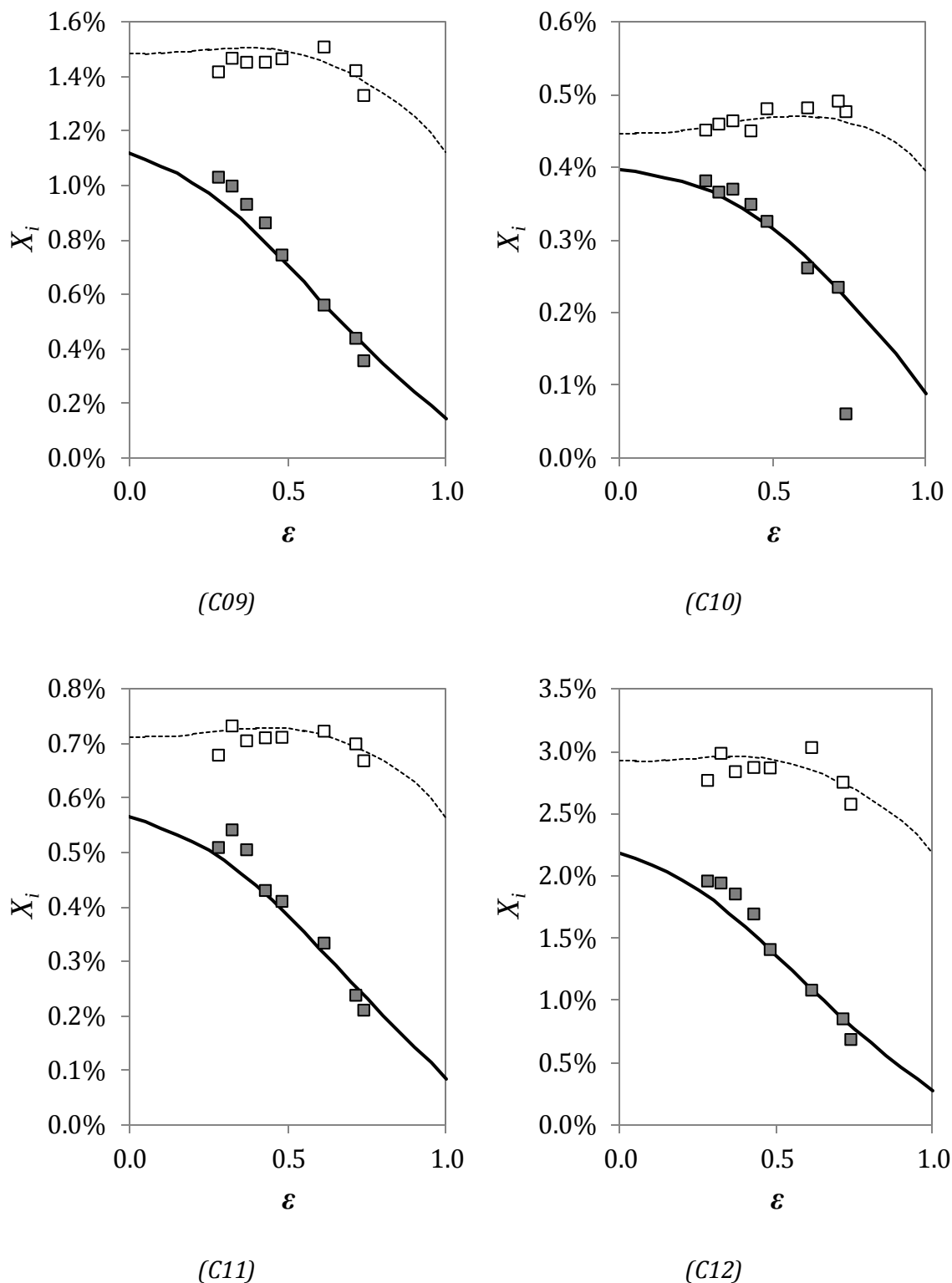


Figure 5.7 (continuation): Evolution of the mass fraction of selected components in the extract and raffinate as a function of the extract yield. Model output is represented by a dashed (extract) and full (raffinate) lines. Squares represent the experimental extract (hollow symbol) and raffinate (full symbol).

