



Cape Peninsula
University of Technology

**MULTI-PRODUCT FRACTIONATION OF ROASTED PEANUTS USING
SUPERCRITICAL CARBON DIOXIDE (SCCO₂): EVALUATION OF PROCESS
ALTERNATIVES**

by

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**In the Faculty of Built Environment and Engineering at the Cape Peninsula
University of Technology**

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DECLARATION

I, Zezethu Siqungathi, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

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ABSTRACT

Peanuts are grown for their nutritional value – the oil is particularly high in monounsaturated fatty acids, and the pulp is high in protein. When roasted, peanuts have a typical aroma that is valued in confectionary. They also contain a range of wax compounds. Peanut oil extraction is a multistep process that includes solvent extraction or cold pressing, degumming, neutralization, winterization, and deodorization. Industrially, hexane is used as the solvent in solid liquid extraction. The process is thus associated with drawbacks such as residual organic solvent persistent in the product, along with an adverse environmental impact and safety issues. Cold pressing is also used, but it is associated with low yields. Consumer trends necessitate exploring sustainable processes with minimum health and environmental risks.

Substituting hexane with a dense form of carbon dioxide, known as supercritical carbon dioxide (scCO₂) yields a process with no risk of residual organic compounds, nor the associated adverse safety or environmental concerns, since CO₂ is generally accepted as safe for use in food and medical products manufacture. CO₂ has a rather poor solvent power, yet it can be recycled without the need for additional process such as distillation to separate the product from the solvent – since the gas spontaneously separates from the liquid upon depressurization. The cost of the solvent is therefore minimum. In addition, its solvent power is a strong function of its density. Hence, its solvent power is easily adjustable through manipulating pressure. As a result, when CO₂ is used as a solvent, high values of selectivity can be achieved.

When these advantages are applied to peanut processing, then a question worthy of research arises: can the high selectivity's obtainable using scCO₂ as a solvent enable the processing of peanuts by successive extraction of each of the product? Hence, a hypothesis can be postulated: The high selectivity's obtainable using supercritical CO₂ can enable the components of peanuts to be removed successively from the feed material at different conditions; thus, peanut oil, free fatty acids, peanut aroma, and the protein rich residual could be obtained successively, and separately, from a batch of peanuts. The overall aim of this work was to prove (or disprove) this hypothesis experimentally. Questions arise from this hypothesis: what are the main compounds making up each of the envisaged products? Are the solubilities of each product in CO₂ sufficiently different as to enable an acceptable separation? If so, what are the conditions under which these different separations can occur?

Can this process compare economically with the above-mentioned current process? These research questions are used to formulate the corresponding objectives.

The typical chemical compositions of each of these was obtainable from the literature. Literature sources were also used to obtain the experimental equilibrium data describing the solubility – or the phase behaviour of the major compounds that make up each of these fractions in scCO₂. These were used to perform an initial prediction of the possibility of separation using scCO₂. The data was also used to perform an initial prediction of the conditions under which this separation could possibly occur. Experimental tests were performed, at pilot plant scale to validate the predictions. Finally, any technically feasible separation was then analyzed for its possible economic viability based on the typical operational costs found in the literature. The results obtained can be summarized as follows: when predicting the feasibility of separation of binary systems, oleic acid and triolein at 40°C produces better chances of enrichment between the concentration ranges of 0.1-0.282. The same behaviour was noticed for linoleic acid in triolein, and assuming that there's no interaction at concentration ranges 0.125 and 0.236, then the mixture can be separated completely due to the dissolution of linoleic acid in CO₂.

Tripalmitate and oleic acid, pressures from 310 bar and above indicate that only tripalmitate can be enriched in mixture while at low pressures of 71 bar to 290 bar only oleic acid is enriched. At pressures above 290 bar up to 500 bar only tripalmitate can be enriched while at low pressure below 200 bar only linoleic acid can be enriched. For the validation of separation efficiency, the highest yield obtained at 150 was 18.39% while at 250 bar the yield increased to 47.8% and finally at 350 bar the highest extracted yield was 75.99%. The curves at 150 and 250 bar show a linear behaviour meaning the increase in the slopes represent a rise in solubility of the oil in solvent. A high temperature of 60°C produced the highest extraction yield by increasing the mass of the carbon dioxide used. The best separation would be obtained at 40°C and varying pressures for different classes of compounds: 150, 250 and 350 bar for aroma compounds, free fatty acids and triglycerides respectively. While there are laboratory bench scale studies on SCF extraction of food grade peanut oil from peanut kernels, there is no information which could be found in the survey of literature on the economic feasibility of such a process. This research would provide reference data and a baseline study on the extraction of triglycerides from the oil in order to determine the techno-economic feasibility of the process. This information will be useful in process scale up.

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DEDICATION

For my late mom, Nosayinethi Mandicate Siqungathi

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GLOSSARY

Terms/Acronyms/Abbreviations

Definition/Explanation

SCF	Supercritical fluid
CO ₂	Carbon dioxide
scCO ₂	Supercritical carbon dioxide
FFA	Free fatty acids
VLE	Vapour liquid equilibrium
FAMEs	Fatty acid methyl esters
GC-MS	Gas chromatography–mass spectrometry
HPLC	High-performance liquid chromatography

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Peanuts, otherwise known as *Arachis hypogea* L. are a large world crop and member of the Leguminosae family native to South America (Sharma and Bhatnagar-mathur, 2006). They are aromatic associated seeds with medium roast having fragrant characters such as methyl pyrazines that boost the flavour of the oil (King, 2002). Worldwide, above one-third of these peanuts are produced for food use because of their nutritional value and high oil content (Sanders, 2003a). To extract oil from these seeds, two primary methods have been identified, mechanical and chemical extraction, which involves a series of steps; cracking into small pieces, mechanical pressing, and solvent extraction (Mukhopadhyay, 2009). The oil obtained comprises aroma compounds, triglycerides, and high portions of unsaturated fatty acids, oleic and linoleic acid. Mechanical pressing does not offer a way of selectively extracting the oil from the seeds and thus removes about 50% of oil and the remaining is extracted using hexane. Nevertheless, solvent extraction has been regarded with circumspection due to intractable and persistent solvent lingering in the final produce (Matricardi, Hesketh and Farrell, 2015).

Physical methods such as cold pressing does not provide a way of selectively extracting the oil from peanuts and thus require another process step after fractionation called degumming. And solvent extraction using hexane have been regarded with circumspection, due to the intractable problem of persistent solvent remaining in the product. The oil produced from these methods contain several impurities and thus has to be sent for further processing. Green innovation in process engineering is the development of new ideas of processing techniques that lead to environmental improvements compared to the previous methods of production. And because of the need for more natural separation processes alleviating organic chemicals in the final product, SCF extraction is used in the study. This separation technique uses supercritical carbon dioxide This is a process that uses supercritical carbon dioxide ($scCO_2$) as a selective solvent for separating flavours, essential oils and waxes from plant materials (Profile, 2016). Compared to other commonly used solvents, $scCO_2$ produces superior results for its selective extraction (Goodrum and Kilgo, 1987).

1.2 PROBLEM STATEMENT

The current methods of peanut oil extraction used in South Africa are multi step processes. These processes are performed with an idea of increasing the oil stability. However, different processing steps affect the quality of the oil and decrease its shelf life. Although accepted and effective in the extraction of food grade oil, they result in low yield, long extraction times and high energy consumption. Consequently, Supercritical Fluid extraction has become a substitute separation technique because of the promising role for being a cost-effective single step separation technique. It is envisaged that such a concept would preclude many of the challenges encountered in the traditional processing routes. The goal of this study is to advance separation techniques from multi-step to single-step processes. None of the reviewed literature could provide adequate information necessary to determine the techno-economic feasibility of producing food grade oil from roasted peanut in a single step fractionation process.

1.3 HYPOTHESIS

The high selectivity's obtainable using scCO₂ can enable the components of peanuts to be removed successively from the feed material at different conditions; thus, peanut oil, free fatty acids, peanut aroma and the protein rich residual could be obtained successively, and separately from a batch of peanuts.

1.4 RESEARCH QUESTIONS

The study attempts to provide clarity and answers to the subsequent demands:

1. What are the main compounds making up each of the envisaged products?
2. Are the solubilities of each in CO₂ sufficiently be different as to enable an acceptable separation?
3. If so, what are the conditions under which these different separations can occur?
4. Can this process compare economically with the above-mentioned current process?

1.5 STUDY AIM AND OBJECTIVES

The aim of this work is to extract four classes of compounds into four product streams – aroma, triglyceride, fatty acid and wax in a single process pass using supercritical CO₂.

The following objectives are formulated as a means to accomplish the overall aim of the study:

1. To predict, the feasibility of separation based on the phase behaviour of relevant systems, using theoretical considerations.
2. To experimentally validate the efficiency of separation (separation factors and selectivity's for the four compounds of interest).
3. To analyse and compare the process economics using process models
4. To use analytical methods to examine the samples

1.6 METHODS

The typical chemical compositions of each of these was obtainable from the literature. Literature sources were also used to obtain the experimental equilibrium data describing the solubility – or the phase behaviour of the major compounds that make up each of these fractions in scCO₂. These were used to perform an initial prediction of the possibility of separation using scCO₂. The data was also used to perform an initial prediction of the conditions under which this separation could possibly occur. Experimental tests were performed, at pilot plant scale, to validate the predictions. Finally, any technically feasible separation was then analyzed for its possible economic viability based on the typical operational costs found in the literature.

This research will provide the following significant novel contributions:

1.7 RESEARCH SIGNIFICANCE AND CONTRIBUTIONS

- Phase equilibria data of relevant systems in CO₂ for the compounds of interest and a baseline study of the techno-economic feasibility of the process. This information will be useful in the process scale up,
- Feasibility experimental results proving a single-step separation of aroma compounds, triglycerides, and free fatty acids from waxes from peanuts using scCO₂,
- A thermodynamic model with aptitude for precise prediction of complex interaction of solute-CO₂ relevant systems,
- A process model with aptitude for precise prediction of performance for the separation of aroma compounds, triglycerides and free fatty acids from waxes using scCO₂.

1.8 RESEARCH APPROACH

The investigation was approached as follows:

1. The theoretical feasibility of separation was investigated based on the phase behaviour of relevant systems by:
 - a) Representing VLE data of relevant binary systems as thermodynamic equations of state
 - b) These were fitted to experimental binary VLE data found in the literature
 - c) Flash calculations were performed with a model mixture as means to determine the effect of process conditions on the separation
 - d) The calculated distribution coefficients for each component enabled the determination of separation factors between any two components.
 - e) A range of parameters spanning the feasible region was noted, and any separation deemed theoretically feasible was tested experimentally at the pilot plant scale.

2. To analyse and compare the process economics (based on process models),
 - a) Kinetic data is recorded and fitted to a suitable extraction kinetics model
 - b) The feasible options are used to develop a plant-wide process model, whose performance is fitted to experimental data and validated with additional experimental data
 - c) The resultant model enables the rapid exploration of the process performance at a wider range of conditions than the ones performed experimentally
 - d) Last, the kinetic data allows for a batch-wise extraction system to be simulated, sized, and scaled to achieve a production capacity, and the economic performance of the resultant system to be investigated and optimized
 - e) Using sensitivity and optimization techniques, such a model gives a deeper insight into performing the conceptual process.

3. The separability of the different compounds in roasted peanuts was investigated as follows:
 - a) Several approaches were adopted such as the total extraction of all soluble materials
 - b) This was followed by partial extraction with fractional separation which works by separating and the deposition of products in the three separators
 - c) And the fractionation by sequential extraction at progressively increasing solvent density.

Relative to the research approach, the subsequent limitations are established as strategies to the research:

1.9 DELINEATION

- The study is limited to the fractionation of aroma compounds, free fatty acids, triglycerides, and waxes from peanuts using scCO₂ as a solvent,
- Experiments are carried out using only standard analytical methods,
- The research will not include a full economic analysis, instead utility costs and solvent consumption will be used as a reasonable basis for comparison of the running costs for each extraction route.

The layout and organization of this thesis into different chapters is subsequently given below to easily address and answer the research objectives.

1.10 THESIS ORGANIZATION

The thesis is divided into the following chapters:

1.10.1 CHAPTER 1 - INTRODUCTION

This is an introductory section of the thesis which aids as a background to the thesis. It describes the rationale of the study by highlighting the objectives. It also outlines the context within which the study is conducted and the thesis outline. Finally, an overview on how the study will be conducted is provided.

1.10.2 CHAPTER 2 - LITERATURE REVIEW

Relevant literature and theoretical background to the study is reviewed and given in this chapter. For this study, theory on traditional methods employed in the extraction of peanut oil is given with emphasis on their drawbacks. Literature on the proposed method is discussed to give perspective to the gap filled by this study. Finally, theory on process modelling and the analytical methods is discussed.

1.10.3 CHAPTER 3 - FEASIBILITY STUDY

This chapter serves as a description to research process and the stages of the research process. It also addresses the methodology tailored to do all the experimental work. A technical study to determine the feasibility of separation and the energy used and thermodynamic model performances for relevant systems.

1.10.4 CHAPTER 4 - EXPERIMENTAL FINDINGS AND DISCUSSION

This section presents the processed experimental results of the study. The results are processed and discussed in detail.

1.10.5 CHAPTER 5 - CONCLUSION AND RECOMMENDATIONS

The chapter concludes on the results presented in the previous chapter. It includes recommendations and possible further research for the study.

1.10.6 CHAPTER 6 - APPENDICES

This is where all the research appendices and data that cannot go into the actual thesis are presented.

1.11 CHAPTER OUTCOMES

- ✓ This chapter allowed for the formulation and introduction of the research topic and the overview of the study. Additionally, the rationale and the objectives of the thesis are stipulated in detail. And the formulation of the study overview

CHAPTER 2

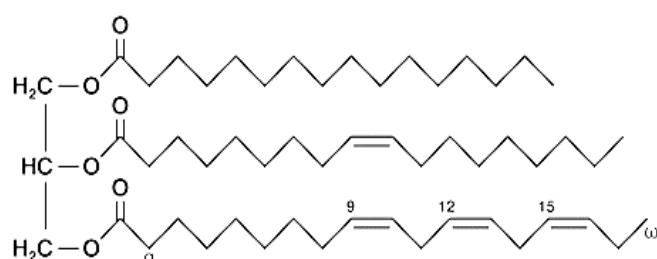
LITERATURE REVIEW

This section of the study aimed at addressing relevant theory required to answer the research objectives one and two. It investigates theory on peanuts, the unique characteristics of a peanuts oil and their applications thereof. The feasibility and viability of peanut oil separation is discussed using conventional methods of extraction. This is intended at establishing the current state of knowledge in the field of extraction. Mathematical modelling and pilot plant scale operation are discussed as methods of operation. Additionally, theory on the methods of analysis and process economics is briefly discussed.

