SCALE-UP DESIGN & SAFETY ANALYSIS OF PALM KERNEL OIL EXTRACTION USING SUPERCRITICAL CARBON DIOXIDE SYSTEM

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by

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيم

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LIST OF SYMBOLS

A_D	Axial dispersion coefficient
A_{int}	Internal cross-sectional area
a_p	Particle specific surface area of the solid volume sphere
CO_2	Carbon dioxide
D_{12}	Binary diffusion coefficient
D_e	Effective diffusivity
d_{int}	Internal diameter extraction vessel
$d_{int1,2}$	Internal diameter small scale, large scale
d_p	Particle size
F_m	Microstructural correction factor
h_{int}	Internal height extraction vessel
$h_{int1,2}$	Internal height small scale, large scale
k_f	Fluid mass transfer coefficient
k_s	Solid mass transfer coefficient
L_m	Length of the model scale
L_p	Length of the prototype scale
M_m	Mass used for model scale
M_P	Mass used for prototype scale
$m_{B1,2}$	Mass bulk small scale, large scale;
$\dot{m}_{f1,2}$	Mass flow rate small scale, large scale
$\dot{m}_f$	Mass flow rate of solvent fluid
M_{CER}	Mass transfer rate at CER period
M_{FER}	Mass transfer rate at FER period
N	Spherical solid particles
P	Pressure
q	Easily soluble fraction on the surface
Q_{BIC}	Dimensionless model parameters
Q_f	Volumetric flow rate of solvent fluid
r_F	Ratio of force
r_L	Ratio of length
r_v	Ratio of velocity

S_{BIC}	Dimensionless model parameters
t	Extraction time
T	Temperature
t_m	Time used for model scale
t_p	Time used for prototype scale
t_{cyc}	Time calculated the equipment will survive until yearly shutdown
t_{res}	Residence time
ν_{int}	Interstitial velocity of solvent fluid
ν_m	Velocity of the model scale
ν_p	Velocity of the prototype scale
ν_{sup}	Superficial velocity of solvent fluid
V_E	Volume of extraction vessel
x_0	Initial concentration of the extract
y^*	Solubility
Y_{CER}	Extraction yield at the CER period
Y_{FER}	Extraction yield at the FER period
Y_E	Extraction yield
Z_k	Dimensionless length coordinate
π	Pi
ε_B	Internal bed porosity
ε_p	Particle porosity
ρ_f	Density of solvent fluid
τ	Tortuosity
τ_{BIC}	Minimal extraction time
ϑ	Dimensionless time
ϑ_k	Time the soluble material disappears
φ	Solids volume fraction
μ_f	Viscosity of solvent fluid

LIST OF ABBREVIATIONS

API	American Petroleum Institute
BPR1	Back pressure regulator 1
BIC	Broken and Intact Core
BIC-SC	Broken and Intact Core + Shrinking Core
CER	Constant extraction rate
CKV1	Check valve 1
CKV2	Check valve 2
CV1	Control valve 1
DA	Dimensional analysis
DC	Diffusion-controlled
DG	Dimensionless group
DOE	Design of experiments
E1	Equipment 1 (Condenser)
ES	Expert System
EV1	Extraction vessel 1
E&P	Exploration and Production
F&EI	Fire and Explosion Index
FER	Falling extraction rate
FIS	Fuzzy inference system
FLD	Fuzzy logic designer
FTA	Fault tree analysis
HAZOP	Hazard and Operability
HE1	Heater 1
HE2	Heater 2
HE3	Heater 3
LPG	Liquefied petroleum gas
MF	Membership functions
OEC	Overall extraction curve
OSHA	Occupational Safety and Health Administration
OREDA	Offshore and Onshore Reliability Data
P1	CO_2 pump

P&ID	Piping and instrumentation diagram
PROBIT	Probability unit
PRV1	Pressure relief valve 1
PRV2	Pressure relief valve 2
PRV3	Pressure relief valve 3
PRV4	Pressure relief valve 4
RAMS	Reliability, availability, maintenance, and safety
SC	Shrinking Core
SC-CO_2	Supercritical carbon dioxide
SF	Supercritical fluid
SFE	Supercritical fluid extraction
SV1	Separation vessel 1
SV2	Separation vessel 2
UNEP	United Nations Environment Programmed
UPV	Unfired Pressure Vessel
V2	Gate valve 2
V3	Gate valve 3
V4	Gate valve 4
V5	Gate valve 5
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REKA BENTUK NAIK SKALA & ANALISIS KESELAMATAN PENGESKTRAKAN MINYAK ISIRONG SAWIT DENGAN MENGUNAKAN SISTEM LAMPAU GENTING KARBON DIOKSIDA

ABSTRAK

Semenjak kebelakangan ini, teknologi pengekstrakan superkritikal karbon dioksida telah digunakan secara meluas sebagai kaedah pengekstrakan alternatif. Walau bagaimanapun, perancangan naik skala yang tidak teratur boleh menyebabkan proses yang tidak effisen dan mengundang bahaya. Oleh itu, objektif kajian ini memberi tumpuan kepada metodologi yang menggunakan kriteria naik skala dalam prinsip persamaan untuk peningkatan proses dan analisa keselamatan sebagai penilaian awal untuk skala besar.yang sangat bermanfaat untuk kerja-kerja masa depan. Empat kumpulan tanpa dimensi telah dipilih dan dikira sebagai kriteria naik skala yang sesuai dengan penilaian perkaitan dan sistem pakar, dengan $\frac{m_f}{m_B}$ malar memberikan kekuatan tertinggi manakala $\frac{d_p}{d_{int}}$ malar terendah, masing-masing dengan $\frac{7.48}{8}$ dan $\frac{3.9}{8}$. Kombinasi $\frac{m_f}{m_B}$ & Re malar merupakan kriteria terbaik untuk skala 0.57 L - 50 L semasa simulasi naik skala kerana ia memberikan jumlah kadar pengekstrakan pantas dan nilai k_f tertinggi., manakala untuk skala 40 ML - 50 L, yang paling rendah didapati dari $\frac{d_p}{d_{int}}$ malar dan Re malar. Penilaian keselamatan sistem dinilai oleh analisis pokok kesalahan di mana 25 set pemotongan minimum yang mendorong kepada tekanan melampau dengan sebab utama iaitu kebocoran paip dan penyambung. Kebarangkalian kegagalan peringkat atas yang dikira untuk analisis set pemotongan minimum dan simulasi Monte Carlo masing-masing adalah 1.241485×10^{-1} and 1.237203×10^{-1}.