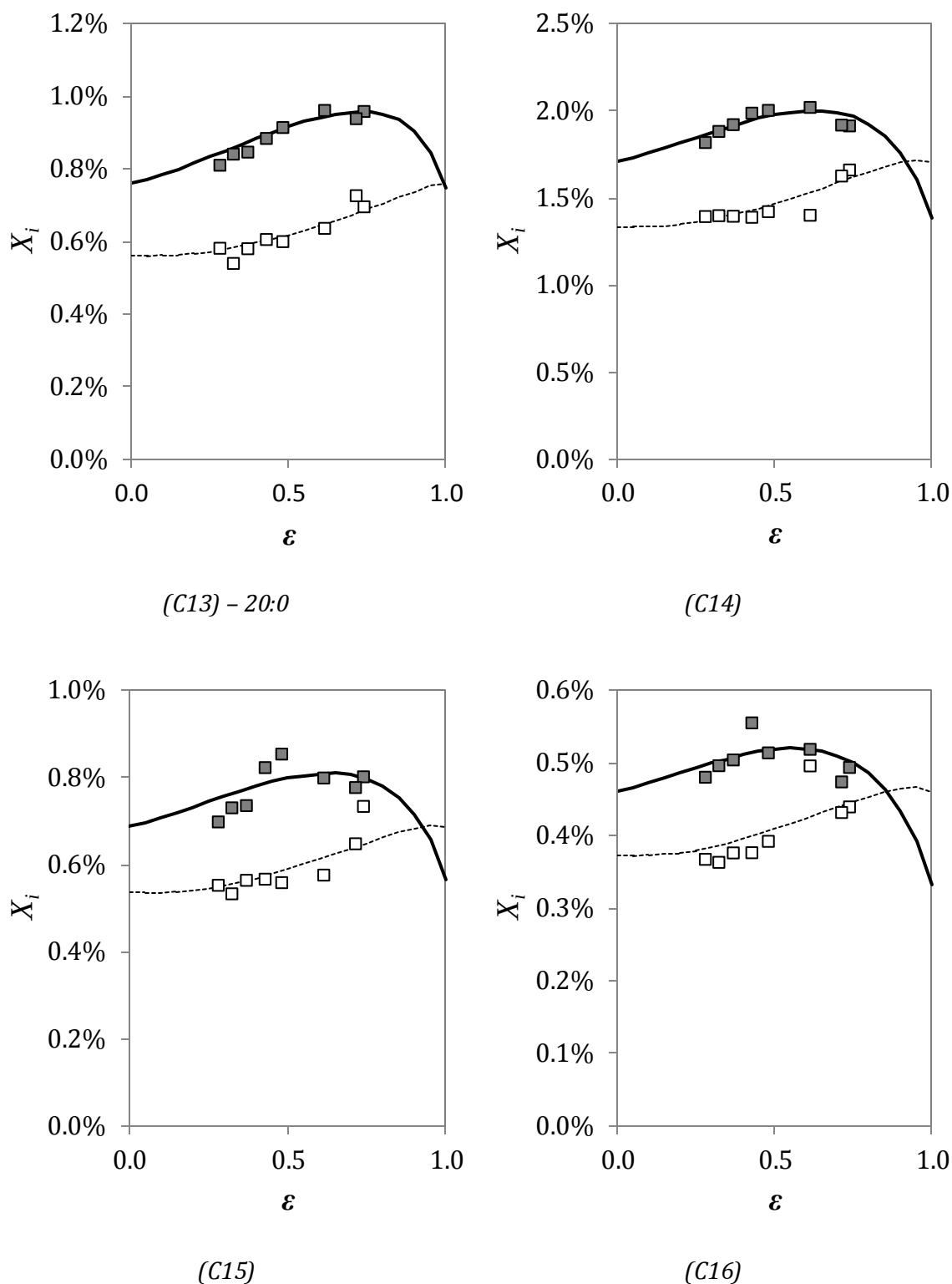
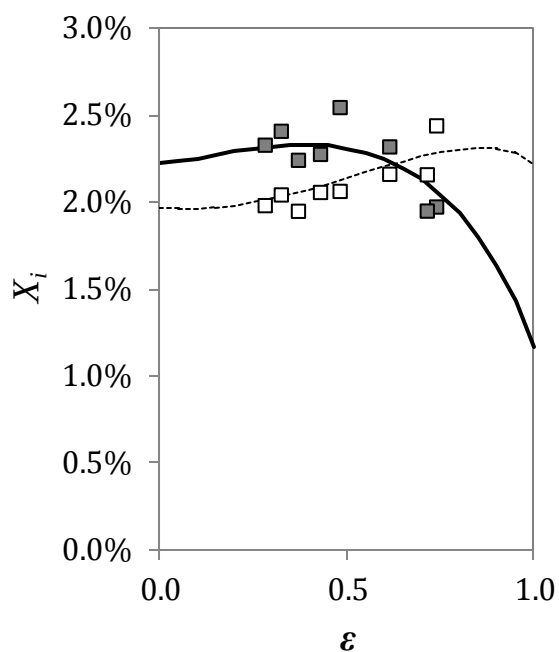
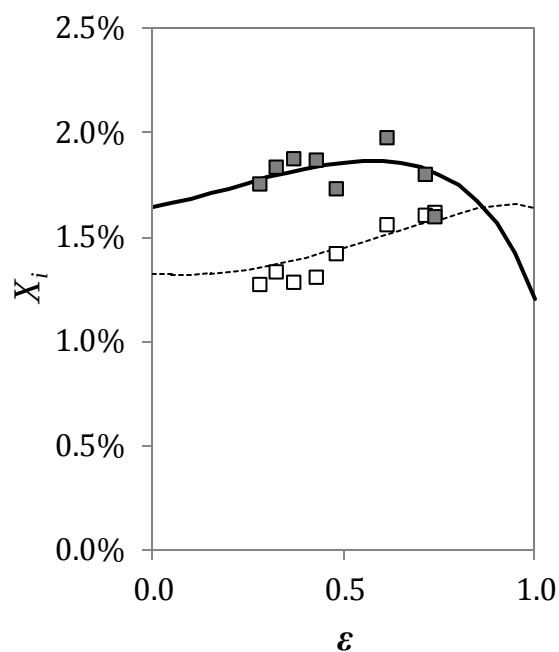


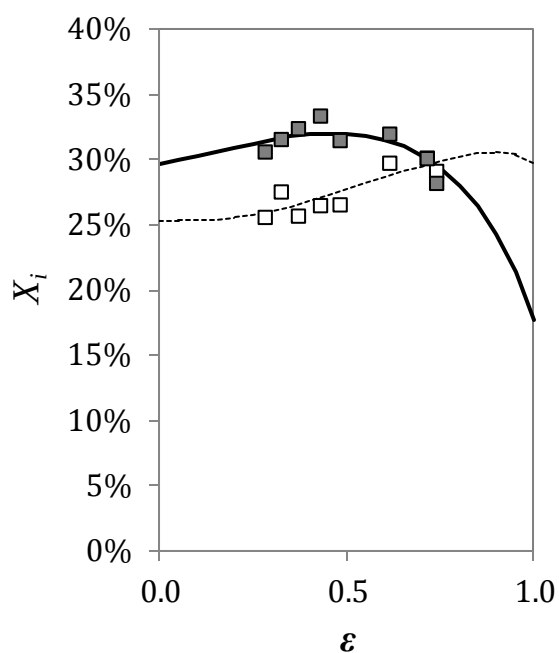
Figure 5.7 (continuation): Evolution of the mass fraction of selected components in the extract and raffinate as a function of the extract yield. Model output is represented by a dashed (extract) and full (raffinate) lines. Squares represent the experimental extract (hollow symbol) and raffinate (full symbol).



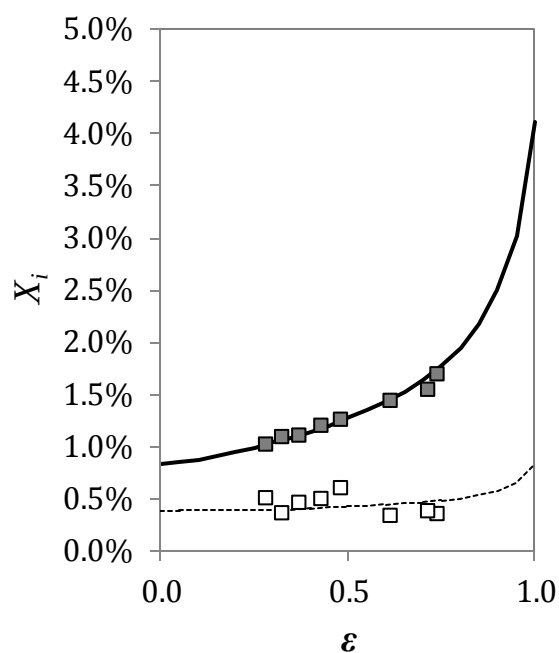
(C17)



(C18)



(C19) – 20:5n3 (EPA-EE)



(C20)

Figure 5.7 (continuation): Evolution of the mass fraction of selected components in the extract and raffinate as a function of the extract yield. Model output is represented by a dashed (extract) and full (raffinate) lines. Squares represent the experimental extract (hollow symbol) and raffinate (full symbol).