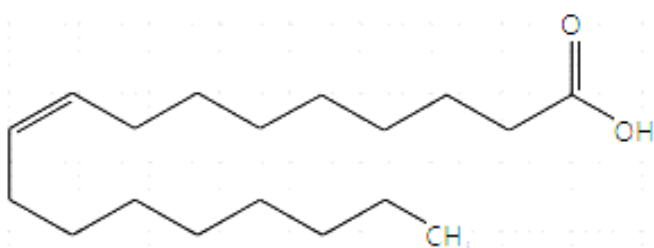
2.1 PEANUTS

Earthnuts are recurrently grown as annual crops in tropical, subtropical, and temperature regions of the world, primarily for their protein-rich seeds which have an oil content ranging between 45% and 55% depending on the variety. Oil from peanuts is generally extracted from the nuts using the common conventional methods i.e., solvent extraction and cold pressing. The pale yellow extracted oil from peanuts is composed of mixtures free fatty acids (mainly oleic and linoleic acid), sterols, phospholipids, triglycerides and aroma compounds (Sanders, 2003a). In this study, roasted peanuts are used because of their unique high level of aromatic compounds also called pyrazines that add flavour to the oil. They are an important source of this research's compounds of interest (List, 2016):

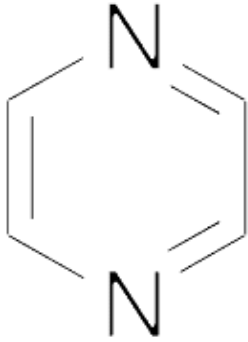
1. Triglycerides:



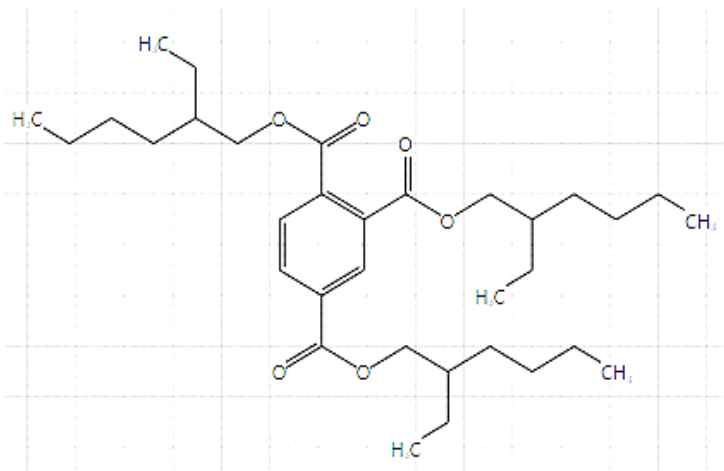
2. Free fatty acids



3. Aroma compound (pyrazines)



4. Wax fractions



5. Protein rich flour



(Nuts.com)

Published literature indicates that Fernandez-Pérez et al., (2008) successfully extracted triglycerides from waxes using an extraction pressure range of range 10-35 MPa and a range of temperatures at 313.15 – 353.15 K. In another work, Spinelli *et al.*, (2016) optimized the extraction conditions of extracting oil compounds and flavonoids from peanuts. They obtained triglycerides and flavour compounds at a pressure of 35 MPa, 40 °C using the fluid CO₂. (Sanders, 2003b) did a study determining the content of fatty acids and other vegetable oils.

The results showed that peanuts have undetectable levels of linoleic acid and they contain higher levels of oleic acid than corn and soybean.

Peanut roasting is a necessary step performed to advance the flavour and aroma of oil.

2.2 PEANUT ROASTING

Roasted peanuts are an important agricultural product because of their unique components that are useful in various industries. This is supported further by a study by Shakerardekani *et al.*, (2011) and (Ozdemir & Devres, 2000; Pittia, DallaRosa, & Lericci, 2001) highlighting the roasting of peanuts as an important processing step in the peanut industry to improve flavour, colour and the texture of the groundnuts. Freitas *et al.*, (2020) further showed the influence of roasting conditions on the quality and acceptance of the peanut paste where the results indicated 140 °C as the optimal roasting temperature with no changes in the tocopherol and oil parameters. Figure 2.2-1 shows the colour of the peanuts during roasting at different temperatures.

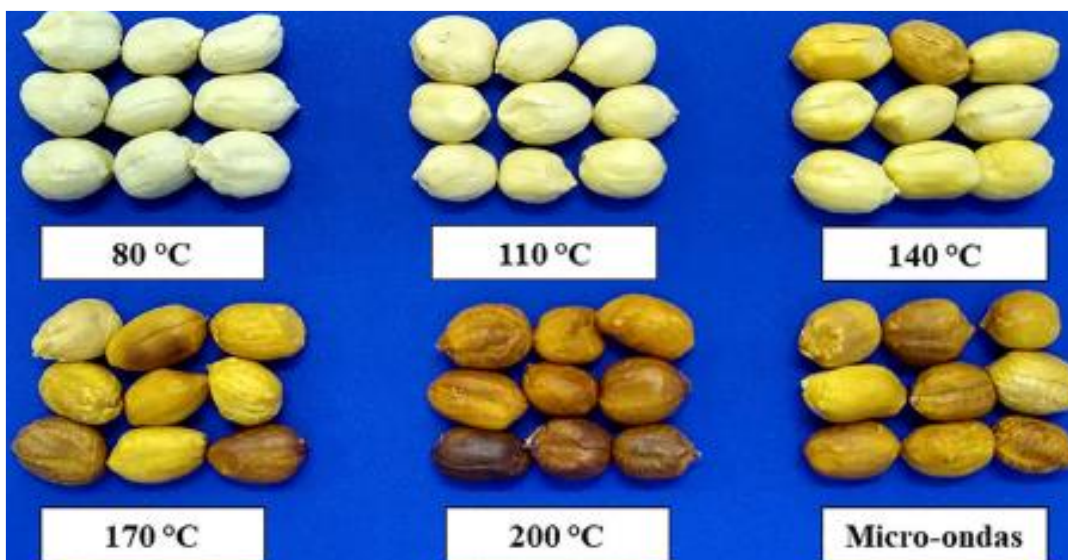


Figure 2.2-1: Roasted peanuts at varying roasting temperatures (Freitas *et al.*, 2020)

2.3 PEANUT APPLICATION

Peanuts are an excellent source of proteins for humans due to their high nutritional percentage of protein by weight. They help improve the quality of diets, especially those based on plant proteins (Arya & Chauhan., 2013). Peanuts are used in different industries:

2.3.1 FOOD INDUSTRY

Traditionally, peanuts were used as the world's source of oil, most of the world's production still goes into cooking oils, margarine, shortenings as well as into the manufacture of soap and other industries (Webb, 2001). Singh *et al.*, (2019) reported on the development of cheese products that are low in fats using supercritical fluid extraction.

The low-fat cheddar and parmesan were treated at the process temperature of 20 °C and 35 MPa and at 40 °C and 35 MPa respectively.

2.3.2 PHARMACEUTICAL INDUSTRY

According to Erdman *et al.*, (2001) processed oil from peanuts is used to lower cholesterol for the reduction of cardiovascular diseases such as heart conditions and for the treatment of cancerous malignant. When applied to the skin, the oil has the capacity to treat enema, joint pains, eczema resulting from dry skins and for the treatment of arthritis. Due to the prudent lipid profile of oil from high contents of oleic acid, it is very beneficial to human health (Arya & Chauhan., 2013). The oil produced from peanuts is rich in monounsaturated fatty acids that decrease the risk of cardiac diseases by dropping the concentration of cholesterol (Sanders, 2003a).

2.3.3 COSMETIC INDUSTRY

Free fatty acids in the oil are used for soap production and the manufacturing of detergents. Some of the uses include converting methyl esters for use as lubricants, detergents, and surfactants (Sanders, 2003a, 2003b). Peanut-derived ingredients are used mainly in the formulation of moisturizers, skincare products, and skin cleansers. However, because of the major allergen in peanuts, compounds extracted from peanuts are mainly not used in cosmetic/personal care products (Oct *et al.*, 2019). Meanwhile, the oil obtained from peanuts usually contains several impurities, it needs further processing and refining to render the oil suitable for use.

Normally, to dissolve a compound, it is important to first select a solvent that has a similar polarity to it and leave the two in contact for a prolonged period. Heating the solvent helps in increasing the number of collisions. One reason liquid is preferred to gases as solvents is that there is a high concentration of molecules attacking the surface of the compound to be dissolved and therefore more solvent-solute bonds can be formed. However, the difficulty with liquid solvents is that, once the compound has dissolved, it needs to separate from the solvent, which is another process step on its own. This separation technique has become prevalent to green technology in different industries. This process is an attractive separation technique over traditional methods because it uses supercritical solvent at high pressures to extract components from plant and animal material. This method is functioned at low temperatures permitting extraction and integrity preservation of thermo-easily altered compounds (Khaw *et al.*, 2017).

2.4 SUPERCRITICAL FLUIDS

According to Mendiola *et al.*, (2003) supercritical fluids are substances with both pressure and temperature higher than its critical values. The dissolving power of a supercritical fluid is vastly dependent on its density which can be influenced by slight changes in the pressure directly affecting the solvent strength. Figure 2.2.4-1 is a typical pressure-temperature phase diagram of CO₂:

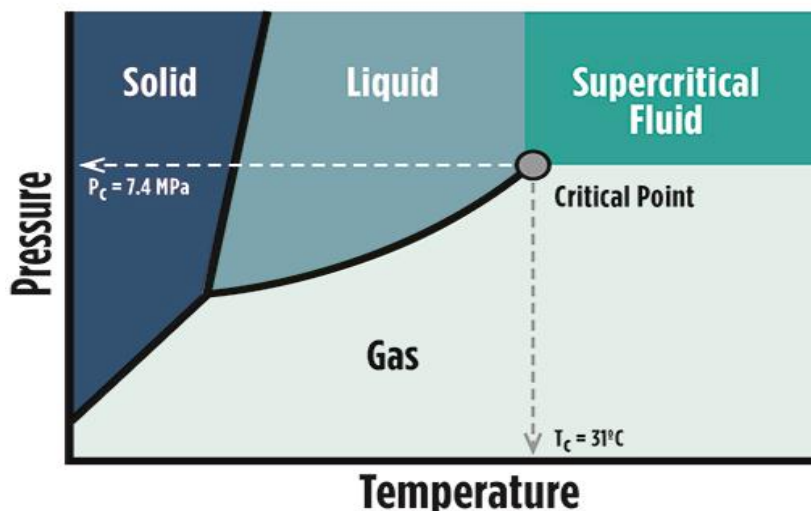


Figure 2.42.4-1: CO₂ pressure-temperature phase diagram (Temelli & Saldaña *et al.*, 2021)

Various supercritical fluids are found in literature and presented in table 2.4-1.

Table 2.4-1: Critical properties of some solvents used in SCF extraction (Mendiola *et al.*, 2003).

Solvent	Critical property		
	Temperature (°C)	Pressure (MPa)	Density (kg/m ³)
Ethene	10.1	5.11	200
Water	101.1	22.0	322
Methanol	-4.4	8.09	272
Carbon dioxide	31.2	7.38	470
Ethane	32.4	4.88	200
Nitrous hexafluoride	36.7	7.26	460
Sulfur hexafluoride	45.8	3.82	730
n-butene	-139.9	3.65	221
n-pentane	-76.5	3.37	237

Even though these compounds are useful in separating techniques, many of them are deemed toxic and hazardous resulting in environmental effects and thus green solvents such as carbon dioxide are an alternative.

2.4.1 CARBON DIOXIDE

For this study, carbon dioxide is proposed and chosen as a supercritical solvent to be used for oil extraction from roasted peanuts. According to Sovová and Stateva, (2011) CO₂ is an easily available, odorless and cheap solvent that doesn't add to the effects leading to ozone depletion.

And due to its low-slung critical properties, carbon dioxide it is suitably used in food, flavour and medicinal industries (Abbas *et al.*, 2008). This solvent is favourable first for its aptitude to yield solvent free products. Moreover, minor variations in its critical conditions results in large deviations in density that allow for solvent strength (Týskiewicz, Konkol and Rój, 2018). Using supercritical fluids over normal liquid solvents is advisable due to their dissolving forte over widespread ranges of temperature and pressure permitting power over properties such as density (Sovová and Stateva, 2011).

2.4.1.1 BENEFITS

Using supercritical carbon dioxide presents the following advantages:

2.4.1.1.1 SOLVENT POWER

The ability of supercritical CO₂ to change density allows for the manipulation of chemical reactions by regulating physical properties including solvent power, diffusivity, and viscosity. Thus, the dissolving power or solvent power can easily be tuned by altering temperature and pressure. This implies that supercritical CO₂ is more favourable for mass transfer than normally used liquid solvents, especially if it is used as a processing medium for extraction and separation (Sovová and Stateva, 2011).

2.5 PROPERTIES OF SUPERCRITICAL FLUIDS

In this study, it is important to have knowledge of the phase behaviour of the process for the determination of the methods to be employed in the SCF extraction. It is significant to know the extraction conditions of oil before the actual process takes place.

2.5.1 SOLUBILITY

The mechanism of SCF extraction is controlled by the pliable solvent density imminent to the critical point (Lombard, 2015). This is defined as the highest dissolvable quantity of a substance in a solvent at a defined temperature (Kalhapure *et al.*, 2019). And this temperature largely affects the ability of a solvent to dissolve a substance by breaking bonds in a solid matrix (Othman, 2012).

Spinelli *et al.*, (2019) optimized the extraction conditions of extracting oil compounds and flavonoids from peanuts. They found out that triglycerides and flavour compounds were obtained at a pressure of 35 MPa, 40 °C using the fluid CO₂. Over time, process technologies have grown and progressed leading to a need for supplementary data in a short space of time. And as such, simulation software and mathematical models have been used by various industries for the prediction of process performances. Extracted oil using SCF extraction at pressures ranges of 10 to 35 MPa and temperatures of 313–353 K and triglycerides successfully separated from waxes (Sovovà and Stateva, 2011).

2.6 SEPARATION TECHNIQUES

Separation processes are aimed at eliminating undesirable components or recovering valuable components to increase the value of products produced. This includes cleaning, sorting, grinding, extracting, and cleansing of different extracts, such as vegetable oils, essential oils, flavours. The specific method of extraction employed depends on the fed plant material and the desired end-product. For this study, the oil to be extracted is not volatile and therefore only a few methods can be used for extraction. Current conventional methods include:

2.6.1 COLD PRESSING

This is a simple method in which the plant material is passed through mechanical spikes that pierce the plant material releasing oil from the cells. The plant material is then squashed to release left over oil which is further separated through a centrifugal process (Mahajan *et al.*, 2015).

2.6.2 DEGUMMING

This process follows extraction and regardless of the process described above (cold pressing), the end product will generally be an impure bio-lipid that contains undesirable contents such as free fatty acids (FFA), tocopherols, waxes, and possibly phosphatides. The latter, if not removed before storage, will produce a thick gum over time. And these waxes are formed when the bio-lipid absorbs water, which causes some of the phosphatides (such as phosphocholine) to become hydrated and thereby lipid insoluble and low temperatures increase the oil viscosity, making phase separation more difficult (Diana da Silva Araújo *et al.*, 2014).

2.6.3 STEAM DISTILLATION

In this process, the plant material is placed into a still where pressurized steam penetrates the plant material, causing internal lipid vacuoles to rupture. Upon exposure to the surrounding environment, the lipid evaporates to form a mixture of easily separable vapours. The vapours condense and concentrate are amassed in a cylinder that is coupled to a condenser.

The major disadvantage associated with steam distillation is the risk of that thermo-labile component being degraded (Saeed Al-hilphy et al., 2015).

2.6.4 SOLVENT EXTRACTION

It is a simple process that separates the wanted product from a solid matrix by means of a liquid solvent i.e., dissolving and separating the soluble desired product (Forde *et al.*, 2014).

The primary aim of every production process is to produce high-quality, minimally processed, and additive-free products. Currently, there is a great demand from consumers for food that has undergone less processing or food with little or no artificial additives. Because of that reason, manufacturing industries have been focusing on improving the quality of food products produced by increasing their shelf life while generating income or making a profit to meet the needs of their customers. The primary aim of every production process is to produce high-quality, minimally processed, and additive-free products.

2.7 ALTERNATIVE SEPARATION TECHNIQUE

The quality of food in the industry is altered during processing because products undergo several processing steps that destroy the quality of products. Food industries are thus looking for alternative separation technologies that will produce products that can be used in several industrial applications. Researchers have been trying to find the best alternative process for oil extraction to minimize environmental effects, decrease toxic residues found in the final product, and produce a high-quality product. The process below has thus been investigated in this study as an alternative method of extraction.

2.7.1 SUPERCRITICAL FLUID (SCF) EXTRACTION

The use of hexane encourages solvent residues in the final product, so the use of scCO₂ would make it easier to separate the solvent from the solute. Under normal conditions, if a gas is compressed too much, it may collapse into a liquid, so careful pressure conditions are chosen (Goodrum and Kilgo, 1987).

2.8 MODELLING TOOLS

Mathematical models are prevailing, and valuable tools used in the scale up and design of SCF extraction techniques. It is impossible to do pilot plant scale up to industrial scales and process cost evaluation without mathematical models. Therefore, the development of modelling tools that will accurately predict the feasibility of peanut oil extraction is essential. These allow the correct design and optimization of the process. Additionally, they are used to optimize and determine the energy requirements of the process.

These help to save cost and time by eliminating long hours in the laboratory for the determination of experimental data. Instead, indispensable data is predicted through modelling tools.