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ABSTRACT

In recent years, supercritical carbon dioxide technology has been widely used as an alternative extraction method. However, improper plan in upscaling can lead to inefficient process and hazards. Therefore, the objective of the study is to focus on the layout of using the scale-up criteria for the principle of similarity in upscaling and the safety analysis as a preliminary assessment for a large scale that would highly be beneficial for future works. Four dimensionless groups were selected and calculated as the suitable scale-up criteria by relevancy evaluation and expert system, as constant $\frac{m_f}{m_B}$ gave the highest strength, while $\frac{d_p}{d_{int}}$ had the lowest with $\frac{7.48}{8}$ and $\frac{3.9}{8}$, respectively. Constant combination of $\frac{m_f}{m_B}$ & Re was the best criteria for 0.57 L – 50 L scale during the scale-up simulation due to the highest total fast extraction rate and k_f, while for 40 ML – 50 L scale, the lowest was obtained from constant $\frac{d_p}{d_{int}}$ and constant Re. The safety assessment of the system was evaluated by fault tree analysis where 25 minimal cut sets led to overpressure mainly caused by leakage of the piping and connector. The calculated top-level failure probabilities for probabilities analysis and Monte Carlo simulation were 1.241485×10^{-1} and 1.237203×10^{-1} respectively.

CHAPTER 1

INTRODUCTION

This chapter presented the foreword of supercritical fluid extraction. This included the main subject for this study and the problems faced in the area. Also, this chapter explained the purpose of this study along with its scope for this study's completion.

1.1 Study background

Over the years, the world sees the increasing number of consumers in consumables, materials, energy, and many more. The numbers can be observed as material flows and resource productivity reported by West and Schandl (2013) focusing on data from Asia and the Pacific. This condition drives the industry especially the manufacturing sector to expand in order to meet the world demands. In doing so, this expansion of production needs to be calculated and planned thoroughly for the purpose of minimizing the risk of loss especially in terms of process design of the system. It goes the same in supercritical fluid (SF) technology such proven by del Valle et al. (2014), Núnez and del Valle (2014), and Núnez (2017). The progressive achievement of SF technology become eye-catching in the section of the renewable industry where it extendedly discussed in Knez (2014). Various studies proved that SF technology is capable to compete with its conventional methodology with the impeccable end result and profitable turnover in economic perspective. This which bring the aspiration for technologist and scientists to bring the technology into the larger scale.

The birth of SF technology refers back to more than a century ago. Early studies on supercritical systems mostly emphasised on purification and matters of solubility in supercritical gases. The earliest industrial development on supercritical technology took place in the mid-1930s in terms of the use of near-critical compressed propane for de-asphalting petroleum (King and Bott, 1993). The development of SF technology has been rapidly and widely adaptable in real-world industry in the recent years, and the application of SF technology has also expanded from various processes such as energy generation (Knez et al., 2014, Zhu, 2017), food engineering of solid and liquid extraction (de Melo et al., 2014b, Capuzzo et al., 2013, Khaw et al., 2017), pharmaceutical and product manufacturing (Clavier and Perrut, 2004, Herrero et al., 2010), high-pressure sterilization (Perrut, 2012), and etc.

The key to SF technology is the principle of supercritical fluid operating under the high-pressure system (Eggers and Lack, 2012). One example of the SF technology process is supercritical carbon dioxide (SC-CO_2) extraction of natural matter, which is one of the earliest and most studied applications in the field of supercritical fluids. In the last 20 years, studies on the extraction of classical compounds like essential oils and seed oils from various sources such as seeds, fruits, leaves, flowers, rhizomes, etc., with or without the addition of a co-solvent have been published and various scale-up methodologies identified in the study of SC-CO_2 extraction. These were discussed by de Melo (2016) and the most widely used method in upscaling is the principle of similarity.

This method is the most common because it is the simplest and easiest to understand. Oldshue (1983) also introduced the concepts of geometric and dynamic similarity and suggested the use of dimensionless groups (DGs) because these are useful in correlating scale-up parameters. Both geometric and dynamic similarity also proven to be the most successful for scale-up of SC-CO_2 extraction of natural matters. However, SC-CO_2 extraction considers to be complicated like any other chemical processing operation. It is nearly impossible to maintain all the governing DG constant. Thus, the justification to select which variables to be scale-up criteria must be sound and well-founded. If not, the expansion attempts will meet failure. In order to achieve a successful scale-up, it is important to know what controls the process (Clavier et al., 1996, Sovová and Sajfrtova, 2017).

Familiarization to the basis of the extraction process is crucial in order to determine the optimal extracting conditions through scanning of the operational parameters. From this, appropriate the scale-up approach is selected. Prediction the behaviour of the process at large scale is made from small data, by considering the differences observed in processes conducted in the small scale using smaller volumes and more basic process design. This kind of familiarization is highly recommended by several publications such as del Valle and De La Fuente (2006), Mezzomo et al. (2009), and Huang et al. (2012). One of the advantages of a simple scale-up was its efficiency (Prado et al., 2012). This is compared by predicting extraction behaviour using more complex mathematical models as the scale increases.

De Melo et al. (2014b) summarized the scale-up criteria from previous studies and these were based on mass transfer, equilibrium, and geometric components. These scale-up criteria can also be used solely and directly to the real process run or with the application of the mathematical model for simulation. These proven by countless examples of scale-up attempts on SC-CO_2 extraction from the 2000s until recent years, such in Table 2.2 – 2.6. However, the list mentioned do not limit on DGs, but some do include the ratio of these variables. Among the scale-up criteria listed, only two pointed out the application of DG as eligible scale-up criteria.

And it is true there are a great number of researches studies that apply the principle of similarity in scale-up SC-CO_2 extraction, yet just several were using only DGs in the upscaling process.