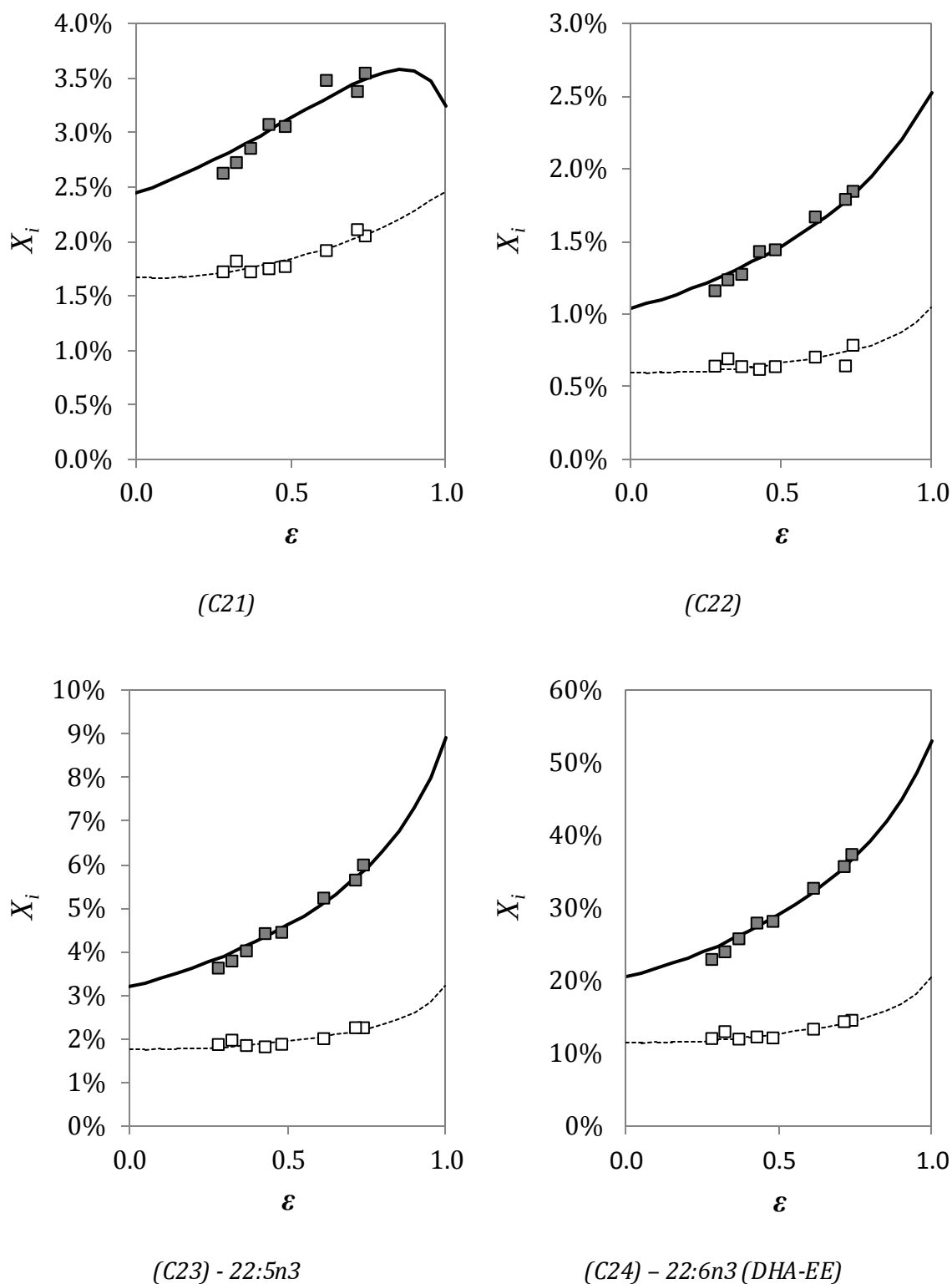


Figure 5.7 (continuation): Evolution of the mass fraction of selected components in the extract and raffinate as a function of the extract yield. Model output is represented by a dashed (extract) and full (raffinate) lines. Squares represent the experimental extract (hollow symbol) and raffinate (full symbol).

A correlation plot between the experimental and modeled values is presented in Figure 5.8.

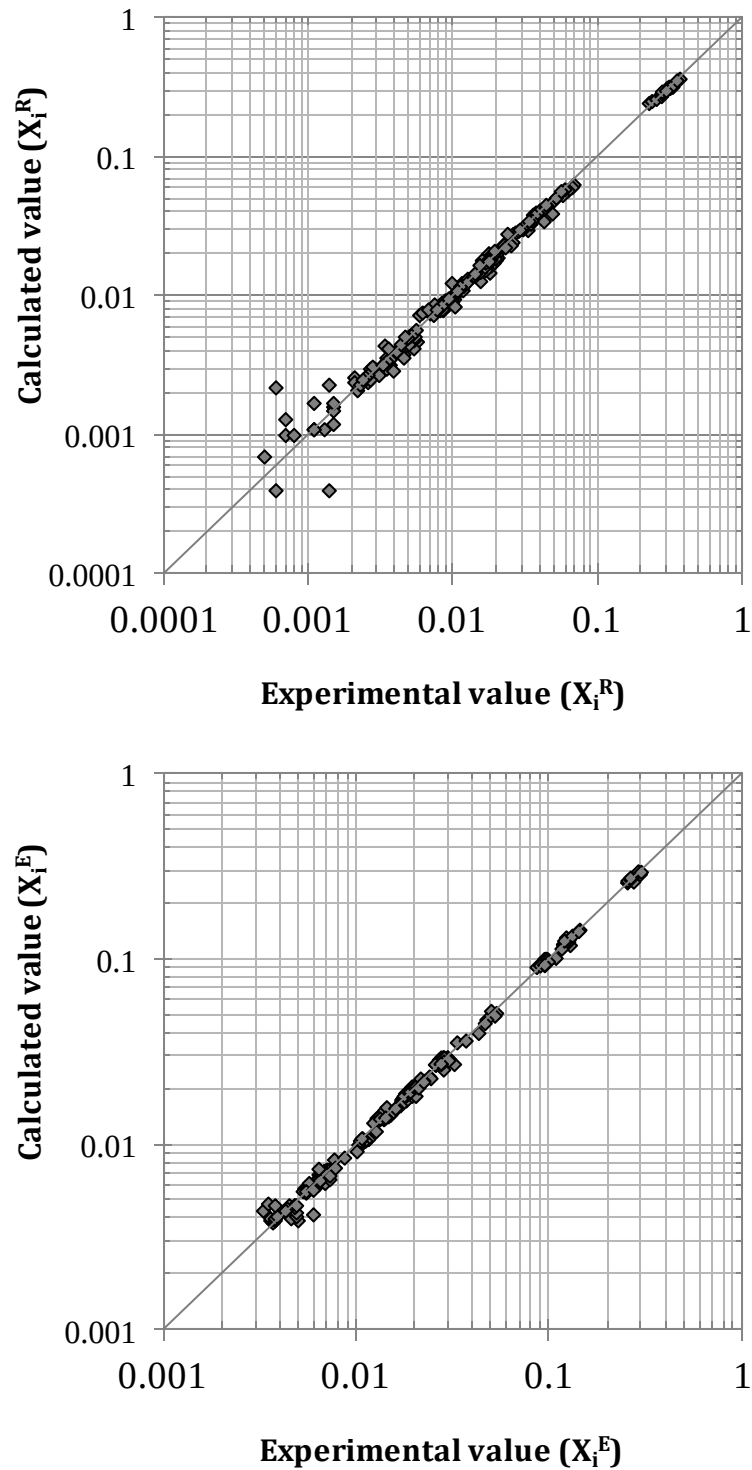


Figure 5.8: Correlation plot between experimental data and model output values.