2.9 MATHEMATICAL MODELLING

Rad et al., (2019) reported on a study by Yu et al., (1994) where the solubility was correlated using theoretical approaches using equations of state, more specifically empirical equations. Therefore, semi empirical or empirical equations are more commonly used for solubility prediction at limited temperature and pressure range. Taseski, (2015) reported on a study by Reverchon & De Marco 2006; Tabernero et al. (2013) where the integration of transfer and mass balance was commonly used for the evaluation of extraction before experimental studies.

2.9.1 VAPOUR LIQUID EQUILIBRIUM (VLE) DATA

This data outlines the disposition of components which between two phases i.e., liquid and vapour phase in equilibrium. Separation processes are founded on the concept of VLE data. It is therefore essential to collect VLE data at specified separation conditions for the development of a process model. This data is plotted into phase diagram that outline the phase behaviour of a model mixture. In the study, the vapour liquid equilibrium data of binary mixtures are collected from literature. This data is then processed by theoretical models and used to plot phase equilibrium diagrams.

2.9.2 PHASE BEHAVIOUR

Phase behaviour can easily be defined as the way components act or conduct themselves in carbon dioxide at equilibrium. This behaviour is seen from two phase equilibrium diagrams that demonstrates the solubility of components over a varied supercritical temperatures and pressures. Based on the understanding of these diagrams, a blueprint for simplifications of the phase equilibrium principles can be formed. This helps save time and energy in the determination of the solubility of a component (Gubbins et al., 1983). Once this is known, thermodynamic modelling is introduced by means of equations of state. Since the everyday running of experiments in SCF extraction plants would be time-consuming and quite costly, the prediction of the feasibility of the process is much cheaper and achieved quickly by the modelling and simulation of the proposed processing scenarios. Thermodynamic modelling thus makes it easier to find the feasibility of the process and these models are useful and significant tools.

2.9.3 THERMODYNAMIC MODELLING

The main idea behind thermodynamics is thermodynamic equilibrium.

Based on the binary data, this part of the research involves fitting thermodynamic modelling interaction parameters such as Peng Robinson. This is meant to properly define the performance of binary systems using equations of state. It is therefore important to model the thermodynamics to enable the fitted equations to be used in a simulator to predict VLE and other physical properties (Eze and Masuku, 2018). There's one useful approach for supercritical extraction modelling (Eze and Masuku, 2018): Experimentation on SCF extraction is very expensive, thus the prediction of the feasibility of the process is much cheaper and quickly achieved by modelling and simulation of the proposed processing scenarios. It is therefore important to explore the mathematical modelling in common use. In literature, the solubility of different components of the oil can be found, but the data found is discreet data points. To convert those values into data for use, modelling is required. Since the everyday running of experiments in the SFE plant would be time-consuming and quite costly, the prediction of the feasibility of the process is much cheaper and achieved quickly by the modelling and simulation of the proposed processing scenarios. Thermodynamic modelling thus makes it easier to find the feasibility of the process. There are three methods used for supercritical extraction modelling (Eze and Masuku, 2018). Different thermodynamic models are used:

2.9.3.1 EMPIRICAL KINETIC EQUATION

This model works by describing experimental data (da Silva *et al.*, 2014; Lombard, 2015). It is founded on empirical kinetic equation used to define the investigational data (Eze and Masuku, 2018). It is normally used and useful where there is no data on equilibrium relation. These models have the advantage of simplicity and because the economics of the process depends on the rate at which the process proceeds. These models are not satisfactory for scaling up but they are advantageous for their simplicity. This model is significant because the economics of the process depends on the rate at which the process proceeds. If the process occurs rapidly then many baths are fit in. If the process is slow then a bigger plant to fit many batches in one is required. The cost of every process is made from both the capital and operational cost. The capital of SCF extraction is very high because the plant operates at very high pressure, requiring thick of the materials of construction to withstand the pressure. However, the operational cost is very cheap because the solvent is recycled.

2.10 PROCESS ECONOMICS

An example of a comparative study focussing on supercritical technology was done by Crause and Nieuwoudt, (2003), who compared the economics of de-oiling and fractionation of paraffin wax using supercritical technology with that using short path distillation and static crystallization. In this study, oil was defined as any paraffin lighter than n-C20.

A minimum of 70% recovery was required where the economic evaluation was based on 100 000 tons per annum of crude wax. It was found that based on economics only, molecular distillation seemed to be the cheapest of the three processes. However, it was also noted that this result would not hold for higher chain length paraffin waxes. The boiling point of paraffin waxes rises quickly with chain length, even at very low pressure, necessitating the use of electricity or furnaces to heat the heat transfer fluid, instead of steam, resulting in a more expensive process. Furthermore, a normal cooling process would cause solidification (congealing) of the wax, necessitating a tempered cooling process, which is an added expense.

2.11 ANALYTICAL METHODS FOR PEANUT OIL

These methods necessitate sensitivity, accuracy and precision for the analysis of the yield. They are used to determine the quality of the products using chromatographic measures. They provide the viability and value of the oil. Different techniques are used:

2.11.1 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

This method is used for quantitative analysis. It works by separating, identifying, and quantifying each component in a mixture. The components in a mixture are identified in terms of peaks in chromatogram. This is an instrumental method that achieves separation that is effectual by employing stationary phases comprising small particles. It has also been known for forcing moveable segment over a motionless stage (Moreno-Arribas and Polo, 2009).

2.11.2 GASS CHROMATOGRAPHY – MASS SPECTROMETRY (GC-MS)

This technique is typically employed in the separation and analyses of compounds from a mixture by means of vaporisation. When GC is coupled with MS there is disintegration or fragmentation of the molecules in the MS, which is used to determine structure and molecular weight of the molecules. A solid would have to go through the process of extraction first. This is however not valid for all liquids but only for volatile and semi-volatile compounds. This is the reason you to derivatize fatty acids to methyl esters to make them volatile. Article (2016) concluded on his study *A. hypogaea* L. oil is a good source of unsaturated fatty acid, his results showed oleic, linoleic, palmitic, and stearic acids as the main fatty acids in the oil.

2.12 CHAPTER OUTCOMES

- ✓ The outcome of this chapter was providing literature on roasted peanuts and the oil characteristics applicable in various industries is discussed. An alternative separation technique that uses supercritical CO₂ as a solvent in a single-step fractionation process for the simultaneous extraction of four compounds of interest is discussed in detail.

- ✓ The development of the model through theoretical models

- ✓ The extraction of data produced by previous authors aids in fulfilling objective 1 and 2. The literature is discussed based on the principles of supercritical CO₂. The oil composition provides the basis for the discussion pertaining to the analysis of results.

CHAPTER 3 FEASIBILITY STUDY

This chapter is aimed at addressing project objective 1, 2 and 3 by investigating the phase behaviour of relevant systems with an emphasis on process feasibility using theoretical considerations. The chapter outlines the precise modelling methodology, experimental validation and economic feasibility approach for addressing project objective 3. The intention is to discuss the experimental design, setup and procedure. The standard material and chemicals used are highlighted including the discussion of the kinetic study methodology. A section on the start-up, step by step method and shutdown procedure is highlighted in the appendix. The development of any product, solution or system should not begin without a clear set of operating standards. And every working system requires a working and feasible slant, this means that all of the project's relevant factors are considered to reach the goal. Therefore, Figure 3.1-1 depicts an approach that is followed in executing the project objectives.

3.1 RESEARCH APPROACH

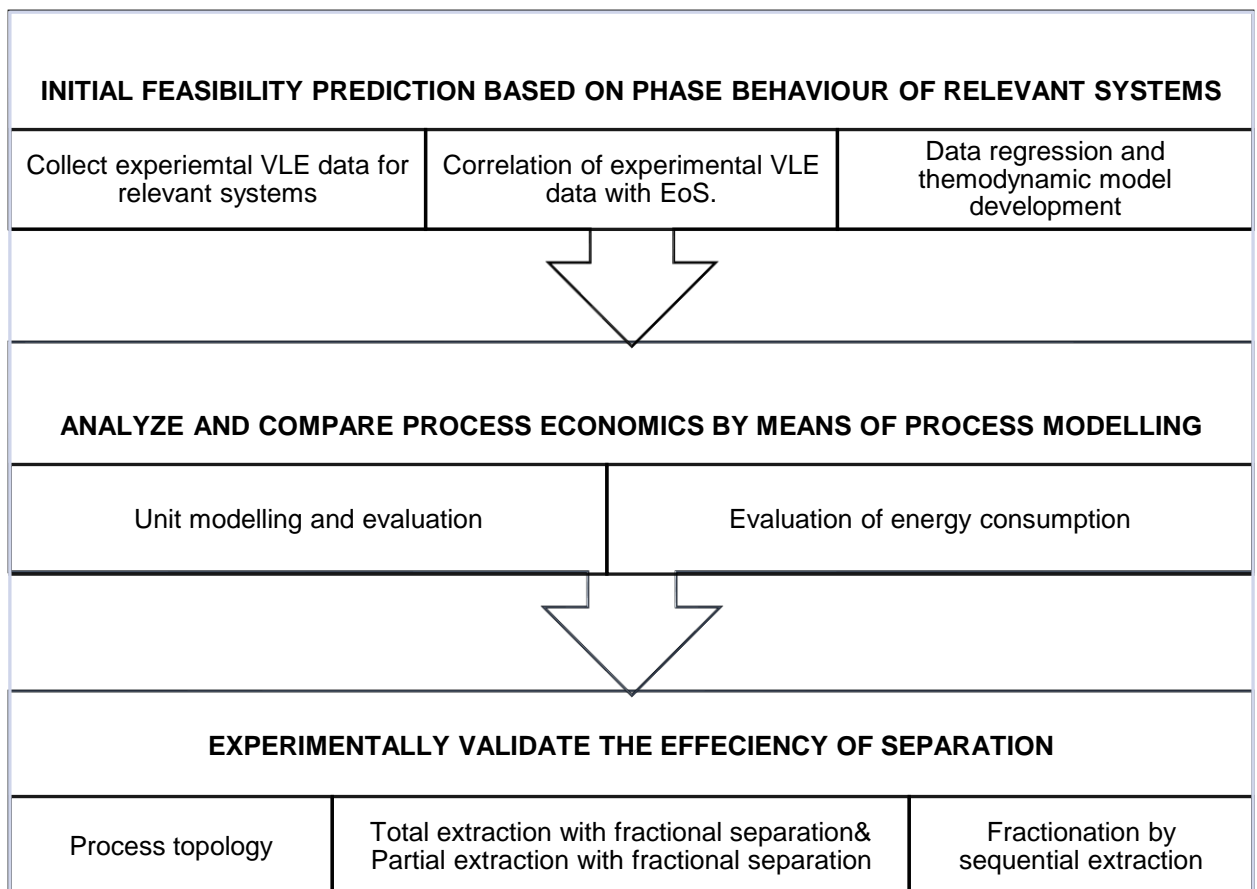


Figure 3.1-1: Research implementation approach

A theoretical prediction of the feasibility of separation of pure fractions from a model mixture composed of triglycerides, fatty acids, and aroma compounds is performed based on the phase behaviour of the binary mixtures of the model compounds with scCO₂. These models enable the correlation and prediction of solubility of solids in scCO₂.

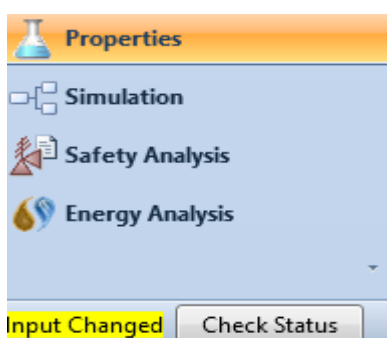
3.2 SEPARATION FEASIBILITY PREDICTION

Thermodynamic modelling makes it easier to find the feasibility of the process. Various thermodynamic models included in the Aspen Plus® software are tested on their predictive capacity with respect to both binary and multi-component systems. For the study, the experimental, kinetic data is collected from available literature and fitted to a suitable extraction kinetics model. The feasible options achieved at this stage results in the develop a plant-wide process model, whose performance is fitted to the experimental data, and validated with additional experimental data. The first step involves predicting the separation feasibility by means of VLE data:

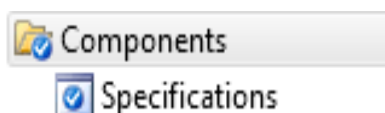
3.2.1 VLE DATA COLLECTION

The vapour liquid equilibrium data is necessary for modelling and controlling the equipment's of different chemical processing. Collecting and sampling at high pressures is not an easy task and can cause disorders in the process equilibrium. Therefore, VLE data is obtained from literature to determine the feasibility of separation of the four fractions of interest by comparing their phase behaviours in CO₂.

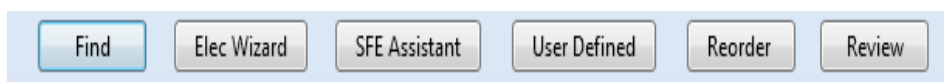
1. Using a process simulator, the method begins by choosing “properties” on aspen plus to fill in the relevant information.



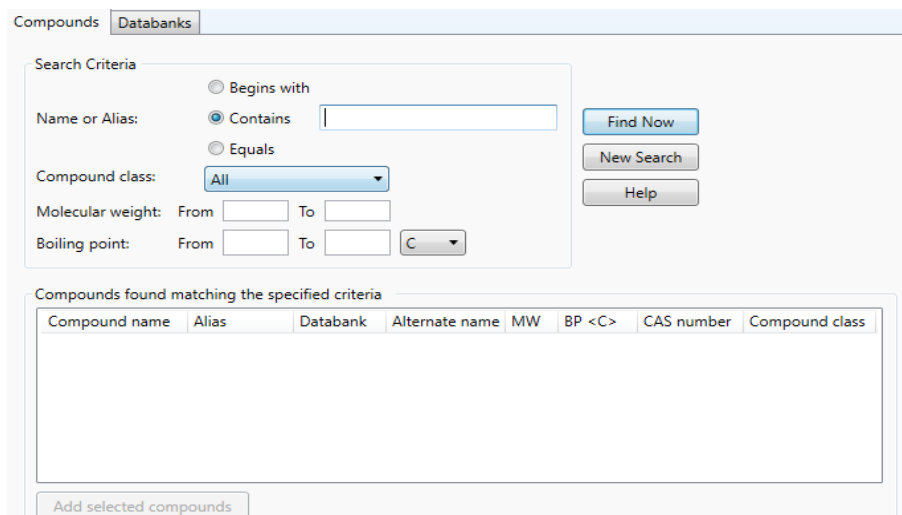
2. And under the properties folder, you choose components. However, it is important to allow the computer to guide you. The easiest way to go about this method is that after you have selected properties, you press next, and the computer will guide you to filling the relevant components for your study.



- The next step will be to find the different components to be used in your study using the Aspen NIST data base.



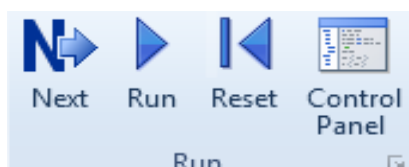
- This is done by going to 'find' on the tab as represented below and you either search the name of the component or the molecular structure of the component. Once the component is found you press "add selected component" at the bottom right of the screen and the component will be added to the list as presented by number 5 below.



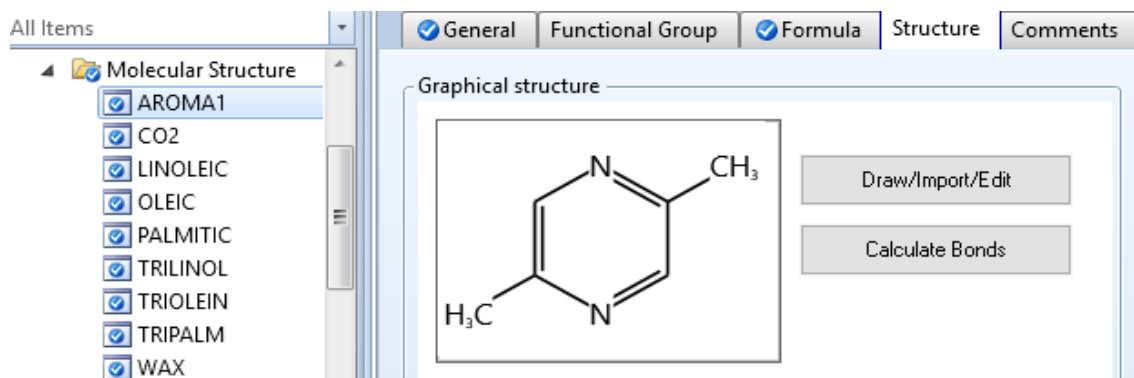
- For my study, the following components were used and determined using the NIST database. The tab written "component ID" allows you to edit the components according to the names suitable for your remembrance or for your use.