One's research study on the scale-up using simple criteria usually have higher percentages to achieve successful attempts. This is because using scale-up criteria provides the freeness of the practitioners to control the conditions of the process in comparison to the technique of direct transfer from the small scale process run to the large scale apparatus utilized by some previously such as Kotnik et al. (2007). A more extensive approach of upscaling such as the application of the mathematical model was proposed since it covers a wider prospect of SC-CO_2 extraction itself. The mathematical model consists of physical correspondence to the materials and the operating conditions of the process studies, so it can well-founded (Reverchon and De Marco, 2006). Thus, it makes a fitting scale-up procedure for a SC-CO_2 extraction process. A mathematical model is best described as sets of equations are developed which representing not only mere mathematical equation but also the information and the knowledge of the process from experimental observations and data. Nonetheless, the application of the mathematical model in SC-CO_2 extraction is known for its meticulous and difficult to solve (time-consuming) even though with computational assistance.

Even numerous research studies using simple scale-up criteria proven successful, there were some differing outlooks on the topic. Del Valle et al. (2004) advised that simple scale-up should be used cautiously. The study asserted that some aspects such as co-extraction of water, mechanical dragging, and efficiency of separator do not cover by simple scale-up criteria. While the scale-up attempt for del Valle et al. (2004) and Kotnik et al. (2007) were deemed to be unsuccessful, the insights of these research studies are considered valuables. As for Kotnik et al. (2007), findings such as the effect on the quantity of separation vessel and its function effectiveness were learned.

On the other hand, Prado et al. (2011) proved that simple scale-up criteria are reliable and more efficient by investigating these three aspects (from the previous paragraph) and their influences toward upscaling. The experiment results show that the yield achieved on a large scale still higher than the small scale. Even water presence in the extract from the pilot scale, the yield of the extract is still superior even after water removal (Prado et al., 2012, Prado and Meireles, 2014). In addition, the study mentioned that the occurrence of mechanical dragging of both extract and water was associated with the increment of the superficial velocity of the fluid.

Although Prado et al. (2011) came up with a positive hypothesis on the influences of mechanical dragging, yet the results of the experiment were inconclusive, therefore Prado et al. (2012) agreed that the topic should be extended to future study. Extract loss by mechanical dragging can be avoided by reducing the wide pressure difference between the extraction vessel and separation vessel. It is because rapid depressurization will cause volumetric solvent flow rate to increase, consequently reduce the time of extract 'detachment' from CO_2 solvent. In addition, Prado et al. (2011) proposed an idea that more than one separation vessel (in series) provides higher chances of higher yield on a large scale. Therefore, it is proven that simple scale-up criteria are fit to be used in upscaling of SC-CO_2 extraction.

Usually, there were two concerns when comes to the upscaling of a process or system. First is the financial aspect and the second is the safety analysis. For this study will focus on the later, on how the topic affects and the significance in the scaling-up process. Several types of methodologies for the safety assessment of SC-

CO_2 extraction were identified. They were carried out by measuring the reliability of the system used. As the SC-CO_2 extraction system scale shifts to much larger capacity with the additional system installed, the system becomes more complex and the risk of a faulty system is easily slipped from attention. Therefore, it is important to perform an analysis mechanism on the possibility of failures which be able to estimate the expected rate of such failures.

1.2 Problem statements

The progression of SC-CO_2 extraction undeniably optimistic since it been developed. However, there is still scarcity and loophole especially the knowledge regarding SC-CO_2 extraction upscaling to a large scale. This matter includes the topics of development of scale-up criteria and the topics of its system safety analysis. On these issues, a few statements were stated which shall highlight the problems.

From the previous research studies, it failed to present the extensive reasoning on how the scale-up criteria/s is/are established in which later selected. Noticeably in previous studies, many only laid out the scale-up criteria (mentioned in Section 1.1) that will be used in the upscaling attempts. The problem with a random selection of scale-up criteria will later depict during the testing in the actual SC-CO_2 extraction. Too many scale-up criteria will increase the time and financial consumption (Worstell, 2014). It is agreeable that a simple scale-up criteria list provides tremendous helps to the research community. However, one's believes that the simple scale-up criteria should be expanded more than not only goes from the list in order to provide broader options of simple scale-up criteria selection.

Furthermore, the published research studies on palm kernel extraction using SC-CO_2 as a solvent on a large scale is rather limited, regardless of oil extraction from the palm kernel state listed. Most research studies recorded were in the small scale and most topics regarding its extract properties and its process optimization. A few publications such as de Melo et al. (2014b), del Valle (2015), and Khaw et al. (2017) were put in the collection, the achievement regarding SC-CO_2 extraction of natural matter and the triumph of this community in effort on expanding the current technology and commercialization.

However, one's could not find or come across any recorded research studies on the topic of scaling up of palm kernel oil by SC-CO_2 extraction. Palm kernel oil can be extracted from many states, for example, as whole palm kernel (Norhuda, 2005), as ground palm kernel, as dehulled ground palm kernel (Zaidul et al., 2007b), as kernel cake (Nik Ab Rahman et al., 2012, Duduku Krishnaiah et al., 2012). For the purpose of this study, one's focuses on the extraction of palm kernel oil from ground kernel since it the most basic. Research studies such as Mohamad Nizar (2000) and Md. Zaidul (2003) are among the earliest works focusing on the oil extraction from ground palm kernel. The following years show the increases in work on process characterization and optimization for SC-CO_2 extraction of palm kernel oil (Zaidul et al., 2007a, Hong et al., 2010, Wahyu et al., 2013).

As for safety assessment for SC-CO_2 extraction, several safety studies on SC-CO_2 extraction were conducted during these previous years. The studies either about analysis on the process and system or hazards detections. A few quantitative tools were deployed for the research. For example, HAZOP analysis was used by Rosenthal (2012) to analyze system design. While Lucas et al. (2003) and Soares and Coelho (2012) utilized the same technique of PROBIT method in order to investigate the hazard vulnerability upon SC-CO_2 extraction system. Another safety analysis such as Fire and Explosion Index (F&EI) also was deployed by Lucas et al. (2003) to rate the potential hazard specifically for fires and explosions. This system's reliability is weighted by the non-failure rate. However, the study is too general (Cheng et al., 2014). Therefore, fault tree analysis is proposed as an alternative approach to carry out a preliminary safety evaluation and its importance before proceeding to the large SC-CO_2 extraction system.