Approximation error

A rigorous calculation can be done taking the fitted distribution coefficients from the approximate model and assuming that there are four theoretical stages. The relative error of the approximate model is under 4% for all compositions, as shown in Figure 5.9.

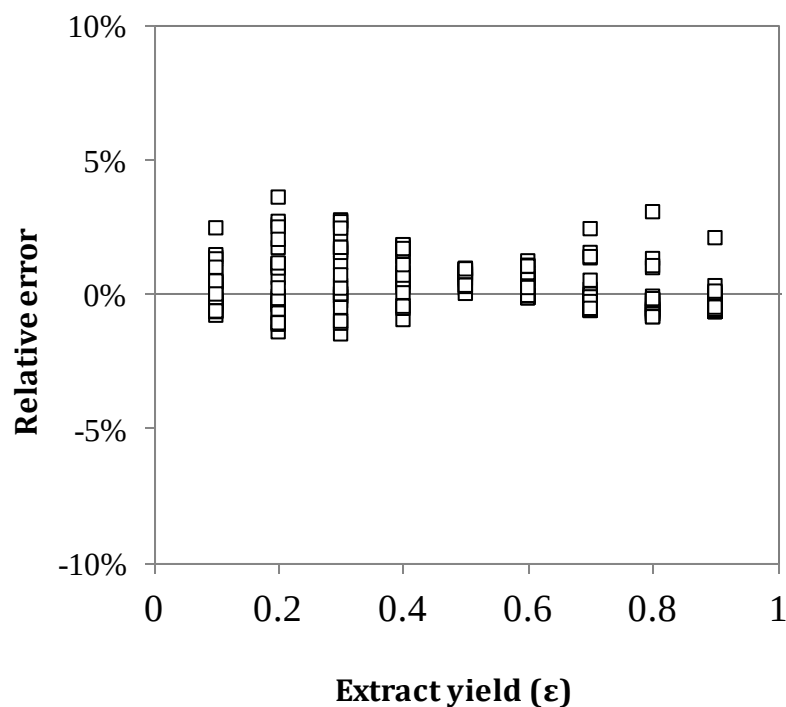


Figure 5.9: Relative error between the approximate and rigorous 4-stage model using the optimized distribution constants.

The resolution of the rigorous model however is iterative on the raffinate composition, which is a problem with $N-1$ variables. On the contrary, the resolution of the approximate model requires no iterations.

5.4. Conclusions

In this work, the fractionation of fish oil FAEEs with supercritical carbon dioxide has been used as a model system to develop a simplified methodological approach.

A mixture of fish oil FAEEs was continuously fractionated with supercritical carbon dioxide at 333 K and 14.5 MPa at a fixed solvent feed rate of 12 kg.h⁻¹ with solvent-to-feed ratios varying from 24.1 to 105. The extract and raffinate mass flow rates were obtained by weight and their composition was determined by chromatographic analysis. An enrichment of ω -3 FAEEs up to a concentration of 74% was achieved in the raffinate, though the solvent was found to be practically unselective towards EPA. This represents an enrichment factor of 1.83. Previous studies have attained higher values [4,5], but the primary goal of this study was not the optimization of this particular operation, but rather the development of a simplified model. Changing the operating pressure and temperature might increase the solvent selectivity. Also, the use of an external reflux should help reduce the concentration of ω -3 FAEEs in the extract.

Modeling of the experimental results ensued. First, the assumption of an ideal mixture behavior was confirmed and the mutual solubilities between supercritical carbon dioxide and the FAEE mixture were estimated to relate the solvent-to-feed ratio to the yield of extract and raffinate (section 5.3.2). Then an approximate model based on the equilibrium stage model was used to correlate the composition of the extract and raffinate to the extract yield (section 5.3.3.3).

In order to reduce the required work load to model the yield and composition of the extract and raffinate for complex mixtures with ideal mixing behavior, the following procedure is proposed:

- 1) The hypothesis of ideal mixture behavior is verified by checking the linearity of the extract yield as a function of the solvent-to-feed ratio Eq. (5.9).
- 2) The solubility of the solvent in the raffinate and of the raffinate in the solvent are calculated according to Eqs. (5.10) and (5.11).
- 3) The composition of the extract and raffinate is correlated by use of Eqs. (5.27), (5.28), (5.41) and (5.42) and fitting the model output with experimental results to obtain the value of the effective distribution coefficients and the number of theoretical stages.
- 4) A rigorous theoretical stage model can be fed with the obtained parameters to model more complex fractionation set-ups, namely for the use of an external reflux.

This procedure is much simpler than the determination of the distribution coefficients by phase equilibrium studies followed by actual fractionation runs. Moreover, it does not require the use of any other equipment to obtain vapor-liquid equilibrium data. By reducing the required time, workload and initial investment for the development of practical applications, the process should become more attractive for potential investors.

5.5. References

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6. Conclusions and perspectives

The goal of the work presented here is to provide some insight to overcome the difficulties encountered when developing applications for the supercritical fractionation process in view of its industrial application.

Four principal subjects have been addressed: a state-of-the-art review, the fractionation of ethanol-water mixtures, the flooding point prediction and the fractionation of a complex mixture of fatty acid ethyl esters.

First, a bibliographic review was conducted. Most of the covered work was found to be exploratory, searching for new possible application or studying the working conditions from an empirical point of view. Modeling of the operation was found to be rather difficult. Equilibrium-stage models used in the literature are very sensitive to the thermodynamical relations used to calculate the solvent selectivity and loading. Thus, it is hard to assess the source of disagreement between experimental and completely predictive simulations.

Fractionation of ethanol-water mixtures was conducted to assess the accuracy of a predictive equilibrium-stage model. The experiments were conducted at 333 K and 10.1 MPa. The ethanol-water-carbon dioxide system has been largely studied and presents a strong influence of the overall ethanol content in both the solvent selectivity and loading. Available VLE data allowed using empirical correlations for the selectivity and solvent load. With this information, a predictive equilibrium-stage model was constructed. A good agreement was found between the predicted and experimental extract and raffinate compositions as a function of the feed composition and solvent-to-feed ratio at laboratory scale. From this series of experiments it can be concluded that equilibrium-stage models are able to predict the composition of the extract and raffinate

at a given feed composition and solvent to feed ratio, but good VLE data is needed since the model output is strongly influenced by the thermodynamic relations used. A very good agreement was also found between experimental results at different scales notably when comparing the extract and raffinate compositions as a function of the extract yield. The overhead load was found to be a useful parameter to determine the hydrodynamic state of the column, since high loads were correlated to droplet entrainment while low loads were due to solvent by-pass. In this study, column flooding was also found at lower solvent velocities than expected compared to the predictions of classical correlations.