Component ID	Type	Component name	Alias
OLEIC	Conventional	OLEIC-ACID	C18H34O2
LINOLEIC	Conventional	LINOLEIC-ACID	C18H32O2
TRIOLEIN	Conventional	TRIOLEIN	C57H104O6
CO2	Conventional	CARBON-DIOXIDE	CO2
PALMITIC	Conventional	TRIPALMITIN	C51H98O6
TRIPALM	Conventional	N-HEXADECANOIC-ACID	C16H32O2
TRILINOL	Conventional	TRILINOLEIN	C57H98O6
AROMA1	Conventional	2,5-DIMETHYLPYRAZINE	C6H8N2-N1
WAX	Conventional	TRIOCTYL-TRIMELLITATE	C33H54O6

- Once all the relevant components have been found then press "next" or "run" on the top ribbon of the Aspen simulator to allow you to move to the next step.



- The next step involves the molecular structures of the chosen components for the study. This is done by ensuring that the tab labelled “general”, “formula” and “structure” have been ticked blue. This means that the necessary information has been filled. At times the molecular structure is provided by Aspen however the bonds have not been calculated so you press “calculate” bonds. But at times the structure is not recorded in the database, you are then required to draw it by pressing “draw/import/edit” tab. Ensure that this step has been completed for all the components and when they are done, the system will mark them blue as shown below. Once this is done press “run”.

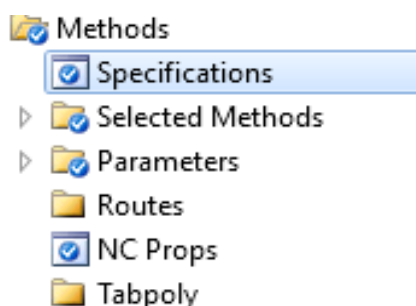


It is important that the data be correlated with equations of state best suit or describe the data based on the phase behaviour of the system.

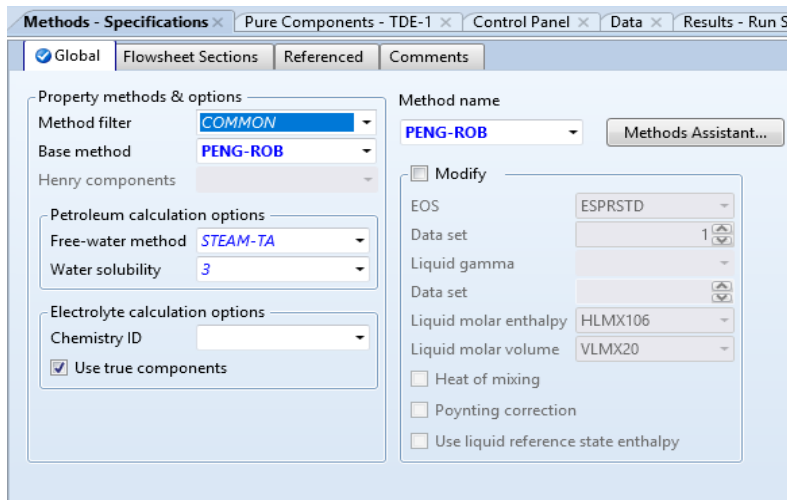
3.2.2 CORRELATION OF EXPERIMENTAL VLE DATA WITH EOS

In Aspen Plus, the estimation methods are stored in what is called a “property method”. A property method is a collection of estimation methods to calculate several thermodynamic (fugacity, enthalpy, entropy, Gibbs free energy, and volume) and transport (viscosity, thermal conductivity, diffusion coefficient, and surface tension). In addition, Aspen Plus stores a large database of interaction parameters that are used with mixing rules to estimate mixtures properties. When you select a property method, you are in effect selecting a number of estimation equations for the different properties. This is done by:

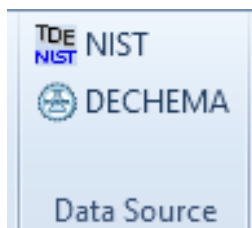
- Choose the type of method you will use to correlate the data by going under specification



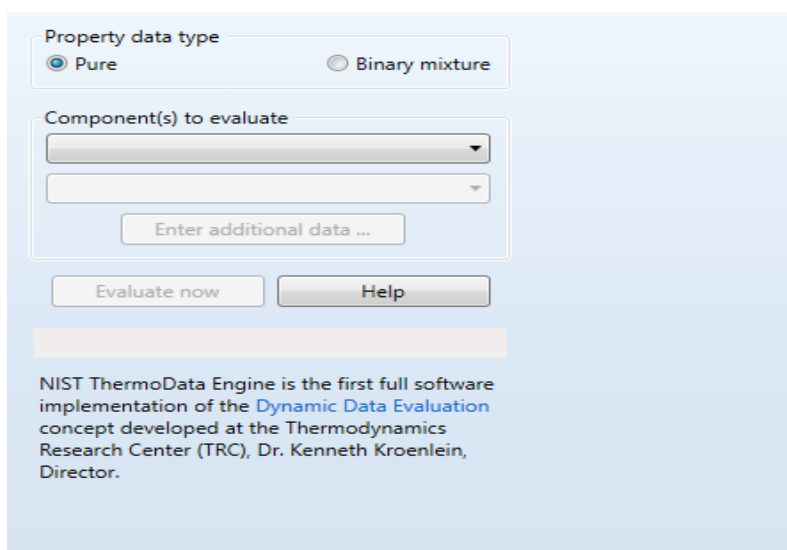
9. Under method specification in the tab labeled “global” you choose the base method and ensure that it is the same as the method name. You are allowed to write something under “comments” that will help you, even if it is the reason behind choosing the method



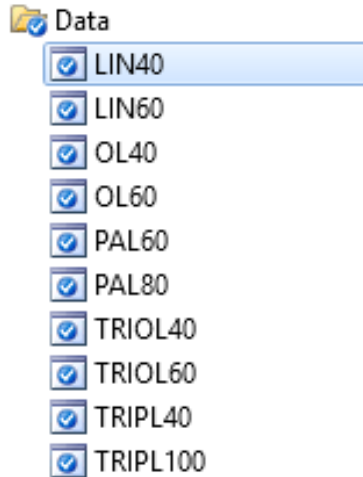
10. Once that step is done then the property data is collected on the NIST data base using the top ribbon on aspen plus



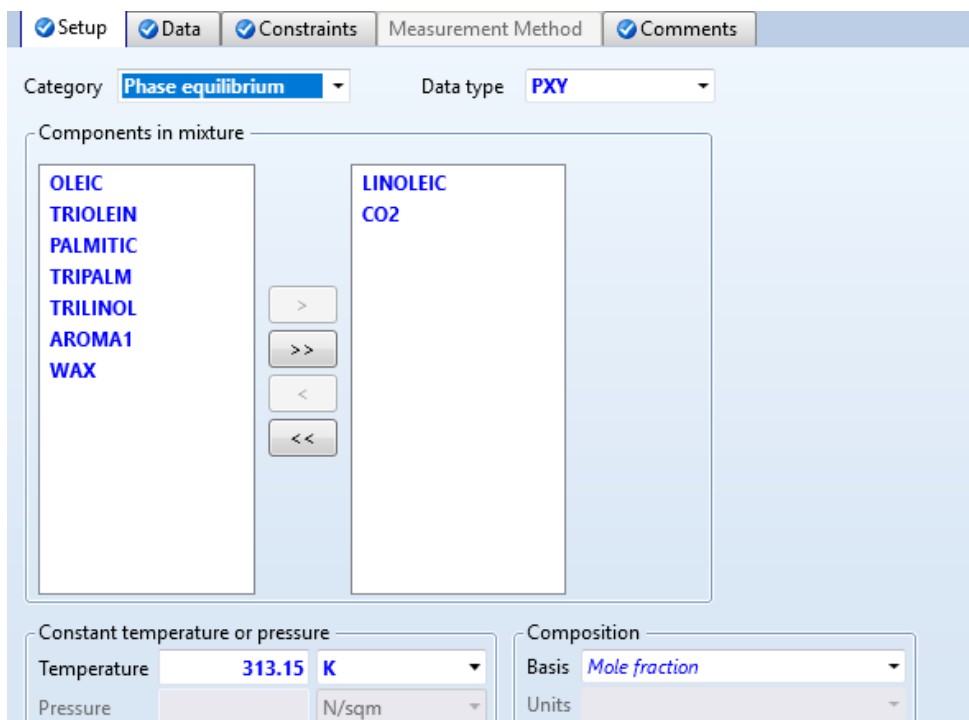
11. This step will lead to dynamic data evaluation tab as represented below. This allows you to collect the data in literature by other authors at different temperature and pressure ranges. It is advisable that you collect both data for pure components and binary components



12. The data should be retrieved and saved according to the name of the component and the chosen temperature range so that it is easy to remember when required to plot the Pxy diagrams. For the study, the data was retrieved and saved as represented below where “LIN40” depicts the binary data of linoleic acid in CO₂ at 40 °C. Then press run.



13. In order to plot the Pxy diagrams that show the behaviour of one component in CO₂ the following is done: under “setup” you ensure the you choose “phase behaviour” and “Pxy” and then choose either the two components or all of them according to your liking. Below make sure that the temperature represented in Kelvins is the same as the one on the saved data, and press run.



14. Under the tab for data, ensure that all the data is appearing both for the CO₂ and the other component before proceeding to plotting the Pxy or phase behaviour diagram.

Setup Data Constraints Measurement Method Comments

Data type PXY Retrieve TDE Binary Data... Generate Data... Clear Data

Experimental data

Usage	PRESSURE N/sqm	X LINOLEIC	X CO2	Y LINOLEIC	Y CO2
STD-DEV	0.1%	0.1%	0	1%	0
DATA	2.65e+07	0.183	0.817	0.0138	0.9862
DATA	2.293e+07	0.194	0.806	0.0115	0.9885
DATA	1.821e+07	0.212	0.788	0.0098	0.9902
DATA	1.412e+07	0.227	0.773	0.0072	0.9928
DATA	1.002e+07	0.25	0.75	0.0054	0.9946
DATA	6.4e+06	0.28	0.72	0.0045	0.9955

15. Once that is done press the Pxy diagrams on the top ribbon of the screen in aspen and press run and the graph representing your results will be shown.

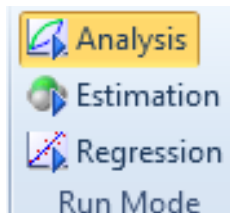


Data regression is the next step that is used to estimate parameters based on the afore collected experimental VLE data. These steps are followed:

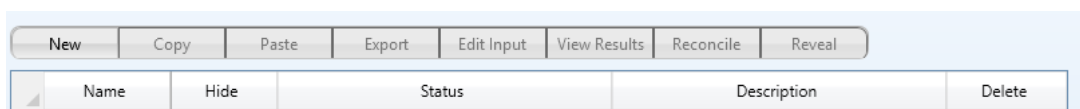
3.2.3 DATA REGRESSION AND THERMODYNAMIC MODEL DEVELOPMENT

The data is retrieved on the Aspen NIST data base to find the binary parameters using equations of state. This is done by:

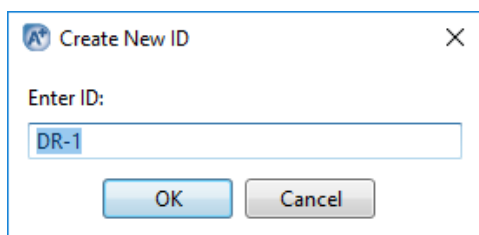
16. Choose “data regression” on the top ribbon on Aspen plus and click “new” and edit in the name for your regression



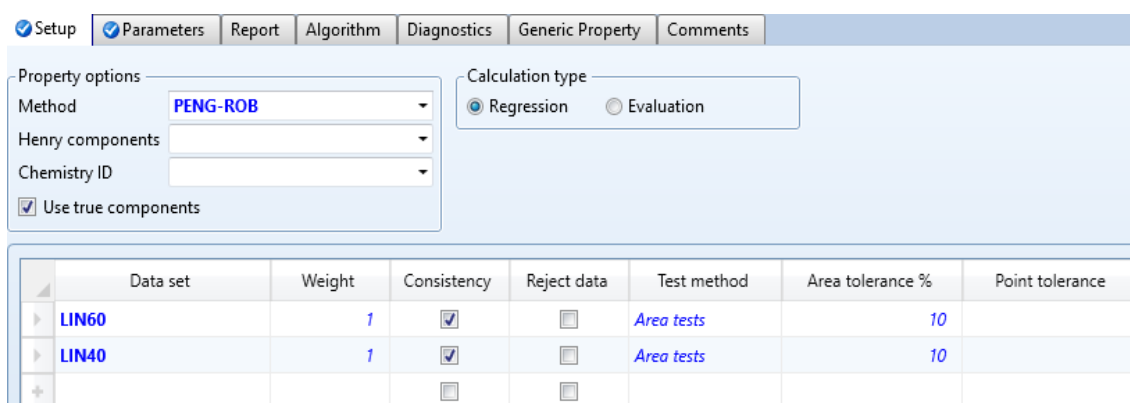
17. Press new as shown below



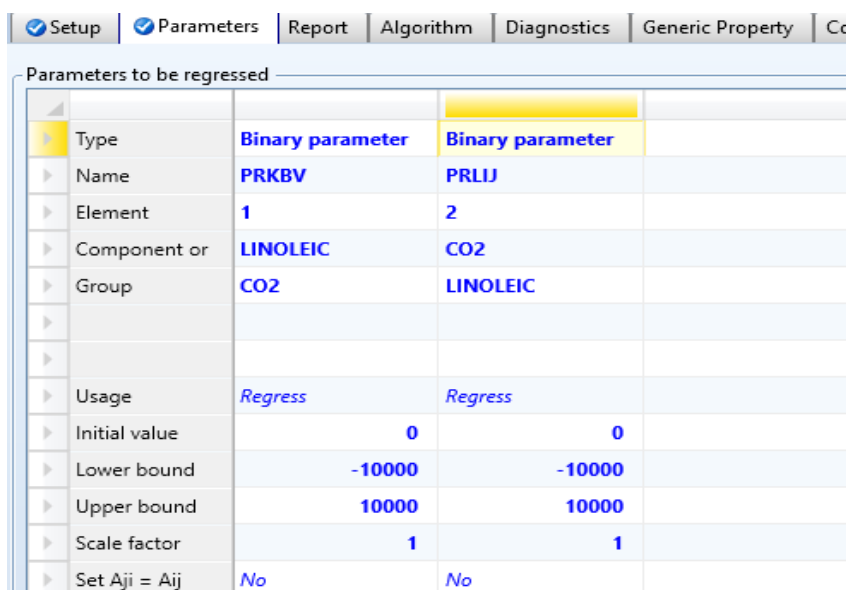
18. A pop-up will appear that will require you to rename the regression you want to make



19. Once all the data to be regressed has been labelled, recover the parameters from the tools bar. Once that is done, check the interaction parameters with equation of state



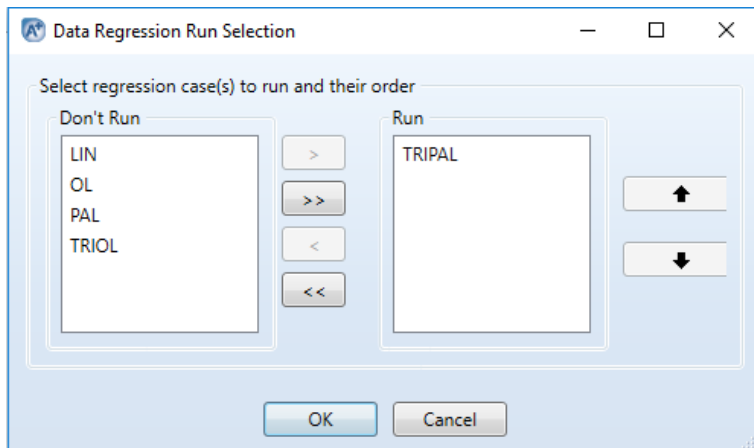
20. Under “parameters” ensure that both columns are made to be binary parameters and the two parts of the peng robinson equations are chosen i.e., PRKBV and PRLIJ. Also choose the binary mixture you want to regress and interchange them under the row labelled binary “group”.