1.3 Objectives of the study

The main objective of this study is to present the scale-up plan of SC-CO_2 extraction with a systematic and reliable designing procedure for a large scale. Below are the sub-objectives of this study:

1. To establish the selected simple scale-up criteria in the form of DGs for SC-CO_2 extraction specifically for palm kernel by theoretical analysis
2. To simulate the scaled process for SC-CO_2 extraction of palm kernel using the simple scale-up criteria established
3. To analyze the probability of overpressure on the scaled SC-CO_2 extraction system using fault tree analysis

1.4 Scope of the study

This elaborates on the study's scopes that were performed in order to achieve the objectives in Section 1.3. This study aims to provide a view of the upscaling of SC-CO_2 extraction on a large scale using constant scale-up criteria. The upscaling runs were attempted on the system ranging between 40 ML scale to 50 L scale. Upscaling criteria were focusing on mass transfer mechanisms and specifically for the static extraction process. Furthermore, this study chose the SC-CO_2 extraction of ground palm kernel as the sample model for the upscaling simulation runs. MATLAB software was used as a calculation tool to emulate the real SC-CO_2 extraction. For the safety section, the assessment is conducted on the 3 L system scale. In order to identify the potential hazards in a thorough manner, the test runs were conducted for static and continuous extraction processes using Agarwood as the sample model. Then, the fault tree is constructed based on the literature review and observational analysis that obtained from the test runs. The failure analysis conducted is based on the equipment failures probabilities. This was assisted with OpenFTA as the tool that provides the complete calculation of failure probabilities such as minimal cut sets, probabilities analysis and Monte Carlo simulation.

1.5 Conclusion

This chapter concluded by describing the organization of the thesis. Chapter 1 provides an overview of the main points of the thesis and introduces the breakdown of studies. Chapter 2 presents the literature review on the scale-up study of SC-CO_2 extraction which includes the topic of process study, previous scale-up attempts, and safety analysis of the system. Chapter 3 describes the methodology used, including the scale-up knowledge retrieval, scale-up criteria selection and process simulation in different scales. In addition, Section 3.2 explains the scale-up criteria selection tool by using the Expert System. This follows with Section 3.3 presents the details about the selected SC-CO_2 extraction model, the variables mathematical equations used, and its application by using MATLAB software. In Section 3.4 explains the method used in the study of safety in the SC-CO_2 extraction system. Chapter 4 presents the results and discussion of the study. It summarizes the theoretical analysis on what variables show included and its relevancy in regards to SC-CO_2 extraction subsequently to its scale-up process. Section 4.1 – 4.2 presents the breakdown of dimension analysis (DA) on finding the scale-up criteria in the form of DG.

Section 4.4 – 4.5 aims at presenting results from Section 4.3 with reasoning on SC-CO_2 extraction and for scale-up prospective. This provides a better interpretation of scale-up criteria selection by going through the technique explained in Chapter 3. These subsections hence comprise the first part of this study's results. The second part of this study's results are put in Section 4.7 – 4.8 where the SC-CO_2 extraction simulation setups in different scales were explained in detail, including the effect of all relevant chosen scale-up criteria. Section 4.6 will be the final input in Chapter 4 describing the results of safety analysis from fault tree analysis. It also discusses in detail by using probabilities set analysis and Monte Carlo simulation. Chapter 5 views the research results in the context of previous findings, comments on possible future applications this upscaling technique and the importance of safety aspects during upscaling. Overall, Figure 1.1 shows the outlines of the thesis.

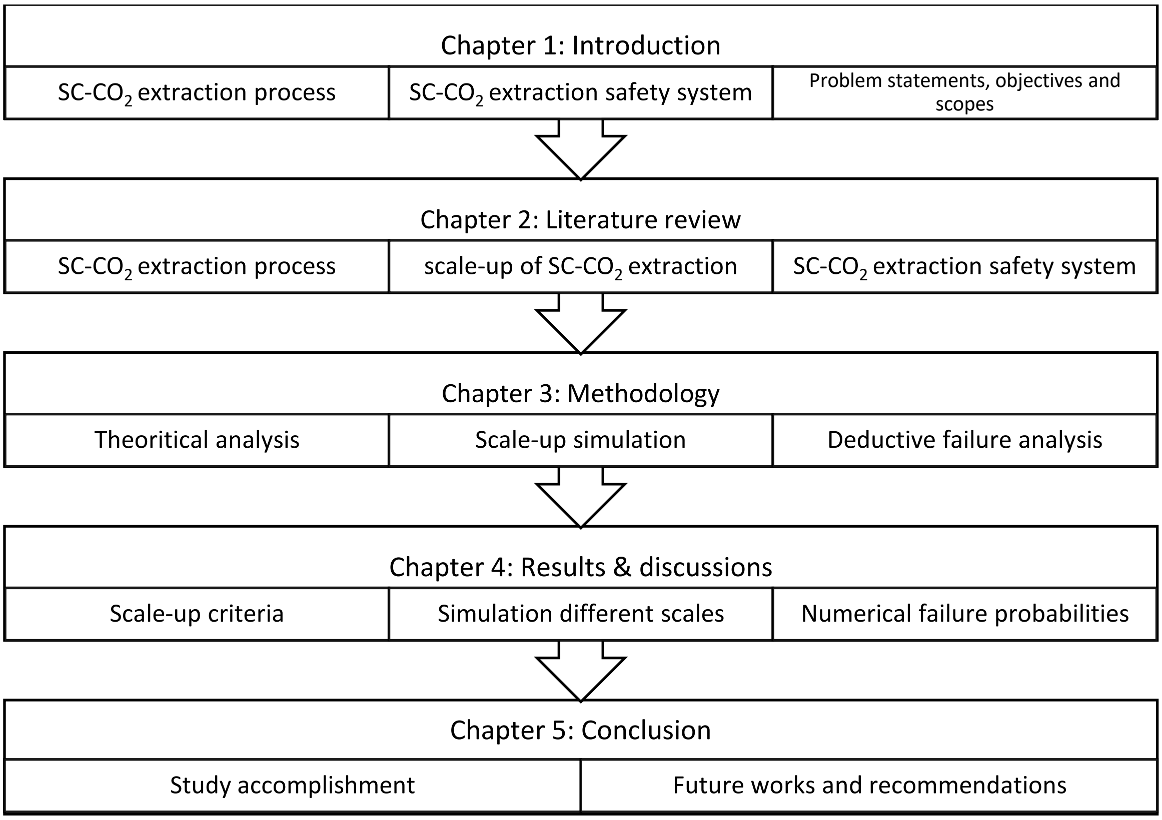

Figure 1.1 The framework of the thesis

CHAPTER 2

LITERATURE REVIEW

This chapter presented an exhaustive review and critical analysis of the available contributions to the theory and practice of scaling-up SC-CO_2 extraction. The significance and limitations of these contributions are compared with one another; moreover, attempts are made to resolve the contradictions among them. This chapter also provided an outlook on the topic of safety assessment of the SC-CO_2 extraction system.