The source of this disagreement was discussed aided by the creation of a database containing available flooding point measurements from the literature. Overall, it was found that the flooding capacity under supercritical conditions was higher than predicted by classical correlations. Hence, a new empirical correlation to estimate the capacity factor as a function of the flow parameter was developed based on this database. Nonetheless, some experimental flooding values, including those obtained in the present study, were found to lie largely below the overall tendency. The source of these deviations was discussed from a theoretical point of view in particular regarding the influence of the physical properties in the flooding point. Overall, the low surface tension values found in most studied systems appear to increase the overall flooding capacity while higher surface tension systems like aqueous systems were found to suffer from early flooding particularly in the case of high surface area packings. This result could be related to a diminished capacity of the column to cope with local holdup increases and flow rate fluctuations at supercritical conditions. Nonetheless, more studies are required to assert the definitive cause of these extreme deviations. Further studies should concentrate on the influence of the surface tension and wettability of the

system in the flooding capacity. Finally, the correlation developed in this study should be acceptable for dimensioning purposes but great incertitude is expected for aqueous systems with high surface area packings since they seem to be subject to particular hydrodynamic phenomena.

Finally, a study on the fractionation of fatty acid ethyl esters issued from fish oils was conducted. Beyond the practical application of the fractionation process for the purification of ω -3 fatty acids, this system's behavior is the opposite of the ethanol-water system previously studied. Fatty acid ethyl esters present an ideal behavior, with an overall solubility independent of the mixture. A simplified stage-equilibrium model was developed, and the overall partition coefficients required were obtained by fitting the experimental data. The new model is much simpler than a classical equilibrium-stage model while presenting low relative deviations. An interesting point raised by these results is the easiness in which systems with constant selectivity and solvent load can be modeled based on experimental fractionation data. In contrast, the ethanol-water system requires a much more precise thermodynamic modeling in order to achieve a similar agreement between experimental and predicted values.

To conclude, the modeling of the extract and raffinate composition was carried out for both a non-ideal system (ethanol-water) and an ideal system (fatty acid ethyl esters). Once the particularities of each system have been taken into account, agreement between equilibrium-stage models and experimental results was found to be satisfactory. Moreover, a correlation was developed to assess the flooding capacity of a supercritical fractionation column. Deviations have been observed for some systems and the possible reasons have been discussed.

Hopefully, the tools developed in this study will provide a basis for the industrial-scale implementation of supercritical fractionation technologies. Overall, the

work presented here has addressed different stages of the conception of an industrial-scale supercritical fractionation process.

Such procedure should start with the laboratory-scale implementation of the selected process. A complete study should include series of fractionation runs conducted at different solvent-to-feed ratios, temperatures and pressures. In the case of a complex mixture, the determination of the relative selectivities could be conducted according to the procedure outlined in Chapter 5. The model could also be used to determine the number of theoretical stages required for the separation and hence provide a way to estimate the required column height.

Then, the correlation proposed in Chapter 4 could be used to estimate the flooding capacity of the column. The diameter of the required columns can be computed from this value and the desired column output. At this point, experimental determination of the flooding point could be useful to ensure that the studied system does not suffer from early flooding.

The results in Chapter 3 have shown that the extract and raffinate compositions of an industrial-scale column presented very good agreement with a laboratory-scale unit (with a factor of scale of 44 between both columns). This comparison shows that laboratory results are reliable for scale-up procedures.

Future works might include systematic studies for the estimation of the Height Equivalent of a Theoretical Stage for supercritical fractionation processes and on the comprehension and characterization of the flooding phenomena under high pressure conditions. HETS values presented in the literature have been obtained in laboratory-scale setups and might not be reliable for larger units. Finally, the determination of the flooding capacity of a supercritical fractionation column has proven to be a complex problem and the influence of the interfacial tension, wettability and liquid holdup on the

flooding capacity should be studied further, according to the discussion presented in Chapter 4.

Appendix A

Use of the surface area fraction as a mass fraction proxy

The best approach to quantify the concentration of each component in a sample by chromatographic analysis is to use an internal standard. This method requires several calibration runs and standards in order to obtain each component relative detector response factors. The response factor is defined as follows:

$$RF_i = \frac{A_i m_{IS}}{m_i A_{IS}} \quad (A.1)$$

where RF_i , m_i and A_i are the response factor, mass and peak surface of component i and m_{IS} and A_{IS} are the mass and peak surface in the chromatograph for the internal standard. When the internal standard method is used, m_{IS} is known beforehand thus the amount of i can be obtained directly from the peak surface ratio and the response factor. Once the surface ratio is known, the mass fraction (x_i) can be computed as:

$$x_i = \frac{A_i}{A_{IS}} \times \frac{m_{IS}}{m_{sample}} \times \frac{1}{RF_i} \quad (A.2)$$

This approach was not possible since the majority of the components detected were unknown and calibration against an internal standard was not possible. Instead, if the response factors are known, it is possible to obtain the mass fraction without an internal standard. Reordering Equation (A.1),

$$m_i = \frac{A_i}{RF_i} \times \frac{m_{IS}}{A_{IS}} \quad (A.3)$$

and using the definition of the mass fraction,

$$x_i = \frac{m_i}{\sum_j m_j} = \frac{\frac{A_i}{RF_i}}{\sum_j \frac{A_j}{RF_j}} \quad (A.4)$$

It is common practice in the analysis of FAME mixtures to consider all response factors equal. In that case:

$$x_i = \frac{A_i}{\sum_j A_j} \quad (\text{A.5})$$

The advantage of this method is that the response factors are not needed, the primary disadvantage is that all areas are used to compute each mass fraction and hence any measuring errors in a single peak will propagate to all components. Moreover, experimental results on FAMES have shown that the FID response is not equal for all compounds. The same behavior is expected for FAEEs.

The second point is debatable. It is known that the FID response is proportional to the number of molecules present and to their capacity to produce ionized CHO^+ ions in the flame. This is roughly proportional to the number of carbon atoms in the molecule, which is in turn proportional to the molecular weight in the case of hydrocarbons. However, the carboxyl group in the fatty acid ester does not interact with the detector; hence the response is proportional to the weight of all non-carboxyl atoms on the molecule instead of the real molar weight [1]. This effect is particularly important for short-chain FAMES [2].

In order to assert the error incurred by the assumption of equal response factors, relative theoretical response factors for the identified molecules were calculated. Stearic ethyl ester was used as a reference. Applying the effective carbon number approach proposed by Ackman and Sipos [1] to FAEEs renders the following relation:

$$\frac{RF_i}{RF_{18:0}} = \frac{60 + 14n - 2I}{312} \times \frac{19}{n + 1} \quad (\text{A.6})$$

where I stands for the number of unsaturations and n is the fatty acid chain length.

The correlation developed by de Saint Laumer *et al.* [3] including the estimation of the combustion energy based on the molecular formula was also used to obtain:

$$\frac{RF_i}{RF_{18:0}} = \frac{60 + 14n - 2I}{312} \times \frac{21.973}{1 + 1.165n - 0.346I} \quad (\text{A.7})$$

The values obtained from these correlations along with some experimental relative response factors are presented in Table A.1. It can be seen that relative response factors are close to unity, the experimental values more so than the theoretical ones.