21. Once all data has been entered, press “binary” on the top ribbon of the screen



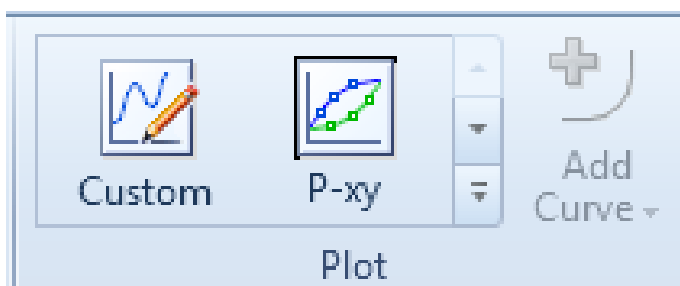
22. The data to be regressed will appear and you can choose if you want to regress everything at the same time or regress the data individually, press okay to continue and then run



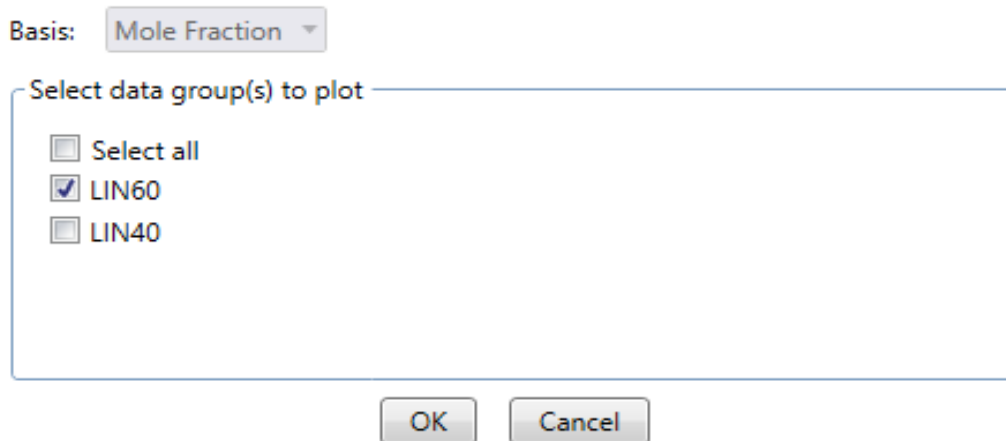
23. The results will be given and under profiles the data of results is given

Parameters										
Consistency Tests										
Residual										
Profiles										
Correlation										
Sum of Squares										
Evaluation										
Extra Property										
Status										
Data set LIN60										
Summary of regression results										
Exp Val TEMP	Est Val TEMP	Exp Val PRES	Est Val PRES	Exp Val MOLEFRAC X LINOLEIC	Est Val MOLEFRAC X LINOLEIC	Exp Val MOLEFRAC X CO2	Est Val MOLEFRAC X CO2	Exp Val MOLEFRAC Y LINOLEIC	Est Val MOLEFRAC Y LINOLEIC	Exp MOLEFRAC
C	C	bar	bar							
60	59.8252	271.4	266.715	0.192	0.185716	0.808	0.814284	0.012	0.0102105	
60	60.2732	218.3	216.145	0.219	0.211718	0.781	0.788282	0.0108	0.00676506	
60	58.5081	181.6	184.047	0.236	0.232433	0.764	0.767567	0.0092	0.00451051	
60	53.5552	138	144.478	0.265	0.260577	0.735	0.739423	0.0065	0.00216179	
60	42.7908	99.4	108.366	0.298	0.277456	0.702	0.722544	0.005	0.00111798	
60	40.5586	63.4	90.0798	0.323	0.327167	0.677	0.672833	0.0035	0.000220986	

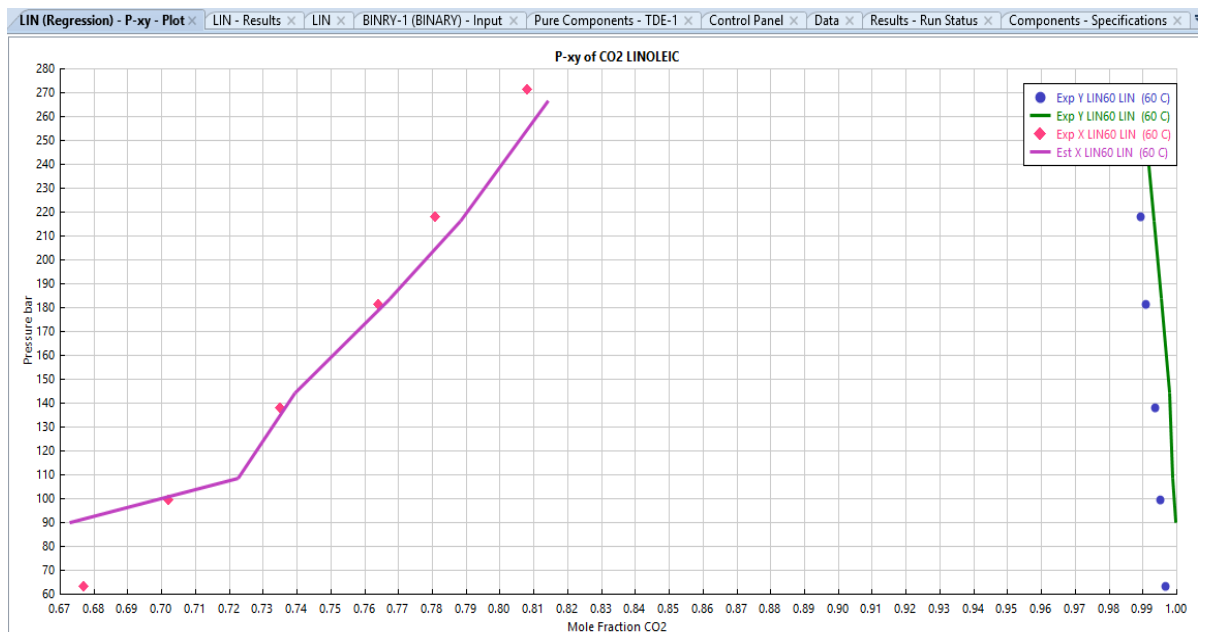
24. The next step is pressing “Pxy” on the top ribbon of the screen



25. A pop-up will appear that allows you to choose which Pxy you want to show, you can either select all or just the one you want to regress and then press okay



26. The Pxy diagram will appear. The data can be plotted well on excel by copying the results under “profiles”



The results before and after regression can be compared. The regressed data will be able to tell us the experimental conditions that should be used for the process model development.

Modelling the process is entirely dependant on accurate presentation of the binary parameters and the behaviour of different systems.

3.3 SIMULATION AND OPTIMIZATION

The goal is to present a methodology where relatively simple thermodynamic and process models are used to accurately predict the separation performance of a SCF extraction process. This is done by developing a process model that regulate the feasibility and separation performance of the process.

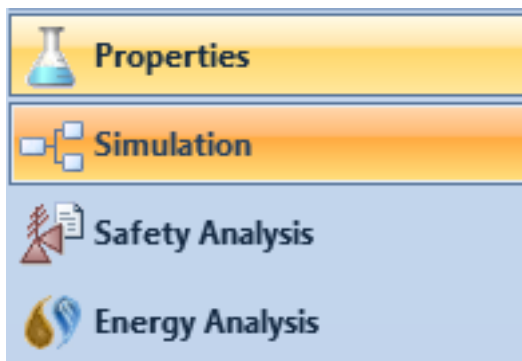
3.3.1 UNIT MODELLING AND EVALUATION

The resultant model will enable the rapid exploration of the performance of the process at a much wider range of conditions than could be performed experimentally. In addition, the kinetic data enables a batch-wise extraction system to be simulated, sized and scaled to achieve a given production capacity, and the economic performance of the resultant system to be investigated and optimized. The model development and evaluation is performed based on the process configurations presented below:

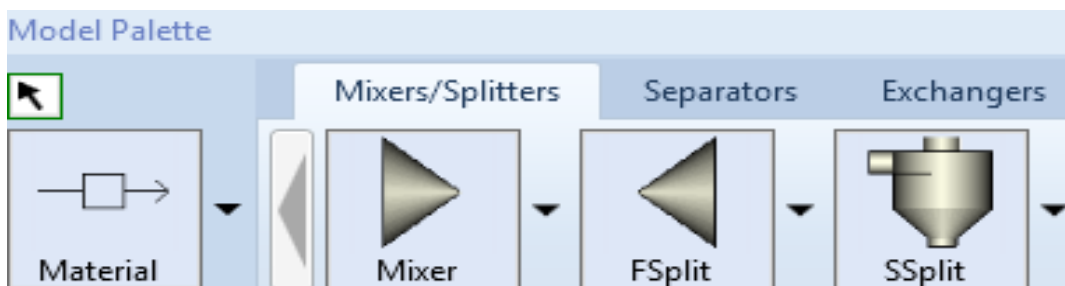
3.3.1.1 FLASH CALCULATIONS

Flash calculations are performed with a model mixture containing a representative sample of the components in the same ratios as present in the raw material. The ratios of the different components in peanuts are found in literature. The calculated distribution coefficients of each component between the liquid and vapour phases as enable the determination of separation factors between any two of the components. The range of parameters spanning the feasible region are noted. A likelihood of a feasible separation is indicated by a selectivity deemed comparable to that achieved in similar industrial processes. The flash calculations are performed following these steps:

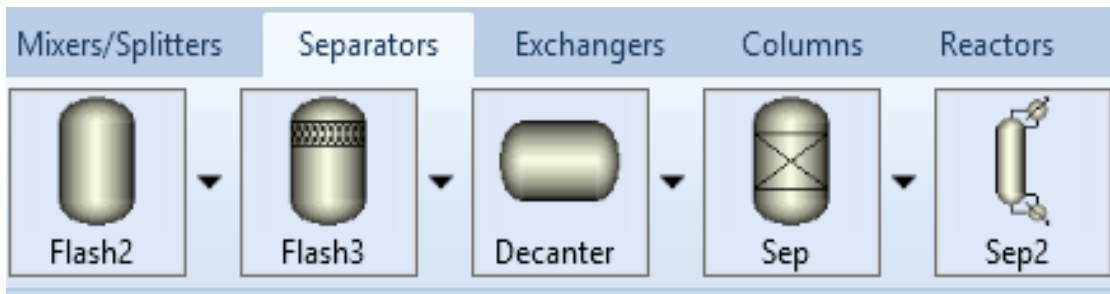
1. In aspen plus a “flowsheet” run is selected by choosing “simulation”



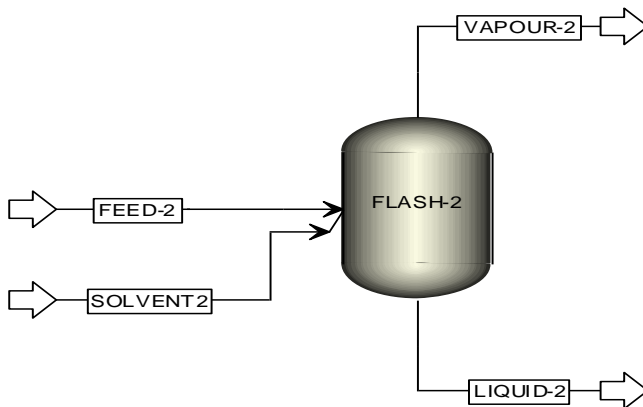
2. Under the model palette, the tab written “separators” is chosen



3. A two-outlet flash drum is used



4. From the model palette using the ribbon written material, the different streams are connected to the flash unit



5. Input the specifications in the flash unit, the fresh feed process conditions, the conditions inside the flash unit and conditions of the stream flowrate. Ensure that the mole fraction of the components added together is equal to one

Mixed CI Solid NC Solid Flash Options EO Options Costing Comments

Specifications

Flash Type: Temperature Pressure

State variables:

Temperature: 40 C

Pressure: 150 bar

Vapor fraction: []

Total flow basis: Mass

Total flow rate: 132 kg/hr

Solvent: []

Reference Temperature

Volume flow reference temperature: [] C

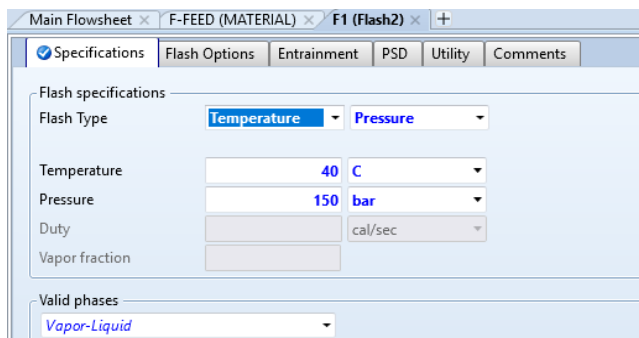
Component concentration reference temperature: [] C

Composition

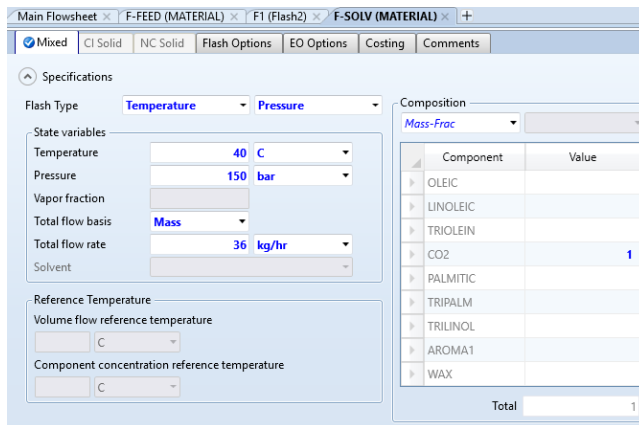
Mass-Frac

Component	Value
OLEIC	0.188
LINOLEIC	0.136
TRIOLEIN	0.042
CO2	0
PALMITIC	0.059
TRIPALM	0.422
TRILINOL	0.051
AROMA1	0.098
WAX	0.004
Total	1

- The same is done for the flash unit, ensuring that the conditions within the flash unit are the same as those in the feed stream



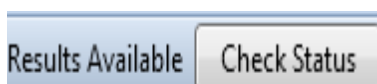
- The solvent flowrate is a different feed stream into the flash unit and the conditions are the same as those in the flash unit. A solvent flowrate is chosen as a basis to the separation in the process unit with a mole fraction of one



- Once all the necessary information has been inputted the system is run



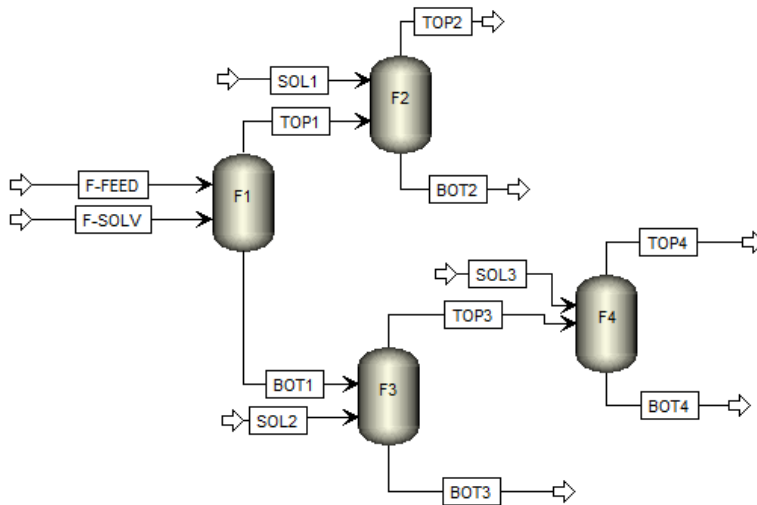
- The results for the separation within the unit will be available and can be checked at the bottom of the screen by pressing "check status"



- The results are represented as shown below with different components listed going to either the bottom or top stream.

Material	Units	F-FEED	F-SOLV	BOT1	TOP1
- Mass Flows	kg/hr	132	36	110.378	57.6221

11. The separation will continue through by adding flash units to the top and bottom streams for further separation. In the study, a multi-stage separation of four units was deemed feasible for separating aromas, free fatty acids from triglycerides and waxes.