2.1 Supercritical fluid extraction

Supercritical fluid extraction (SFE) is a technique that utilizes a fluid phase. Sovová and Sajfrtova (2017) explained the characteristics of this technique are in between the characteristics of gas and liquid to induce the solubilisation of solutes in a matrix. Extraction is defined as the process of removing soluble material from insoluble matter, which may be either solid or liquid, for the creation of a new product. Through time the treatment uses a liquid solvent, which influenced by the mass transfer mechanism. Somehow the conventional extraction method, in particular, the usage of or organic solvent – screw press, solvent extraction, and screw press followed by solvent extraction arose environmental concerns overtime. For example, the palm oil extraction, the endproduct from this process requires additional purification and refining processes such as degumming, bleaching, and deodorization (Md. Zaidul, 2003). As for food processing, fractionation, and hydrogenation were added to further oil refining process (Norhuda and Jusoff, 2009).

There are several types of solvent used in SF technology such as water or nitrogen, however, carbon dioxide (CO_2) is popular among those since its properties are more superior compares to others. As an intermediate medium of this process, CO_2 can diffuse through solids like a gas and dissolve materials like liquid when its pressure and temperature above it the critical point (Sapkale et al., 2010). Thus, this type of SF becomes a good solvent for solutes with chemical compatibility. Table 2.1 shows the critical properties of commonly used supercritical fluids (Sapkale et al., 2010). CO_2 becomes the most common use in various sector including food engineering because of it safe, cheap, and have low critical temperature and pressure of which make it an ideal medium for processing volatile products. SC-CO_2 have low viscosity allows it to penetrate the solid raw material, low latent heat of evaporation, and high volatility mean it can be easily removed without leaving a solvent residue (Sovová and Sajfrtova, 2017). Also, SC-CO_2 is a non-polar solvent and most apt for organic compound extraction. Occasionally, SC-CO_2 is modified with polar solvents such as ethanol to lower the polarity and enable extraction of raw materials extensively. Water sometimes to a certain extent deemed as a natural modifier since water always presents in plants even dry.

Table 2.1 Critical properties for some components commonly used as supercritical fluids referred from Sapkale et al. (2010)

Solvent	**Molecular Weight (g/mol)**	**Critical temperature (K)**	**Critical pressure MPa (atm)**	**Critical density (g/cm^3)**
Carbon dioxide (CO_2)	44.01	304.1	7.38 (72.8)	0.469
Water (H_2O)	18.015	647.096	22.064 (217.755)	0.322
Methane (CH_4)	16.04	190.4	4.60 (45.4)	0.162
Ethanol (C_2H_5OH)	46.07	513.9	6.14 (60.6)	0.276

The usage of CO_2 as a solvent is highly selected due to its environmentally friendly behaviour. The CO_2 used is the byproduct from the fermentation process, thus the extraction solvent does not increase the amount of CO_2 already present in the atmosphere and consequently, no overall detrimental effect on the earth's ozone layer from the use of this CO_2 (Moyler, 1993). Today, the formation of the programme such as the United Nations Environment Programmed (UNEP) was to monitor the pollution prevention and green technology initiative all around the world (West and Schandl, 2013). In the manufacturing of foams and aerogels, CO_2 was used replacing CFC (R12, then R22) which has been banned (Perrut, 2000). In the food industry, SC-CO_2 was used for the decaffeination of coffee in the manufacturing industry nowadays widely. Plus, the number of studies on extraction and sterilization of natural matters were conducted with very much promising results to serve as an alternative for the conventional methods (Reverchon and De Marco, 2006, Perrut, 2012).

The solvent power of SFs is strongly influenced by pressure and temperature based on de Melo et al. (2014). The early stages of SFE use normally occur in high-pressure systems, with pressure value higher than 35 MPa although the relatively SC-CO_2 soluble compounds, including terpenes, sesquiterpenes, and fatty acids, need to be extracted (Reverchon and De Marco, 2006). Following that, the principle of optimization between solvent power and selectivity is applied. The SFE of solid raw materials is operated at a small scale during the early stages before it is brought to large scales such as pilot, industrial, and commercial. Notably, as some industrial-scale plants implement a system that utilizes different types of gas for the isolation or fractionation of components (Knez et al., 2014), the use of SFE is not limited to the extraction of crude end products.

$SC\text{-}CO_2$ extraction, is a complicated process, simplest to describe the nature of the process is by a couple of key elements, which are mass transportation mechanism and phase equilibrium (Brunner, 1987, Sovová, 1994, Hong et al., 1990, Goto et al., 1993, King et al., 1997, Goto et al., 1996, Song et al., 2017, Huang et al., 2012, del Valle and De La Fuente, 2006, del Valle et al., 2005). Sovová and Sajfrtova (2017) proposed that the flow pattern of the solvent in the extraction vessel regards as an important component in regard process and was considered to be included in the $SC\text{-}CO_2$ extraction phenomenological model. Thus, various studies regarding optimization and scale-up are related to these components. The feed (solid raw material) utilized in $SC\text{-}CO_2$ extractions were either in the original state or pre-treated. In $SC\text{-}CO_2$ extraction which usually uses vertically position extraction vessel, the solvent flows through a fixed bed formed by feed particles where it gradually saturated with the extracted material.

Mass transport or known also as mass transfer depends on the raw material matrix since the mechanism of extraction can be different. In $SC\text{-}CO_2$ extraction of solid raw material, the kinetic movement between extract, solute, and solvent were described by externally and internally. Sovová and Sajfrtova (2017) explained that the system of the feed, solute, and solvent consist of two phases; one is the fluid phase, also known as the supercritical phase which is the solvent containing the solubilized solute and the other one is the solid phase in which the raw material matrix form where the solute is extracted. The transports of the components occur by convection and dispersion in the fluid phase, mass transport in solid-fluid interface and diffusion of the solute-solvent mixture in the solid phase when contacts between the phases happen (Zabot et al., 2014a).