Table A.1: Response factors relative to stearic acid ethyl ester

Corresponding lipid	Experimental RF	Theoretical RF	
		Ref. [1] Eq. (A.6)	Ref. [3] Eq. (A.7)
14:0	0.999	1.039	1.041
16:0	0.990	1.017	1.018
18:0	1	1	1
18:1n9	0.990	0.994	1.009
20:0	—	0.986	0.985
20:5n3	—	0.957	1.030
22:5n3	—	0.948	1.012
22:6n3	—	0.943	1.021

The response factors from Table A.1 can be used to estimate the mass fraction of the identified components in the feed and compare them to the assumption of equal response factors, as it is shown in Figure A.0.1. For this calculation, experimental factors were used when available. It can be seen that taking the surface fraction as equivalent to the mass fraction introduces relative errors under 3.5% for all components. Hence, the error introduced by using the area fraction as a proxy of the mass fraction is considered acceptable, as long as the overall peak surface is well measured.

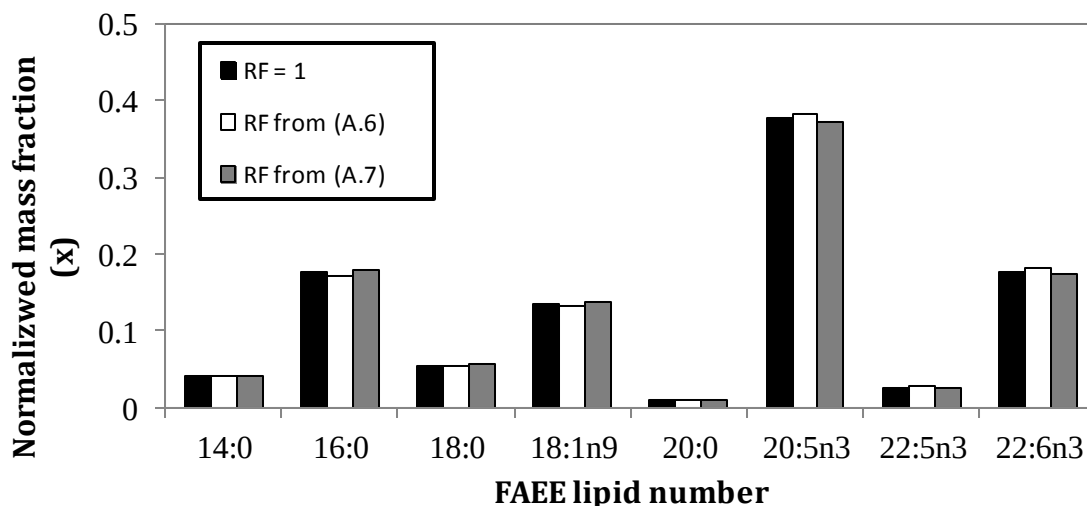


Figure A.0.1: Estimated mass fraction of the identified compounds in the feed calculated using different response factors from Table A.1.

Nomenclature

Latin symbols

A_i	Peak surface area	<i>counts.s</i>	
I	Number of insaturations	—	
n	Number of carbon atoms	—	
RF_i	Response factor of component i	—	$RF_i = \frac{A_i}{A_{IS}} \frac{m_{IS}}{m_i}$
t_R	Relative retention time	—	

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Appendix B

The group method for a stripper column

A multiple stage stripper is considered and conceptualized according to the classical equilibrium-stage model. Some further assumptions are taken:

(H1) that the solvent and feed are pure;

(H2) that the solubility of the solvent in the raffinate is negligible;

(H3) that the solubility of the feed in the solvent is unaffected by the overall composition.

In the group method, the ratio between the mass flow rate of the component i in the vapor and liquid exiting a stage m ($v_{i,m}$ and $l_{i,m}$, respectively) is defined as the stripping factor (S_i):

$$S_i = \frac{v_{i,m}}{l_{i,m}} \quad (\text{B.1})$$

Using the definition of the distribution constant (K_i) renders

$$S_i = K_i \frac{V}{L} \quad (\text{B.2})$$

Since the liquid and vapor mass flow rates are constant along the column according to the initial hypothesis, then the V/L ratio is equal to the E/Z ratio. Hence,

$$S_i = K_i \varepsilon \quad (\text{B.3})$$

Let us consider the mass balance of a component between an arbitrary stage m and the bottom of the column:

$$l_{i,m+1} - v_{i,m} = r_i \quad (\text{B.4})$$

Using the stripping factor, the equation can be rearranged to yield

$$\frac{l_{i,m+1}}{r_i} = 1 + S_i \frac{l_i}{r_i} \quad (\text{B.5})$$

This equation can be used recursively to tie the liquid mass flow of a component between stages. However, this equation cannot be used to link the liquid from the

second stage to the raffinate, since the first stage is a particular case given that the solvent enters the column pure. For the first stage:

$$\frac{l_{i,2}}{r_i} = 1 + S_i \frac{1}{1 - \varepsilon} \quad (\text{B.6})$$

Combining the last two expressions,

$$\frac{l_{i,2}}{r_i} = 1 + S_i \frac{1}{1 - \varepsilon} \quad (\text{B.7})$$

$$\frac{l_{i,3}}{r_i} = 1 + S_i + S_i^2 \frac{1}{1 - \varepsilon} \quad (\text{B.8})$$

$$\frac{l_{i,4}}{r_i} = 1 + S_i + S_i^2 + S_i^3 \frac{1}{1 - \varepsilon} \quad (\text{B.9})$$

Generally, it can be stated that

$$\frac{l_{i,m}}{r_i} = \sum_{j=0}^{m-2} S_i^j + \frac{S_i^{m-1}}{1 - \varepsilon} \quad (\text{B.10})$$

Multiplying this expression by the stripping factor,

$$\frac{v_{i,m}}{r_i} = \frac{l_{i,m}}{r_i} S_i = \sum_{j=1}^{m-1} S_i^j + \frac{S_i^m}{1 - \varepsilon} \quad (\text{B.11})$$

Applying the relation to the last stage N ,

$$\frac{e_i}{r_i} = \sum_{j=1}^{N-1} S_i^j + \frac{S_i^N}{1 - \varepsilon} \quad (\text{B.12})$$

With some algebraic work this expression can be simplified to render

$$\frac{e_i}{r_i} + 1 = \frac{z_i}{r_i} = \frac{S_i^{N+1} - 1}{S_i - 1} + \frac{\varepsilon}{1 - \varepsilon} S_i^N \quad (\text{B.13})$$

This is the inverse of the stripping loss, which is defined as

$$\phi_{S,i} = \frac{r_i}{z_i} \quad (\text{B.14})$$

Finally, the model can be expressed as:

$$\frac{1}{\phi_{S,i}} = \frac{S_i^{N+1} - 1}{S_i - 1} + \frac{\varepsilon}{1 - \varepsilon} S_i^N \quad (\text{B.15})$$

or

$$\phi_{S,i} = \left(\frac{S_i^{N+1} - 1}{S_i - 1} + \frac{\varepsilon}{1 - \varepsilon} S_i^N \right)^{-1} \quad (\text{B.16})$$