3.3.1.2 MASS TRANSFER ANALYSIS

A component dispenses either in the light or in the heavy phase, this is determined by calculating the distribution coefficients and separation factors through a process simulator. The light phase components have k values higher than one while those in the heavy components have k values lower than one. Where: $K_i = y_i / x_i$ and the separation factor is calculated by $SF_{ij} = K_i / K_j$ using the data below:

Parameters	Consistency Tests	Residual	Profiles	Correlation	Sum of Squares	Evaluation	Extra Property	Status
Regressed parameters								
Parameter	Component i	Component j	Value (SI units)	Standard deviation				
PRKBV/1	LINOLEIC	CO2	0.0778817	0.0407003				
PRLIJ/2	CO2	LINOLEIC	-0.000423893	0.00415576				

3.3.2 EVALUATION OF ENERGY CONSUMPTION

The energy consumptions and product quality will then be evaluated in order to optimise the model. This will be done using sensitivity and optimisation techniques and therefore give insight on the energy demands of the process and the process cost estimation.

3.3.2.1 PROCESS ECONOMICS

Should the obtained results of theoretical prediction indicate that separation of any two components is indeed feasible then, the experimental separation step will be taken. The process practical viability is verified through pilot plant trials.

The results of such tests will also share light on the energy demands of the process, so as to enable order of magnitude in the process cost estimation. A more detailed step by step procedure for the experimental work is given in Appendix 1 at the end of this chapter.

3.4 VALIDATION OF SEPARATION EFFICIENCY

This section provides details on how the experiments are carried to respond to the research objectives. Several approaches are adopted, including: the total extraction of all soluble material followed by their separate deposition in three separators, and sequential extraction at progressively increasing solvent density.

3.4.1 TOPOLOGY, EQUIPMENT AND STREAM INFORMATION

The primary reference for the processes to be developed is the topology of the pilot plant, and various topologies are then developed based on those suggested in the literature such as supercritical fluid extraction. The topology gives the arrangement of the process, for this process, supercritical carbon dioxide is fed into the plant, the solvent is cooled to change its state from gas to a liquid as it passes through the pump and then the heater. This then enters at the bottom of the extraction setup at a pressure and temperature higher than its critical conditions. And allowed to percolate through and extract compounds of interest which are deposited in the separators for collection. This is, however, better explained and illustrated in Appendix B. This project concerns SCF extraction, the process where a solute is extracted from a fixed bed of roasted peanuts with a solvent in a supercritical state.

3.4.1.1 MATERIAL PREPARATION

The feed investigated, roasted peanuts is an agricultural product bought and supplied by Alibaba.

3.4.1.1.1 DRYING

The peanuts are firstly rinsed to remove any form of dust and then dried in an oven to a constant moisture content using a tray dryer. The tray dryer is filled uniformly flat at the top to maintain constant drying at 80 °C for 24 hours. To ensure constant moisture content the pan was dried in an oven and stored in a desiccator prior to use to ensure that no residual moisture is attached to them. The specific drying times were not determined experimentally and hence the drying kinetics were not obtained. The dry roasted peanuts are then sealed in a container until further experimental use. Figure 3.4-1 below represents the feed used.



Figure 3.4-1: Peanuts inside the drying oven

3.4.1.1.2 ROASTING

The dried peanuts of about 4 kg are roasted in oven at 140 °C in portions. The mass of the peanuts was not weighed but rather uniformly distributed on the tray to ensure no seed was on top of the other. The drying was time-based i., hourly at different temperatures. The samples were allowed to cool down and were wrapped in a foil so they may retain moisture until the day of experimentation. On the day of the run, the roasted peanuts were grinded using a small coffee grinder to a particle size below 80 μm using sieves.

3.4.1.2 SUPERCRITICAL FLUID EXTRACTION PROCESS

A classic pilot plant SCF extraction process is presented in figure 3.4-2:

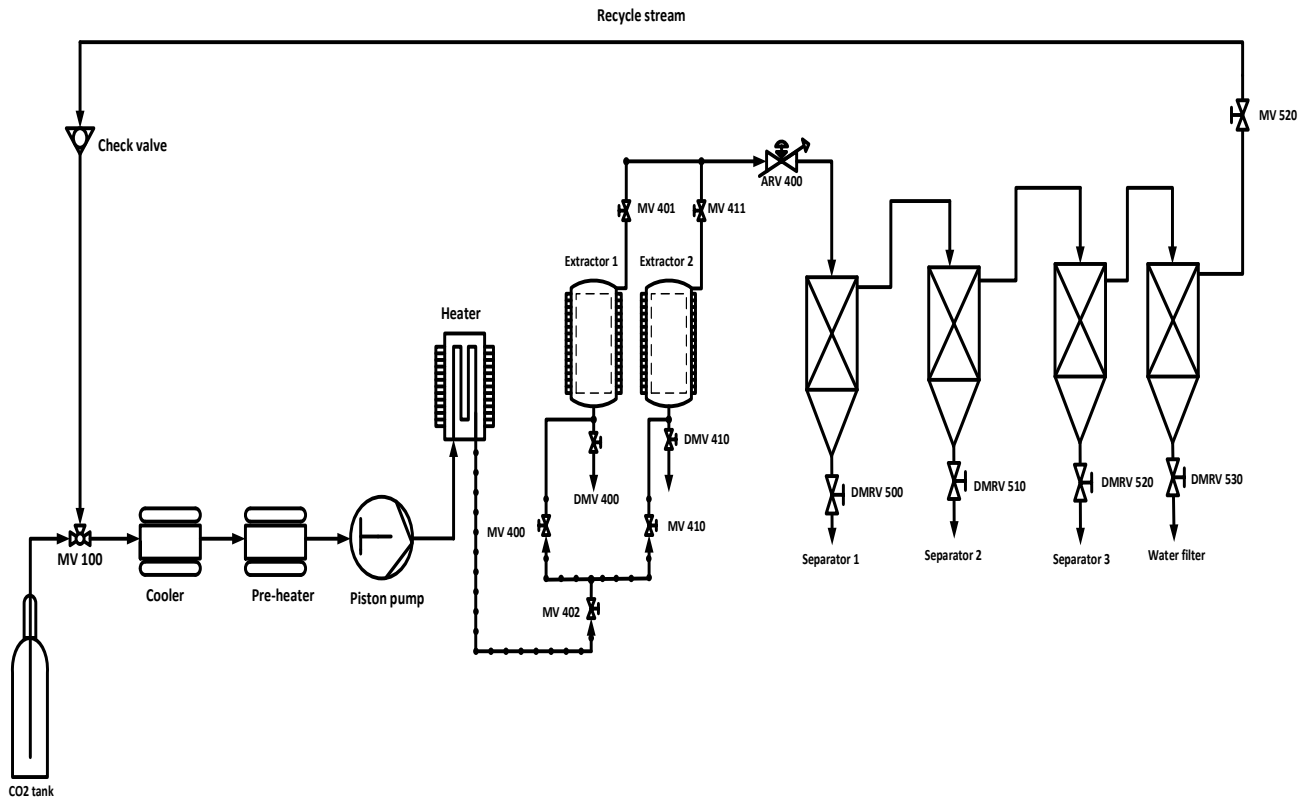


Figure 3.4-2: SCF extraction flow process diagram

In the process flow diagram shown on figure 3.4-2, supercritical carbon dioxide is fed into the plant from a cylindrical storage tank supplied by Air Liquid. The carbon dioxide enters the extraction setup from a cylinder as a gas at approximately 80 bars, it is then cooled by water and propylene glycol in the chiller to a temperature of about -5°C and sent to an eccentric disc pump. With time the pump may begin to heat up due to the moving piston and the liquid may start to become a gas again which may lead to pump failure. Because of that reason, the carbon dioxide temperature was adjusted since the pressure in the cylinder tanks cannot be decreased. This compensates for the heat produced during the mechanical operation of the pump. From the pump, this liquid is sent to a heater (which uses a coil to maximize heat transfer) where it is heated to a temperature of operation above its supercritical conditions (74 bar and 31 °C) turning it into a vapour. This vapour is fed at the bottom of the extractor through permeable discs and the solvent is allowed to be saturated with the solutes and sent to the separators. The pressure is reduced to 50 bar so the solvent may discard the extracts in the respective separators. The temperatures in the separators are set at 100 °C to decrease the solvent affinity. The solvent is the allowed to recycle back into the system.

3.4.1.3 SYSTEM INFORMATION

The equipment used for the extraction of oil from roasted peanuts is a typical Supercritical Fluid (SCF) extraction plant. The experiment is carried out in the SEPAREX SFE-5 pilot plant located in the High-Pressure laboratory in the Chemical Engineering Department of Cape Peninsula University of Technology. The plant is designed to process both solids and liquids using a supercritical solvent, in this case, supercritical carbon dioxide (scCO₂). The plant consists of two parts: an extraction section for solid processing and a counter-current fractionation section of liquid feed. The two sections use the same separation vessels for the disengagement of the extract from the solvent. For this reason, the two sections cannot be operated simultaneously. Figure 3.4-3 shows the SCF extraction pilot plant used in the study.



Figure 3.4-3: SCF extraction pilot plant

3.4.2 EXPERIMENTAL SEPARATION

To determine the experimental separation factors and selectivity's for the four commercially marketable products, three separations strategies will be attempted:

- I. Total extraction with fractional separation - this is an extraction done by maintaining process conditions in the extraction vessels at the highest solvent power while varying conditions in the separation vessels so as to discriminate the deposition of solutes based on the temperature and pressure in each vessel.
- II. Partial extraction with fractional separation - this is an extraction done by varying process conditions in both the extraction vessels and the separators.
- III. Fractionation by sequential extraction - this is an extraction done by varying process conditions in the separators, the fractions are extracted from the vessel one by one by means of varying the density.

The above-mentioned steps will then provide answers to the following research questions: product quality, total value of products and energy requirements?

3.4.2.1 EXPERIMENTAL PROCEDURE

The roasted peanuts were placed in an extraction vessel and the solvent which is above its critical point is fed at the bottom of the extractor and the process conditions are chosen and set for the fractionation of the four components of the desired peanut oil.

When the extraction pressure and temperature are reached and at equilibrium, the experiment begins. The experiments are run under different conditions and the product is collected for analysis in the separators where the pressure is dropped to 50 bar. This section gave a brief experimental procedure, a more detailed step-by-step procedure for the experimental work is given in Appendix B. Experimental were run at constant flowrate of 5 kg/hr, the conditions are summarized in table 3.4-1. The extraction temperatures were kept constant at 40 and 60°C while the pressures ranges were varied at 150, 250, 350 bar. Samples were individually weighed after every 16 minutes to determine the quantity of oil extracted.

Table 3.4-1: Experimental conditions

Time (m)	40 °C			60 °C		
	150 bar	250 bar	350 bar	150 bar	250 bar	350 bar
0						
16						
32						
48						
64						

3.4.2.2 DATA MEASUREMENT

The data collected from the experimental runs was measured to estimate the reliability of the experiment, this includes finding the confidence error and standard error of the data. This data was measured in terms of:

1. Yield (by measuring mass in grams using a balance scale)
2. Extraction time (in minutes or hours)

The collected samples from experimental runs were analysed to determine the components found in the mixture and to determine the reliability of extraction.

3.5 EXPERIMENTAL ANALYSIS

All the chemicals or standards used in this study were purchased from Mineral Innovation Technologies South Africa MIT-SA, and proper storage was followed.

3.5.1 CHARACTERISATION OF EXTRACTS BY GC-MS

Fatty acids methyl esters (FAMES) were characterised following the method by Firl, Kienberger and Rychlik, (2014) where they validated the sensitive and precise quantification of fatty acid distribution in bovine milk.

3.5.1.1 SAMPLE PREPARATION

5 ml (2:1 chloroform: methanol) was added to ca. 250 mg sample. The sample was vortexed and sonicated at room temperature for 30 minutes. The sample was centrifuged at 3000 rpm for 1 minute. 130 μ l of the bottom layer (chloroform) was entirely dried with a mild nitrogen stream and vortexed with 100 μ l of methyl tert-butyl ether (MTBE) and 30 μ l of trimethylsulfonium hydroxide (TMSH). 1 μ l of the derivatized samples was injected in a 5:1 split ratio onto the GC-MS.

3.5.1.2 CHROMATOGRAPHIC SEPARATION

Separation was performed on a gas chromatograph (6890N, Agilent technologies network) coupled to an Agilent technologies inert XL EI/CI Mass Selective Detector (MSD) (5975, Agilent technologies Inc., Palo Alto, CA). The GC-MS system was coupled to a CTC Analytics PAL auto-sampler. Separation of the FAMES was performed on a polar RT-2560 (100 m, 0.25 mm ID, 0.20 μ m film thickness) (Restek, USA) capillary column. Helium was used as the carrier gas at a flow rate of 1.2 ml/min. The injector temperature was maintained at 240°C. 1 μ l of the sample was injected in a 5:1 split ratio. The oven temperature was programmed as follows: 100°C for 4 min, ramped to 240°C at a rate of 3 °C/min and held for 10 minutes. The mass spectrometer detector (MSD) was operated in scan mode and the source and quad temperatures were maintained at 240°C and 150°C, respectively. The transfer line temperature was maintained at 250°C. The mass spectrometer was operated under electron impact (EI) mode at ionization energy of 70eV, scanning from 40 to 650m/z.

3.6 CHAPTER OUTCOMES

This chapter's outcome is as follows:

- ✓ To fulfil objective 1 and 2, the feasibility of separation was predicted using a combination of literature data, theoretical modelling, simulation, optimization and validation of the selected conditions by means of flash calculations. A range of parameters spanning the feasible region is noted and any separation deemed theoretically feasible is tested experimentally at the pilot plant scale. The experimental validation of selected conditions using a pilot plant facility will fulfil the first objective. This will provide new high-pressure data for a single-step four-way fractionation of vegetable oil.
- ✓ To fulfil objective 3, the range of parameters are tested experimentally at the pilot plant scale. This ensures adequate set of data is available to enable a comprehensive analysis of the data with regard to the influence of the relevant parameters on the composition of the various fractions.

- ✓ This is a way to validate the effect of varying process conditions (temperature, pressure and flowrate) based on the extraction kinetics and the period of extraction.

- ✓ To fulfil objective 4, the different extracts of oil are sent for analysis. The volatile fractions are analysed using the gas chromatography, while the non-volatile are analysed using the HPLC.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter is aimed at addressing and discussing the processed results of designed experiments for the research. These results will aid understanding into the single-step, multi-product fractionation of roasted peanuts using carbon dioxide as a supercritical solvent. It includes results on preliminary experiments, effects of process conditions on the feasibility of separation, process modelling, analysis, and process economics.

4.1 PRELIMINARY RUNS

In the experiments ran, the following process parameters were optimised: operating solubility, extraction pressure, extraction temperature, extraction time and yield. The solvent flowrate was kept constant to minimize the number of factors investigated. The extraction temperatures were maintained within a range above the solvent's supercritical condition i.e., 45°C and 70°C respectively. The pressure range was maintained between 200 – 400 bar based on revised literature and limits imposed by equipment design.