The study about the phenomenological insights of SC-CO_2 extraction processes can be studied by the extraction curve (Sovová and Sajfrtova, 2017). Generally, the extraction rate is a function of solubility of the solute in the chosen solvent and follows by the limiting factor, diffusion. Figure 2.1 illustrates the dependency of the extraction process by the extraction curve. The dependency in solubility happens during the first region of the extraction process where the linear increase in yield, that is, the higher pressures or temperatures creating faster extraction (Eggers and Lack, 2012). In principle, the elevated pressures result in higher densities and elevated temperatures result in an increase in vapor pressure (Sovová, 1994). Nonetheless, the influence of vapor pressure at higher pressure and temperature is more powerful compared to decreased fluid density.

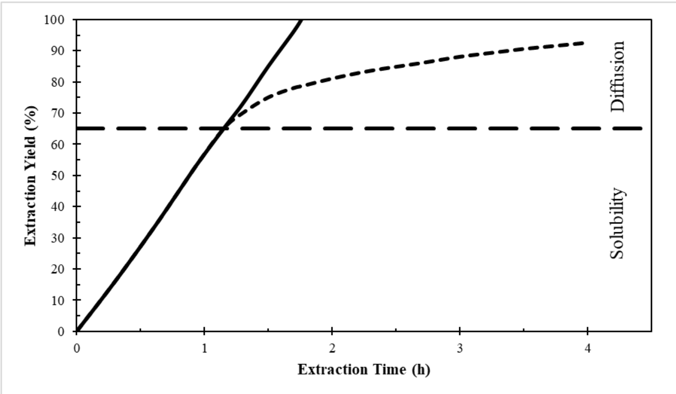

Figure 2.1 The curve above illustrates the rate of SC-CO_2 extraction described by Sovová and Sajfrtova (2017)

The second region is controlled by diffusion. Once the extract on the surface 'drained out', the outer layer diminished, the solvent mobilized in penetrating the core to extract the solute inside it (del Valle and De La Fuente, 2006). To maximize the extract result, usually, the solid raw material will undergo pre-treatment for removing the diffusion barrier and reduce the diffusion distance on the other. The diffusion time relies on the corresponding distribution ratio of the extract within the solid matrix and if adsorbed in it or not (Eggers and Lack, 2012). A few assumptions regarding transport phenomena in solid raw materials are (Eggers and Lack, 2012); 1) The raw material absorbs the fluid, swelling the raw material particles, and expands the pores, improve the movement of extract and solvent; 2) The extract dissolves in the solvent and diffuses to surface layer and passes through it; and 3) The extract passing the surface layer is separated by upstreaming CO_2. Diffusion velocity relays on present extract concentration difference (within particle structure and CO_2).

Like mentioned in the previous paragraph regarding the dependency of CO_2, the best state of extraction seldom produces solubility of the endproduct in solvent that passes a few mass percent (Eggers and Lack, 2012). There is some portion of the endproduct that does not dissolve freely during the interaction between the solute and the matrix of raw materials. This is due to the raw material matrix whether it is absorb or adsorb. In SC-CO_2 extraction phase equilibrium, Perrut et al. (1997) proposed that if the initial concentration in the extracted material is high enough, the equilibrium fluid phase concentration equals to the solubility of the solute concentration in the solvent when the extraction begins until the solid phase concentration decreases the solute concentration in the solid controlling the transition in the equilibrium curve. Then, the remains of solute interact with the raw material matrix and the equilibrium is characterized by a linear relationship with the equilibrium constant for low solute concentrations. In addition, if the extraction begins with solid phase concentration lower than the solute concentration in the solid controlling the transition in the equilibrium curve, the linear equilibrium relationship exerted from the starting point.

In order to developed extraction using SC-CO_2, the knowledge of solubility is vital. Therefore, the design of supercritical fluid requires the solubilities of each component in the supercritical fluid (Wahyu et al., 2013). Many of the solubility and phase equilibrium measurements were conducted to fulfill the necessities for fundamental data for process design purposes and the analytical application. The data are important in determining the optimal operating condition, the selectivity of the extracted solute, and the scale-up criteria. In the process run, the solubility of the solute is represented by extract concentration that can be found at the exit of the extraction vessel (Eggers and Lack, 2012). Most behaviour on solid raw material (seeds) solubility observed that it increases along with temperature and the pressure (Hassan et al., 2000, Nik Norulaini et al., 2004, Akanda et al., 2012, Jokic et al., 2012, Wahyu et al., 2013, Duba and Fiori, 2015b, Cunha et al., 2016).

2.2 Established empirical studies of scaling-up

The study of the scale-up starts with the basic principle of gathering data from process runs in small scale A repetitive set of small scale process run and calculations will be engaged in designing the large scale plant. With advanced mathematics and computation, the design of the commercial scale process configuration, commonly known as a full production scale is made easier for example in del Valle (2012). A systematic process in designing a large scale can be achieved provided with detailed calculations, improvement and fine-tuning from small scale i.e laboratory, pilot. The easy scale-up procedure as described by Akanda et al. (2012) for $SC\text{-}CO_2$ extraction consists of two steps, one is to perform small scale assays in order to define the optimal conditions through screening of operational parameters and the second is to select the scale-up method based on the kinetic limiting factors.

In scale-up terms to achieve a successful design, it requires empirical information that secured experimentally in with a small scale (i.e laboratory scale) and theoretical analysis. Analysing the scale-up criteria of SC-CO_2 extraction grants the prediction of the performance of the process at large scale derived from the small scale data. Since multiple research conducted on the scale-up are specific to the conditions and designed outputs of the researchers, it is a more judicious move to initiate collection of own set of laboratory tests for the purpose of the accumulation of data to support the specific scale-up (Sharif,2012). Nonetheless, data on scale-up expounded a guide to bring the laboratory or pilot scale to an even larger size at the commercial level.

There were several ways of scale-up methodology identified based on previous studies and summarized in Figure 2.2 in which later also included in Table 2.2 – 2.6. The scale-up of SC-CO_2 extraction is either by direct knowledge transfer from a small scale or using constant criteria as a component for upscaling. Alternative 1 and Alternative 4 respectively described upscaling by utilizing only simulation assisted by process simulation programming and software. Alternative 2 and Alternative 5 respectively described the upscaling by conducting real process runs i.e experiment without the process simulation. Alternative 4 and Alternative 3 respectively described the upscaling by utilizing both real and simulation of the extraction process. From Table 2.2 – 2.6, the most widely used effective method for upscaling is the “principle of similarity”. It shows examples of SC-CO_2 extraction upscaling for the bioactive compound from various plant matrix. From previous researches divulged that more prominent scale-up criteria were the usage of mathematical models, empirical equations of the bed geometry as well as kinetic parameters, such as pressure, temperature, extraction period and supercritical fluids used.