It should be noted that $\phi_{S,i}$ is a continuous function ε so that if

$$S_i = 1 \Leftrightarrow \phi_{S,i} = \left(N + \frac{\varepsilon}{1 - \varepsilon} \right)^{-1} \quad (\text{B.17})$$

In turn, the stripping losses can be used to determine the extract and raffinate compositions:

$$x_i^R = \frac{\phi_{S,i} x_i^Z}{\sum_j \phi_{S,j} x_j^Z} \quad (\text{B.18})$$

$$x_i^E = \frac{(1 - \phi_{S,i}^{-1}) x_i^Z}{1 - \sum_j \phi_{S,j}^{-1} x_j^Z} \quad (\text{B.19})$$

To conclude, the model equations are:

$$S_i = K_i \varepsilon \quad (\text{B.3})$$

$$\phi_{S,i} = \begin{cases} \left(N + \frac{\varepsilon}{1 - \varepsilon}\right)^{-1} & \Leftrightarrow S_i = 1 \\ \left(\frac{S_i^{N+1} - 1}{S_i - 1} + \frac{\varepsilon}{1 - \varepsilon} S_i^N\right)^{-1} & \Leftrightarrow S_i \neq 1 \end{cases} \quad (\text{B.16})$$

$$x_i^R = \frac{\phi_{S,i} x_i^Z}{\sum_j \phi_{S,j} x_j^Z} \quad (\text{B.18})$$

$$x_i^E = \frac{(1 - \phi_{S,i}^{-1}) x_i^Z}{1 - \sum_j \phi_{S,j}^{-1} x_j^Z} \quad (\text{B.19})$$

Model limits

It should be noted that the following useful limits apply:

$$\lim_{\varepsilon \rightarrow 0} x_i^R = x_i^Z \quad (\text{B.20})$$

$$\lim_{\varepsilon \rightarrow 1} x_i^E = x_i^Z \quad (\text{B.21})$$

It's physical implication is that when all the feed is extracted ($\varepsilon = 1$) the extract composition matches the feed while the raffinate composition matches the feed when nothing is extracted ($\varepsilon = 0$).

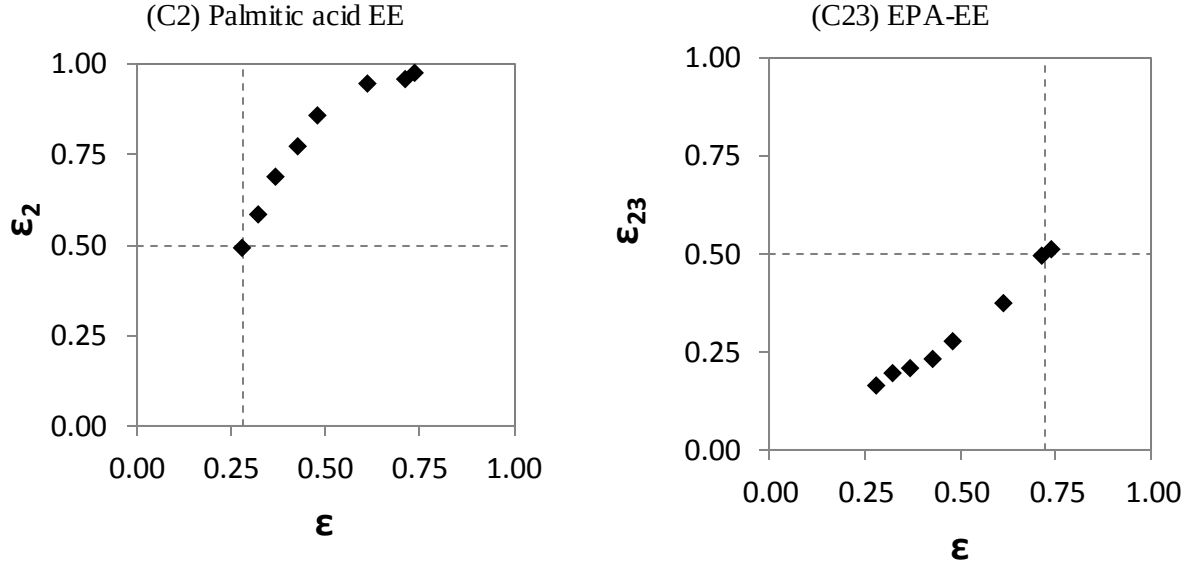
K_i values estimation

Fitting the K_i coefficients required an initial estimate. To obtain it, the following method was used.

Let's consider the extract yield of component i , defined as follows,

$$\varepsilon_i = \frac{e_i}{z_i} = \frac{x_i^E}{x_i^Z} \varepsilon \quad (\text{B.22})$$

which is a function of the global extract yield ε . This value can be easily computed from experimental data. Figure B.1 shows such a plot for two different components.



B.1. Experimental extract yield of two components as a function of the overall extract yield. Feed = Fish oil ethyl esters. T = 333K . P = 14.6 MPa.

It can be proven using the model equations that

$$\lim_{\varepsilon \rightarrow 0} \varepsilon_i = 0 \quad (\text{B.23})$$

$$\lim_{\varepsilon \rightarrow 1} \varepsilon_i = 1 \quad (\text{B.24})$$

It is interesting to note that the extract yield of i will be superior to the global extract yield if $K > 1$ and inferior if $K < 1$.

Let's now consider the case when $\varepsilon_i = 0.5$, as marked in Figure B.1. Since ε_i is a monotonically increasing function of ε that starts at 0 and ends at 1, there will always be a value of ε (that we will call $\varepsilon^{(i)}$) so that $\varepsilon_i = 0.5$; i.e.

$$\exists \varepsilon^{(i)} \in]0,1[, \quad \varepsilon_i(\varepsilon^{(i)}) = 0.5, \quad \forall i \quad (\text{B.25})$$

Let us consider the two extreme columns that may exist: a single stage flash (N=1) and an infinite column (N $\rightarrow\infty$). First, if $\varepsilon_i = 0.5$,

$$\frac{z_i}{r_i} = \frac{1}{1 - e_i/z_i} = 2$$

Using Equation (B.13),

$$2 = \frac{S_i^{N+1} - 1}{S_i - 1} + \frac{\varepsilon^{(i)}}{1 - \varepsilon^{(i)}} S_i^N \quad (\text{B.26})$$

a) First, let's assume $N=1$,

$$2 = \frac{S_i^2 - 1}{S_i - 1} + \frac{\varepsilon^{(i)}}{1 - \varepsilon^{(i)}} S_i \quad (\text{B.27})$$

$$2 = S_i + 1 + \frac{\varepsilon^{(i)}}{1 - \varepsilon^{(i)}} S_i \quad (\text{B.28})$$

$$1 = \frac{S_i}{(1 - \varepsilon^{(i)})} \quad (\text{B.29})$$

reordering and using Equation (B.3),

$$K_i^{(1)} = \frac{1 - \varepsilon^{(i)}}{\varepsilon^{(i)}} \quad (\text{B.30})$$

which gives a first estimate $K_i^{(1)}$.

b) Now, let's assume $N \rightarrow \infty$.