4.1.1 EXTRACTION PARAMETER OPTIMIZATION

The first part of the experiments was aimed at optimising process parameters. Preliminary experiments were performed based on research done by Taribak et al., (2013) investigating the Argan oil extraction. In the study, a feed of approximately 2,2 kg of roasted peanuts was used in the extraction vessel. A batch SCF extraction process for the determination of process feasibility for the extraction of aromas, free fatty acids, triglycerides, and waxes was investigated. The experiments were performed on an extraction vessel at solvent flowrates of 13 kg/hr. Two sets of experiments were examined, the first at 45°C and the other 70°C. The pressures were varied at 200, 300 and 400 bar. The sample masses were collected at 15-minute intervals to determine the extraction yield. Raw data is given in the appendices from appendix C to I. The effect of extraction conditions is represented by figure 4.1-1 and 4.1-2:

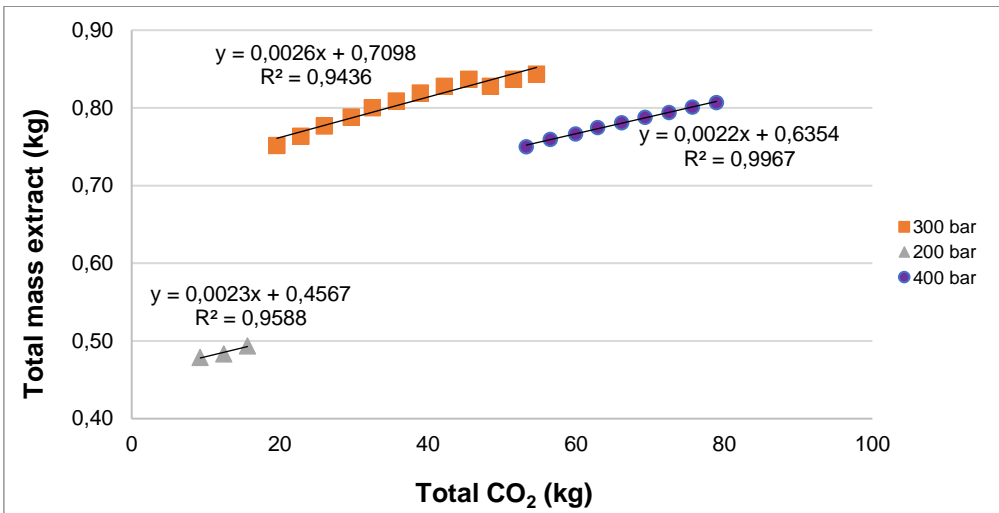


Figure 4.1-1: Solute deposited per kg of CO₂ at 45°C

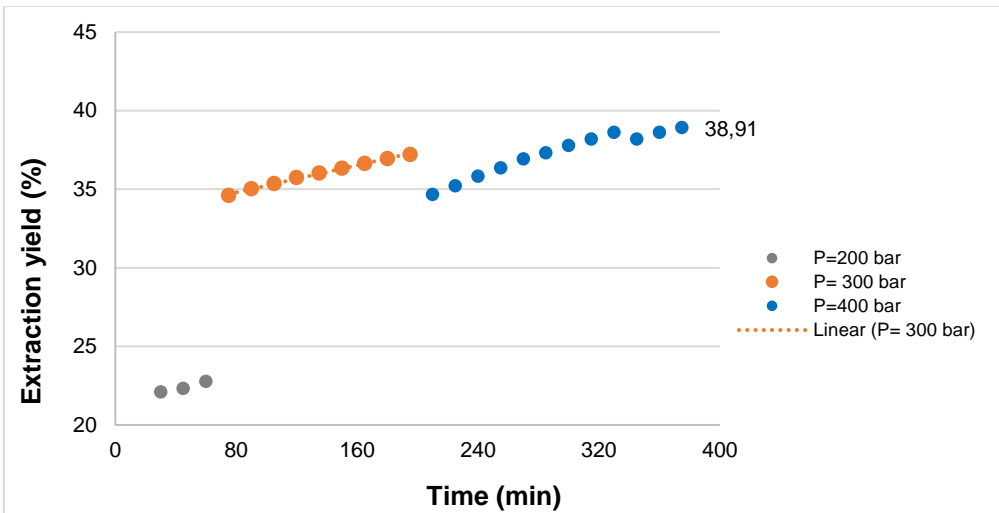


Figure 4.1-2: Extraction pressure effects on extraction yield at 45°C

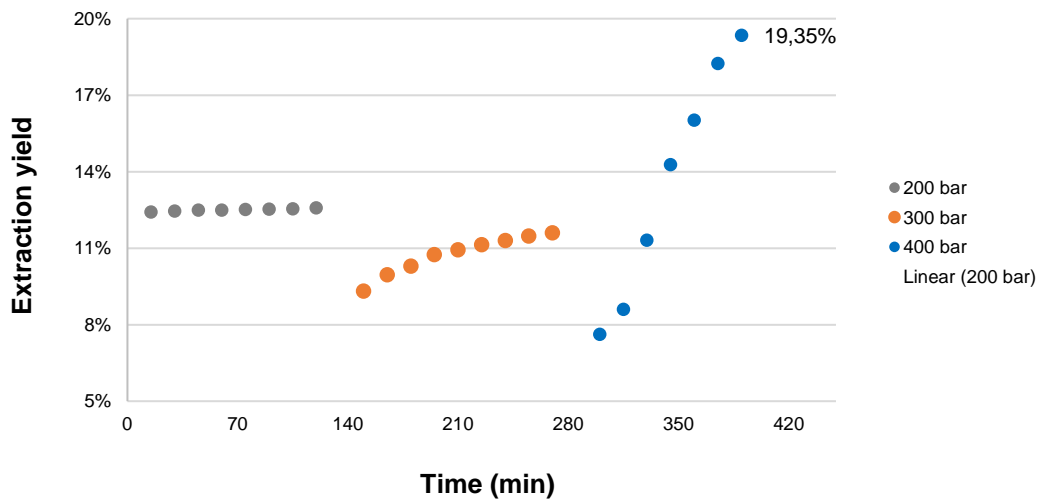


Figure 4.1-3: Extraction pressure effects on extraction yield at 70°C

4.1.1.1 OPERATING SOLUBILITY

The goal of the first experiment was to extract the highest concentration of aroma compounds in the solute. A comparable relationship was reported by Ziegler and Liaw (1993) where he used dense carbon dioxide to investigate deacidification of edible oils. The results showed that at constant temperature, the solubility of aroma compounds was directly related to their volatility. Ziegler and Liaw (1993) mention that the fatty acids concentration derivatives improved with increasing temperature and pressure at constant fluid-phase density.

4.1.1.2 INFLUENCE OF EXTRACTION PRESSURE

Figures 4.1-1 and 4.1-2 show that a pressure increase having an extreme influence on the rate of extraction and the yield at 45°C and 70°C. This effect is credited to the density increase of the solvent CO₂ that rises with pressure increase and thus increases the solvent power. When the solvent power increases it means that the solvent has more affinity to dissolve and to selectively dissolve the desired compounds. The extraction yield follows the same pattern both 45°C and 70°C. The constant temperature of 45°C indicates a linear curve at 300 bar, representing a controlled equilibrium extraction during the 120 minutes. The same pattern is noticed in figure 4.8 at 200 bar. The curves at 400 bar displays both the linear and the diffusion-controlled stage meaning that towards the end the extraction is slower. At 400 bar there is a sudden drop in the extraction yield and then a rise again above the yield obtained at 300 bar. This is reported in a study by Taribek et al (2013) on the SCF extraction of plant flavours. The study reports that above 300 bar, the supercritical solvent solubility is independent of the pressure. They also reported that above 300 bar, there is an overturn. A study done by Ziegler and Liaw (1993) reveals that because of the decrease in temperature and pressure, at constant fluid-phase density, the concentration of the flavours drops though that for fatty acids increased. It can thus be deduced that the crossover pressure for peanut oil extraction at 45°C and 70°C is 300 bar.

4.1.1.3 INFLUENCE OF EXTRACTION TEMPERATURE

The extraction yield increase is caused by an increase in temperature from the presented diagrams. The highest yield obtained at 45°C is 38.91% while at 70°C it is 19.35%. This can be accredited to a smaller difference in solubility at higher temperatures. And the solvent affinity is a function of solvent density, therefore a decrease in the solvent density means that the solvent has less affinity to dissolvent compounds of interest. At 300 bar, the extraction conditions had no influence on the extraction yield. It can therefore be concluded that an increase in temperature at varying pressures comes with a solvent density reduction effect resulting in a decrease in the extraction yield.

4.1.1.4 INFLUENCE OF EXTRACTION TIME

Time has been found to have a maximum effect on total yield (%). Long extraction times result in an increase in the extraction. However, it is advisable to manipulate process conditions to obtain the highest yield possible instead of long extraction times. Often, low solvent flowrates result in long extraction times but allow for more contact time between the solvent and the feed matrix. This goal of this section of the experiments is determining the feasibility of separation using phase equilibria data available in literature.

4.2 SEPARATION FEASIBILITY PREDICTION

Theoretical VLE data was collected to determine the feasibility of separation of the four fractions of peanut oil by comparing their phase behaviours in supercritical CO₂. The available phase behaviour data is compiled and presented in Appendix B.

4.2.1 PHASE BEHAVIOUR OF RELEVANT SYSTEMS

VLE data of free fatty acids specifically oleic, linoleic, and palmitic acid in carbon dioxide is used to plot the two-phase equilibrium diagrams. These represent the behaviour of the different solutes in the solvent.

4.2.1.1 OLEIC ACID

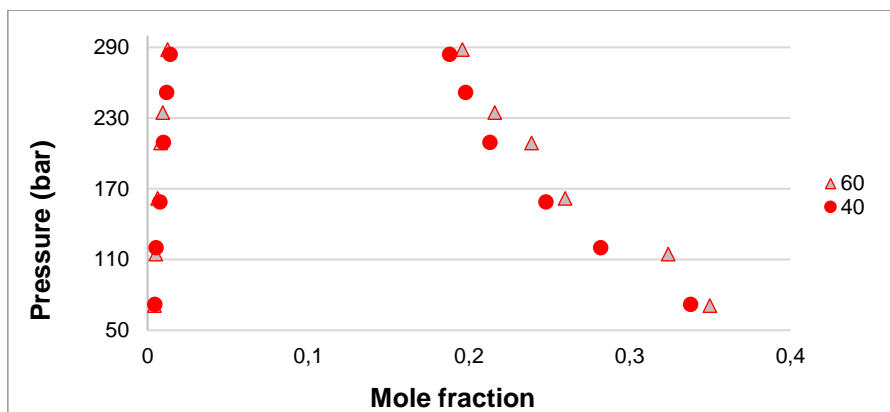


Figure 4.2-1: Oleic acid/CO₂ phase separation at 40 and 60°C

Figure 4.2-1 shows two-phase separation diagram of oleic acid in scCO₂. Carvalho et al., (2011) reports on sesame seeds suggested that free fatty acids can be extracted at 35°C and 200 bar. The vapour liquid equilibrium data plotted shows that carbon dioxide can be enriched in oleic acid at pressures of 70 bar $\geq P \leq$ 300 bar. However, it can also be depicted that the behaviour of oleic acid in scCO₂ at 40°C and 60°C does not differ much. From the graph it can be noticed that the solvent is more enriched with oleic acid in the liquid phase and that the percentage difference for oleic acid at 40°C and 60°C is 1.2%.

4.2.1.2 LINOLEIC ACID

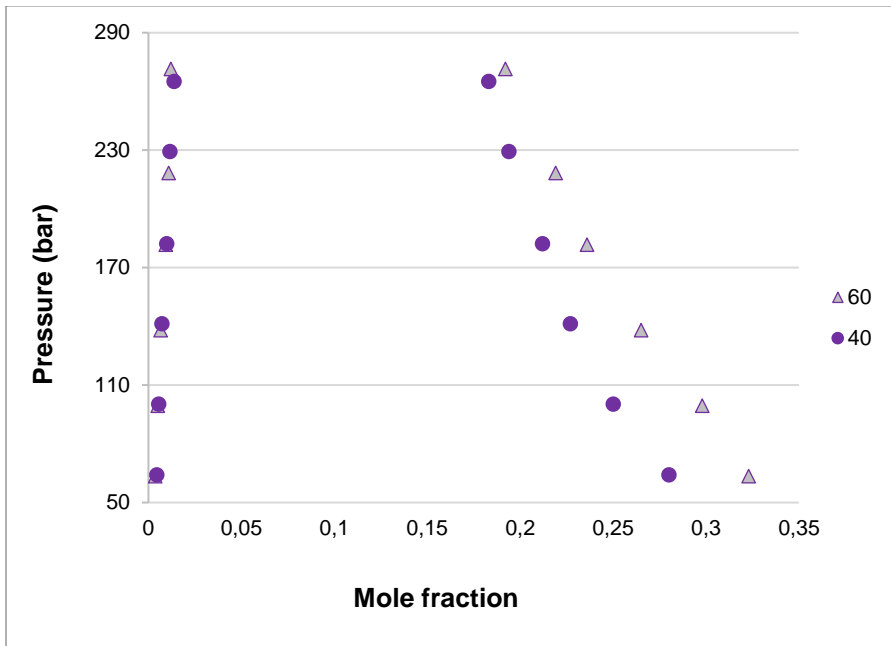


Figure 4.2-2: Linoleic acid/CO₂ phase separation at 40 and 60°C

Figure 4.2-2 shows a two-phase separation diagram of linoleic acid in scCO₂ at 40°C and 60°C. The behaviour of linoleic acid in CO₂ at these two temperatures does not differ much. The solvent is less enriched in linoleic acid in the vapour but more enriched in the liquid. The same behaviour was noticed for linoleic acid, an increase in pressure resulted in solvent power increase. The highest mole fraction obtained at 40°C is 0.28 and at 60°C its 0.323 with a percentage difference of 4.3%.

4.2.1.3 PALMITIC ACID

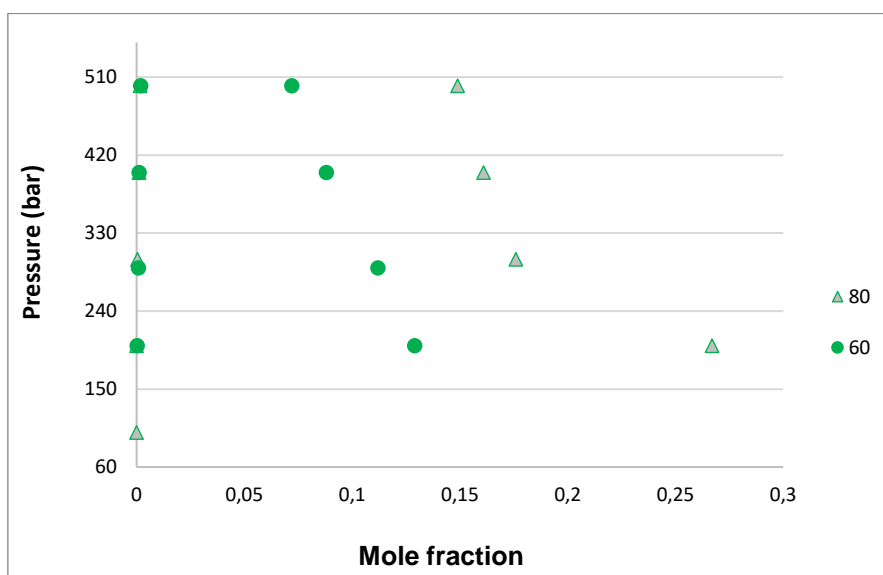


Figure 4.2-3: Palmitic acid/CO₂ phase separation at 60 and 80°C

Figure 4.2-3 represents the two-phase separation diagram of palmitic acid in scCO₂. VLE data for palmitic acid-CO₂ at 60°C and 80°C. Palmitic acid is more enriched in CO₂ in the liquid. Vapour liquid equilibrium data of triglycerides specifically triolein and tripalmitate in carbon dioxide is obtained from literature and presented as phase behaviour diagrams. Data for trilinolein could not be found on the NIST database:

4.2.1.4 TRIOLEIN

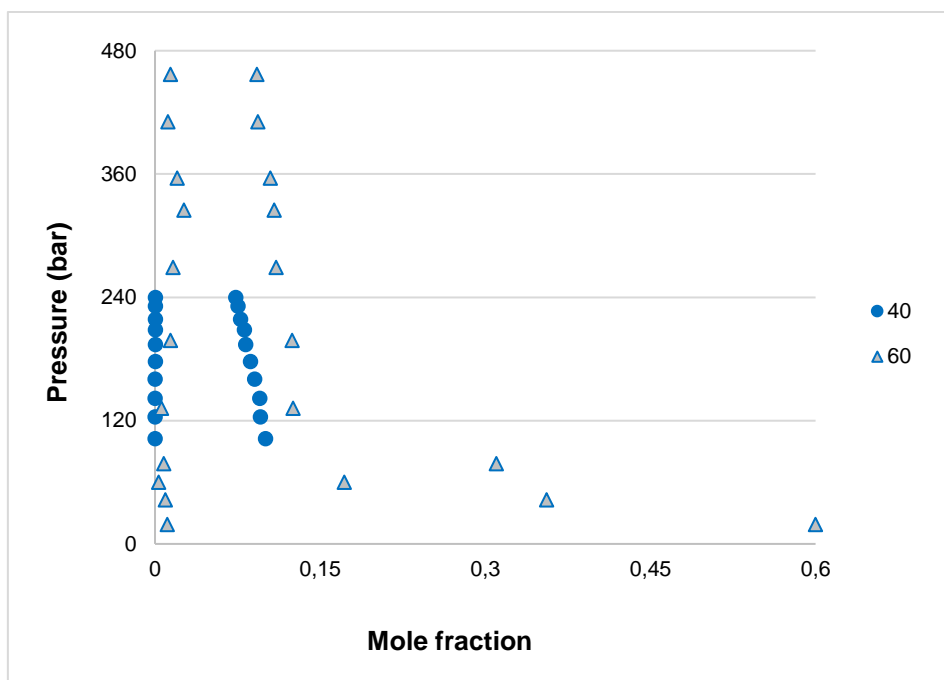


Figure 4.2-4: Triolein/CO₂ phase separation at 40 and 60°C

Figure 4.2-4 represents the two-phase separation diagram of triolein in scCO₂. Manna et al., (2015) on valorisation of hazelnut, coffee and grape wastes suggested that triglycerides are extracted at 60°C and 500 bar. The graph below shows a significant difference in the behaviour of triolein in carbon dioxide between the two temperatures of 40°C and 60°C. It can be noted that at 60°C triolein is more enriched in carbon dioxide in the liquid than in the vapour. Triglycerides have complex structures, and it is not a surprise that at 60°C that is how it behaves in CO₂. At 40°C, pressures below 100 bar do not show any behaviour of triolein in carbon dioxide.