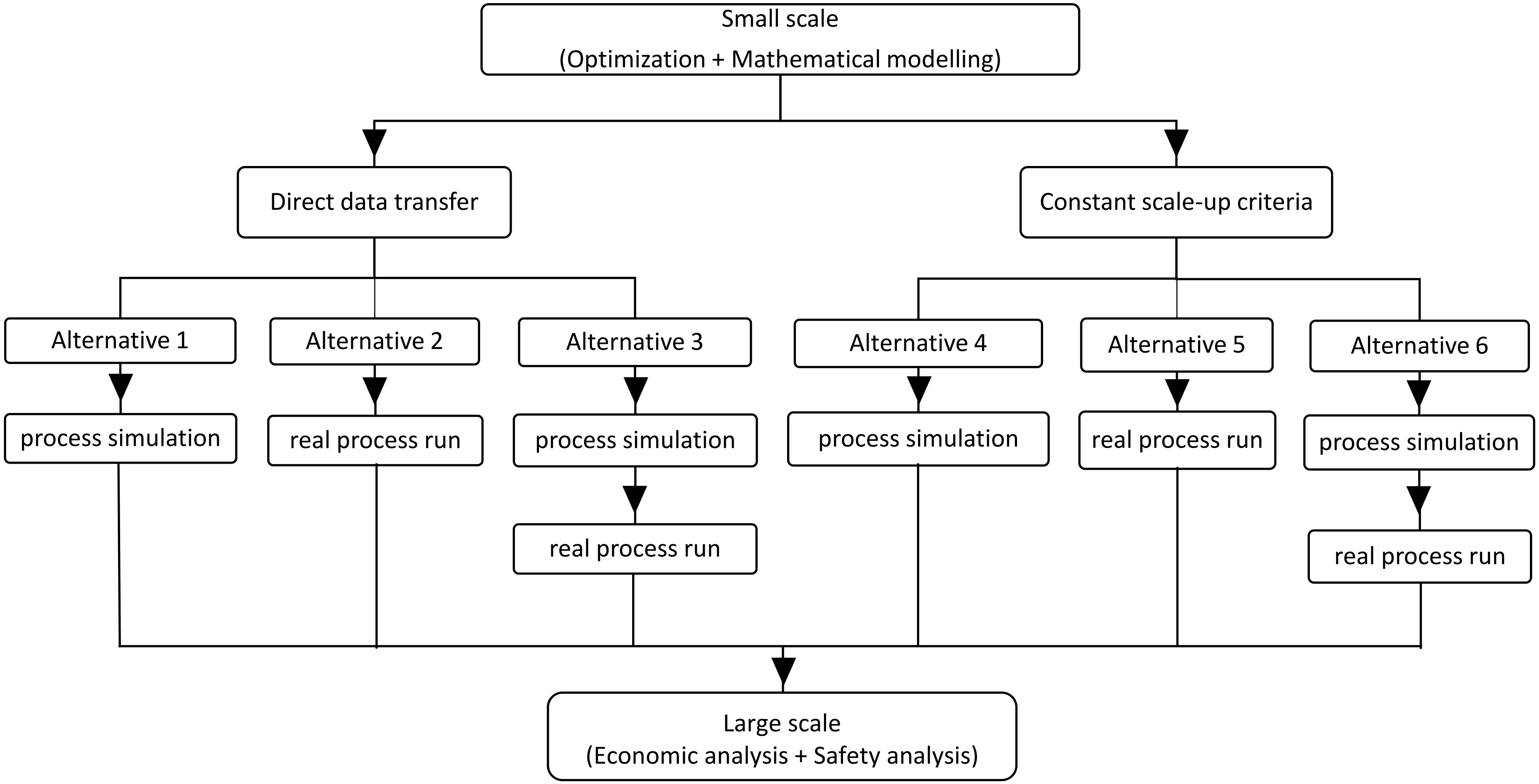

Figure 2.2 Summarised the scale-up methodology process based on previous studies

Table 2.2 Scale-up studies for SC-CO_2 extraction from 2000s – recent year

Raw Material	**Scales**	**Unit Capacity**	**Scale-up Method**	**Scale-up Criteria**	**References**
Annatto *(Bixa orellana L.)* Seeds	Laboratory Laboratory	0.00657 L 0.29 L	Alternative 5	Constant $\frac{m_f}{m_B}$	Albuquerque and Meireles (2012)
Artemisia annua L. Leaves	Laboratory Pilot	0.05 L 50 L	Alternative 5	Constant $\frac{\dot{m}_f}{m_B}$	Baldinoa et al. (2018)
Chamomile *(Matricaria chamomilla)* Flower Heads	Laboratory Intermediate	0.06 L 5 L	Alternative 3	Application model by Hong et al. (1990) and Brunner (1987)	Kotnik et al. (2007)
Clove *(Eugenia caryophyllus)* Buds	Laboratory Intermediate	0.29 L 2 x 5.15 L	Alternative 5	Constant $\frac{m_f}{m_B}$	Prado et al. (2011)
Clove *(Eugenia caryophyllus)* Buds	Laboratory Laboratory	0.005 L 0.3 L	Alternative 6	Application BIC model (Sovová, 1994) with constant value of constant ν_f and constant $\frac{\dot{m}_f}{m_B}$	Martínez et al. (2007)
Clove *(Eugenia caryophyllus)* Buds	Laboratory Intermediate	0.005 L 0.3 L	Alternative 6	Application desorption–dissolution–diffusion (DDD) Mechanism model with constant ν_f and constant $\frac{\dot{m}_f}{m_B}$	Hatami et al. (2010)
Feverfew (*Tanacetum parthenium*) Flower Heads	Laboratory Intermediate	0.06 L 4 L	Alternative 3	Application model by Hong et al. (1990) and King et al. (1997)	Cretnik et al. (2005)
Ginger *(Zingiber officinale var. Amarum)*	Laboratory Pilot	2 x 1 L 2 x 50 L	Alternative 5	Application of DOE's Taguchi method: $L_9(3^3)$ orthogonal array with constant $\frac{m_f}{m_B}$	Salea et al. (2017)