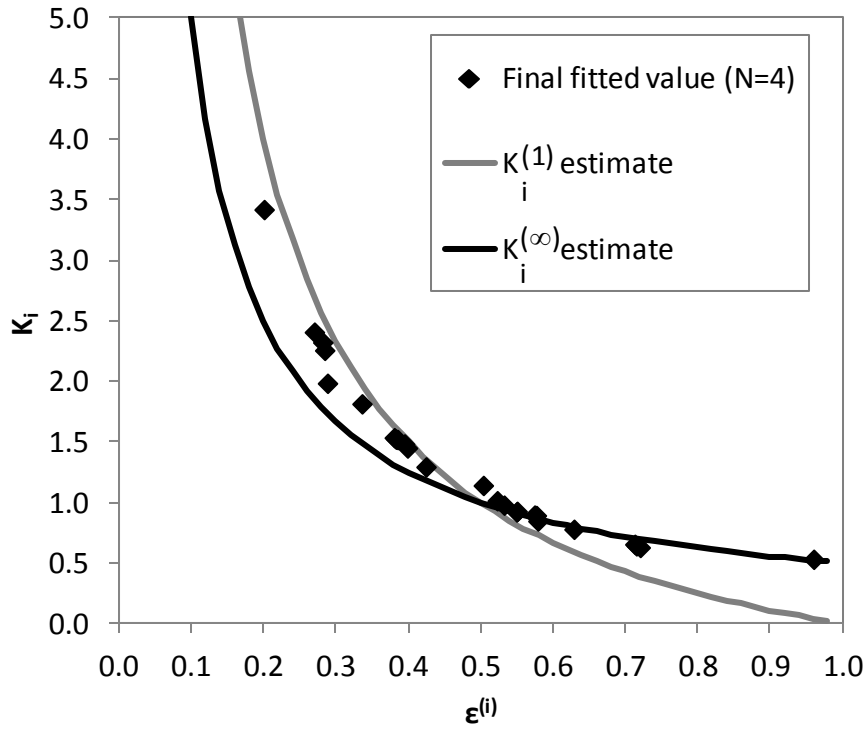
In this case, in order for the system to have a solution, the stripping factor must be less than unity (if not, the right-hand terms go to infinity). Under that conditions, the limit when $N \rightarrow \infty$ of Equation (B.26) is

$$2 = \frac{1}{1 - S_i} \quad (\text{B.31})$$

Reordering, the following estimate can be found,

$$K_i^{(\infty)} = \frac{1}{2 \varepsilon^{(i)}} \quad (\text{B.32})$$

Figure B.2 compares the two initial estimates with the optimized values obtained in Chapter 4 for fish oil FAEs.



B.2: Comparison between K_i fitted values and initial estimated values.

Since the $K_i^{(1)}$ values are better estimates at low $\epsilon^{(i)}$ values and $K_i^{(\infty)}$ works best for high $\epsilon^{(i)}$ values, a weighted mean $(K_i^{(m)})$ is proposed:

$$K_i^{(m)} = \epsilon^{(i)} K_i^{(\infty)} + (1 - \epsilon^{(i)}) K_i^{(1)} = \frac{1}{2} + \frac{(1 - \epsilon^{(i)})^2}{e^{(i)}} \quad (\text{B.33})$$

From our experimental data, the relative error in this initial estimation is less than 15% with a mean 5.5% deviation.

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DEVELOPPEMENT D'OUTILS POUR L'IMPLEMENTATION D'UN PROCEDE DE FRACTIONNEMENT SUPERCRITIQUE A L'ECHELLE INDUSTRIELLE

Résumé :

Le fractionnement supercritique est un procédé prometteur avec un potentiel certain d'application encore peu exploité à grande échelle. Les travaux expérimentaux et la discussion théorique qui font l'objet de cette thèse ont pour objectif d'apporter des outils fiables permettant d'effectuer la mise en œuvre d'un procédé de fractionnement supercritique à l'échelle industrielle, en abordant le changement d'échelle et la modélisation du procédé. Cette étude comporte plusieurs volets. La première partie du travail de thèse porte sur le fractionnement de mélanges éthanol-eau en utilisant du dioxyde de carbone supercritique à 333 K et 10 MPa, sur des unités de fractionnement à échelle du laboratoire, pilote et industrielle, avec des diamètres de colonne respectivement de 19, 58 et 126 mm. Les compositions d'extraits et de raffinats obtenues à différentes échelles, ainsi que les prédictions d'un modèle d'étages d'équilibres, montrent une bonne concordance. Le phénomène d'engorgement est discuté suite à son observation sous certaines conditions de travail. Une corrélation permettant d'estimer la capacité d'engorgement d'une colonne garnie à contre-courant sous pression est proposée, après avoir exprimé l'ensemble des données répertoriées dans la littérature sous forme adimensionnelle. Les possibles sources de déviations observées sont également discutées afin de proposer des perspectives à ce travail. Enfin, le traitement de mélanges complexes est abordé par la mise en œuvre et la modélisation du fractionnement supercritique d'éthyl esters issus d'huiles de poisson, sous des conditions de 14.5 MPa et 333 K, en variant le rapport solvant sur charge entre 21,8 et 143. Un modèle simplifié dérivé de la méthode des groupes est développé afin de représenter l'influence du taux d'extraction sur la composition de l'extrait et du raffinat.

Mots-clés : fractionnement supercritique, modélisation, changement d'échelle, capacité d'engorgement.

DEVELOPMENT OF TOOLS FOR THE IMPLEMENTATION OF AN INDUSTRIAL-SCALE SUPERCRITICAL FRACTIONATION PROCESS

Abstract:

Supercritical fractionation is a promising process with a great potential but with little current large-scale applications. The experimental work and theoretical discussion in this dissertation aim providing tools for the implementation of an industrial-scale supercritical fractionation process by covering aspects such as scale-up and process modeling. In order to do so, three principal axes are discussed. Firstly, the fractionation of ethanol-water mixtures by supercritical carbon dioxide at 333 K and 10 MPa was studied using fractionation units at laboratory, pilot and industrial scale with column diameters of 19, 58 and 126 mm, respectively. The extract and raffinate compositions obtained show good agreement between different scales and with the predictions of an equilibrium-stage model. The flooding phenomenon is also discussed after being detected under certain conditions. A correlation to estimate the flooding capacity of a countercurrent column at high pressure conditions is proposed following a dimensionless representation of the available experimental results presented in the literature. The possible sources for deviations found are also discussed in order to propose future works. Then, the treatment of complex mixtures is tackled by modeling and supercritical fractionation of fatty acid ethyl esters derived from fish oil under 14.5 MPa and 333 K, varying the solvent-to-feed ratio between 21.8 and 143. A simplified model derived from the group method is developed to represent the influence of the extract yield on the composition of the extract and raffinate.

Keywords: supercritical fractionation, process modeling, scale-up, flooding capacity.

Discipline: **GENIE DES PROCEDES**

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