Table 2.3 Table 2.2. Continued

Raw Material	Scales	Unit Capacity	Scale-up Method	Scale-up Criteria	References
Ginger *(Zingiber officinale var. Amarum)*	Laboratory Pilot	2 x 1 L 2 x 50 L	Alternative 5	Application of DOE's Taguchi method: $L_9(3^3)$ orthogonal array with constant $\frac{m_f}{m_B}$	Salea et al. (2017)
Grape *(Vitas vinifera)* Seeds	Laboratory Intermediate	0.29 L 2 x 5.15 L	Alternative 5	Constant $\frac{m_f}{m_B}$	Prado et al. (2012)
Grape *(Vitas vinifera)* Seeds	Laboratory Intermediate	0.001 L 2 L	Alternative 2	Extrapolation by DOE's Taguchi method: $L_9(3^3)$ orthogonal array	Cao and Ito (2003)
Lemon Verbena *(Aloysia triphylla)* Leaves	Laboratory Intermediate	0.29 L 2 x 5.15 L	Alternative 5	Constant $\frac{m_f}{m_B}$	Prado and Meireles (2014)
Mampat *(Cratoxylum prunifolium)* Dyer Leaves	Laboratory Intermediate Industrial Industrial Industrial	0.001 L 2 L 124 L 209 L 291 L	Alternative 2	Extrapolation by DOE's Taguchi method: $L_9(3^3)$ orthogonal array	Cao et al. (2000)
Mango *(Mangifera indica L.)* Leaves	Laboratory Intermediate	0.1 L 5 L	Alternative 6	Application of BIC model (Sovová, 1994) with constant value of $\frac{m_f}{m_B}$, $\frac{\dot{m}_f}{m_B}$, $\frac{\dot{m}_f \cdot d_{int}}{m_f}$, Re	Fernández-Ponce et al. (2016)
Marigold *(Calendula officinalis L.)* Flowers	Laboratory Intermediate	0.022 L 6.5 L	Alternative 2	Extrapolation direct from small scale's data	Baumann et al. (2004)
Marigold *(Calendula officinalis L.)* Flowers	Laboratory Laboratory Intermediate	0.27 L 1.35 L 5.19 L	Alternative 6	Application of BIC model (Sovová, 1994) with constant value of constant ν_f and constant $\frac{\dot{m}_f}{m_B}$	López-Padilla et al. (2017)

Table 2.4 Table 2.2. Continued

Raw Material	**Scales**	**Unit Capacity**	**Scale-up Method**	**Scale-up Criteria**	**References**
Orange *(Citrus snninensis L.)* Peel	Laboratory	0.36 L	Alternative 6	Application of BIC model (Sovová, 1994) with been developedconstant value of $\frac{m_f}{m_B}$ and $\frac{\dot{m}_f}{m_B}$	Berna et al. (2000)
	Intermediate	5.18 L			
Peach *(Prunus persia)* Kernels	Laboratory	0.1 L	Alternative 6	Application of BIC model (Sovová, 1994), Logistic model, and Diffusion model (Crank, 1987) with constant value of $\frac{m_f}{m_B}$, $\frac{\dot{m}_f}{m_B}$, both latter, and the former two with Re	Mezzomo et al. (2009)
	*NS	*NS			
Pelletized *(Solanum lycopersicum)* tomato	Laboratory	0.05 L	Alternative 2	Extrapolation by DOE's full factorial design	Núñez et al. (2011)
	Intermediate	0.5 L			
	Intermediate	1.3 L			
	Intermediate	4 L			
Pine *(Pinus brutia)* Bark	Laboratory	0.3 L	Alternative 5	Constant $\frac{m_f}{m_B}$	Yesil-Celiktas et al. (2009)
	Intermediate	6.5 L			
Rice *(Oryza sativa L.)* Bran	Laboratory	0.1 L	Alternative 3	Extrapolation model by Brunner (1987)	Danielski et al. (2005)
	Intermediate	4 L			
Rosehip *(Rosa moschata)* Seeds	Laboratory	0.05 L	Alternative 3	Application model that described to be one –dimensional, unsteady state with axial dispersion of solute with BIC model (Sovová, 1994)	del Valle et al. (2004)
	Intermediate	1.9 L			

Table 2.5 Table 2.2. Continued

Raw Material	Scales	Unit Capacity	Scale-up Method	Scale-up Criteria	References
Safflower *(Carthamus tinctorius L.)* Seeds	Laboratory	0.5 L	Alternative 1	Extrapolation by BIC model (Sovová, 1994)	Han et al. (2009)
	Pilot	260 L			
Soybean *(Glycine)*	Laboratory	0.2 L	Alternative 6	Application of BIC model (Sovová, 1994) with constant value of $\frac{\dot{m}_f}{m_B}$ and $\frac{h_{int}}{d_{int}}$	Jokic et al. (2012)
	Intermediate	5 L			
Striped weakfish *(Cynoscion striatus)* Wastes	Laboratory	0.0056 L	Alternative 6	Application of BIC model (Sovová, 1994), Crank model (Crank, 1987), Lee et al. (1986) model with constant value of $\frac{\dot{m}_f}{m_B}$	Aguiar et al. (2012)
	Laboratory	0.3 L			
Sugarcane *(Saccharum officinarum)* Filter Cake	Laboratory	0.29 L	Alternative 5	Constant $\frac{m_f}{m_B}$	Prado et al. (2011)
	Intermediate	2 x 5.15 L			
Sunflower *(Helianthus annuus L.)* Leaves	Laboratory	0.0001 L	Alternative 5	Constant Re , $\frac{h_{int}}{d_{int}}$, $\frac{\dot{m}_f \cdot d_{int}}{m_f}$	Casas et al. (2005), Casas et al. (2009)
	Intermediate	2 L			
	Intermediate	6.5 L			
Tasmanian bluegum *(Eucalyptus globulus)* Bark	Laboratory	0.5 L	Alternative 6	Application model by Brunner (1987), Cocero and García (2001) model, Simple single plate model (Gaspar et al., 2003), Diffusion model (Crank, 1987) with constant $\frac{\dot{m}_f}{m_B}$	de Melo et al. (2014a)
	Intermediate	5 L			
	Pilot	80 L			