4.2.1.5 TRIPALMITATE

The two-phase diagram for tripalmitate shows that the solute is more enriched in solvent in the liquid phase. There is no behaviour noted at 60°C for pressures below 200 bar. A percentage difference for mole fraction of 13.8% is noted which can be advantageous for enrichment.

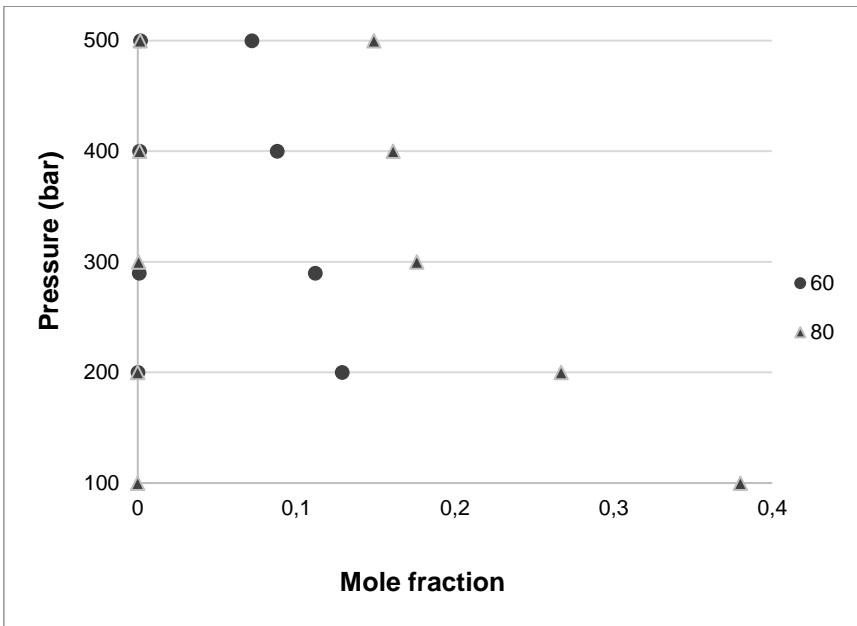


Figure 4.2-5: Tripalmitate/CO₂ phase separation at 60 and 80°C

4.2.2 SEPARABILITY OF BINARY SYSTEMS

The data was plotted on the same pair of axes in order to determine the components are separable at different conditions.

4.2.2.1 TRIOLEIN/OLEIC ACID

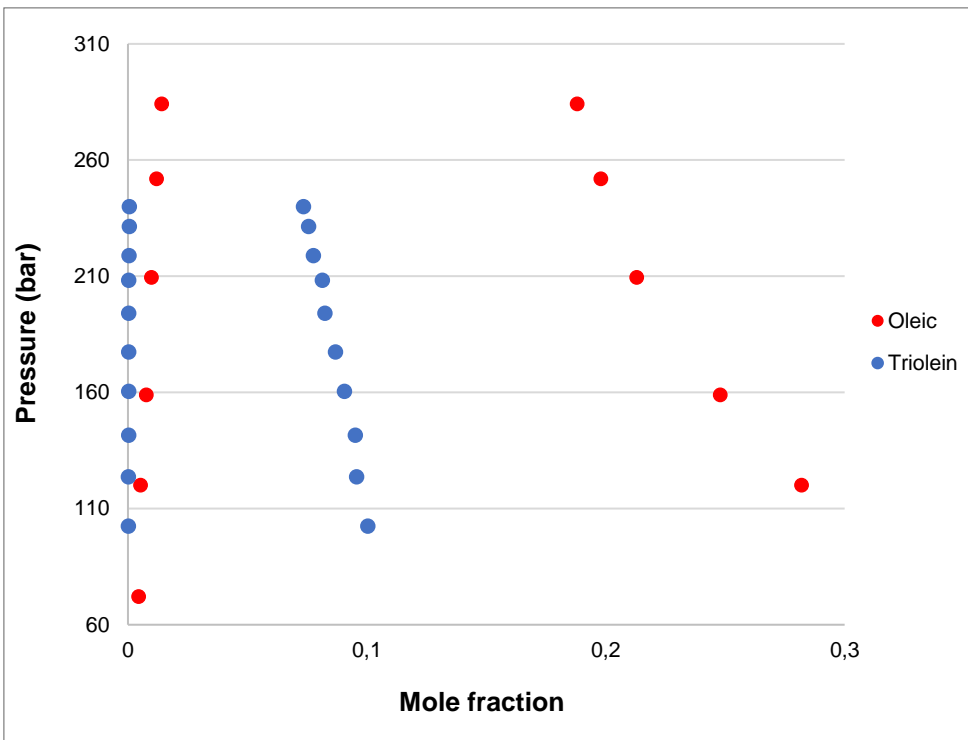


Figure 4.2-6: Triolein/oleic acid at 40°C

Figure 4.2-6 shows the the behaviour of oleic acid/triolein in CO₂ at 40°C. The highest mole fractions obtained for oleic acid and triolein are 0.282 and 0.1 respectively. It can then be deduced that oleic acid is more enriched in CO₂ in the liquid phase than triolein. Therefore separation of one component from the other happens within the range of 0.1 – 0.282. At 250 bar and above, only oleic acid can be separated from the binary mixture while at pressure ranges of 100 – 130 bar only triolein can be separated.

If the two-phase equilibrium curves are superimposed and a line at 200 bar is used to illustrate the relationship between the conditions in an extraction vessel. It can be inferred that at 200 bar when measured separately; the binary systems composed of oleic acid with CO₂ and triolein with CO₂ reach saturation (bubble point) at 0.220 and 0.075 respectively. And they become one vapour phase (dew point) at concentrations of CO₂ less than 0.018 and 0.001 respectively. The concentration ranges of the solute lying between 0.018 - 0.220 and 0.001 and 0.075 show that the binary system exist as two-phase systems. It can thus be deduced that, assuming no interaction between oleic acid and triolein, between the concentration ranges 0.075 and 0.220, a mixture of triolein and oleic acid can be separated completely because of the dissolution of oleic acid in the CO₂ phase while triolein remains in the liquid phase. Similarly, triolein can be precipitated from a single vapour phase made up of a mixture of triolein and oleic acid by increasing the solute concentration to above 0.001 and 0.075 respectively. It can thus be concluded that a mixture of oleic acid and triolein can be separated completely.

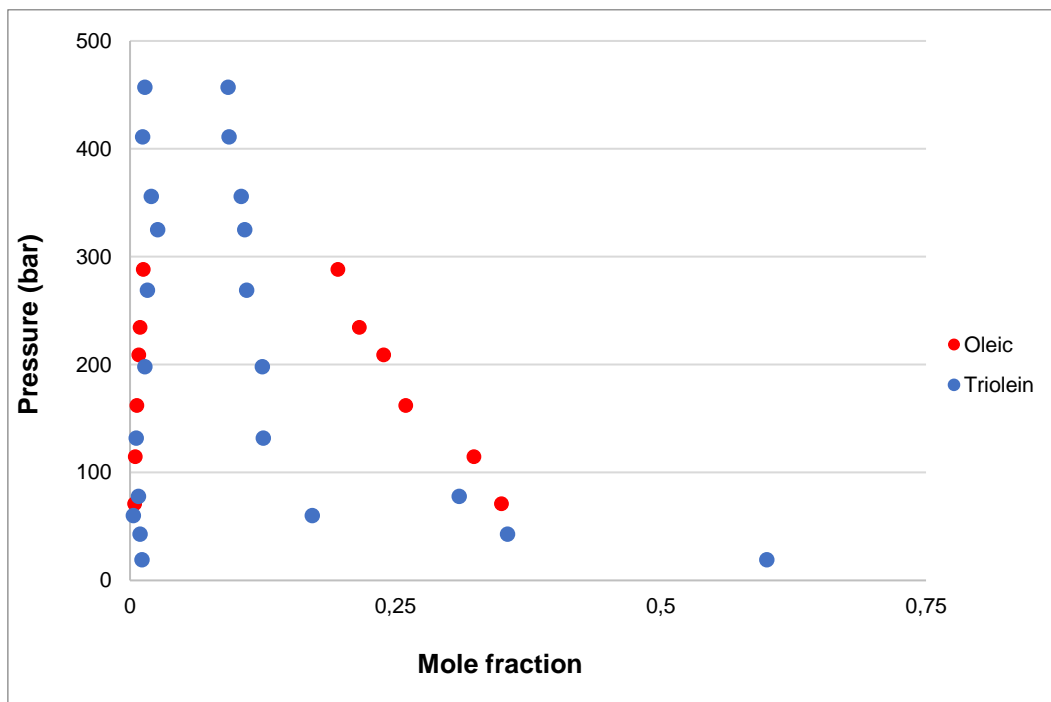


Figure 4.2-7: Triolein/oleic acid at 60°C

Figure 4.2-7 indicates the the behaviour of the binary systems of oleic acid/triolein in CO₂ at 60°C. This diagram represents a possible enrichment of one solute in the solvent than the other. It can be noticed that the two curves in the vapour phase are somewhat connected which helps draw an assumption that it would not be easy to one component in the solvent than the other. The liquid phase however shows oleic acid is more enriched in the solvent than triolein, this is seen from the solute concentration regions of 0.35 and 0.172 of oleic acid and triolein respectively. At pressures above 300 bar the bianary mixture does not show any behaviour of oleic acid in the solvent, this allows the possibility of speculating that only triolein can be separated from the mixture.

Suppose the two phase equilibrium curves are superimposed and a line representing 200 bar pressure is shown to illustrates the distribution of the components present in the extractor between the two phases. When measured separately, the binary systems composed of oleic acid with CO₂ and triolein with CO₂ reach saturation (bubble point) at 0.239 and 0.125 respectively with the dew point at concentrations of CO₂ less than 0.014 and 0.001 respectively. The binary systems exist as two phase systems in the concentration ranges of the solute lying between 0.014 - 0.239 and 0.001 and 0.125. It can therefore be deduced that, assuming no interaction between oleic acid and triolein, between the concentration ranges 0.125 and 0.239, a mixture of triolein and oleic acid can be separated completely as a result of the dissolution of oleic acid in the CO₂ phase while triolein remains in the liquid phase.

Similarly, triolein can be precipitated from a single vapour phase made up of a mixture of triolein and oleic acid by increasing the solute concentration to above 0.001 and 0.014 respectively. It can thus be concluded that a mixture of oleic acid and triolein can be separated completely. Additionally, a two phase mixture contains both components in both phases, and thus an efficient separation can be achieved using a multistage process. Finally, if a comparison is to be made between the separation of oleic from triolein in carbon dioxide the temperature of 40°C produces better chances of enrichment than 60°C.

4.2.2.2 TRIOLEIN/ LINOLEIC ACID

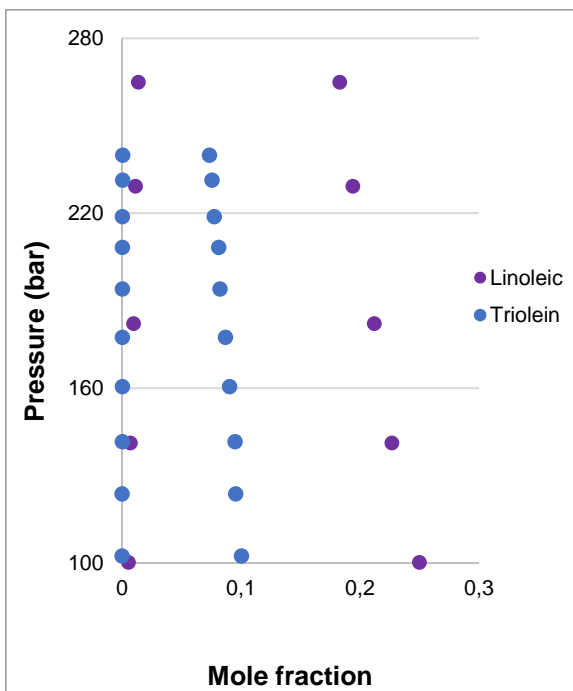


Figure 4.2-8: Triolein/linoleic acid at 40°C

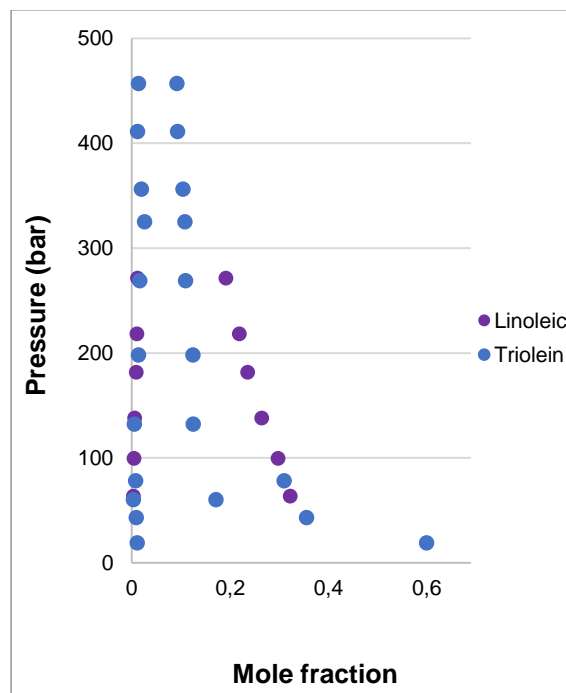


Figure 4.2-9: Triolein/linoleic acid at 60°C

Figure 4.2-8 and 4.2-9 show the behaviour of the binary systems of triolein /linoleic acid in carbon dioxide at 40°C and 60°C respectively. The percentage difference between the two allows for an assumption that in the liquid phase, linoleic acid is more enriched in the solvent than triolein because of its higher concentration. If a line is to be drawn at 200 bar illustrating the relationship between the conditions in an extraction vessel; the first drop of triolein in the vessel is obtained at a concentration of 0.078 while the for linoleic acid it is obtained at 0.194. It can thus be presumed that, if no interaction between linoleic acid and triolein, between the concentration ranges 0.078 and 0.194, a mixture of triolein and linoleic acid can be separated completely due to the dissolution of linoleic acid in the CO₂ phase while triolein remains in the liquid phase.

The dew point of triolein and linoleic acid at this pressure inside the vessel happen at the concentrations of 0.0005 and 0.0115 respectively. Triolein can be precipitated from a single vapour phase made up of a mixture of triolein and linoleic acid by increasing the solute concentration to above 0.0092 and 0.014, respectively. And assuming that there is no interaction between triolein and linoleic acid, between the concentration ranges 0.125 and 0.236, then the mixture can be separated completely due to the dissolution of linoleic acid in the CO₂ phase while triolein remains in the liquid phase. Finally, if a comparison is to be made between the separation of linoleic from triolein in carbon dioxide the temperature of 40°C produces better chances of enrichment than 60°C.

4.2.2.3 TRIPALMITATE/ OLEIC ACID

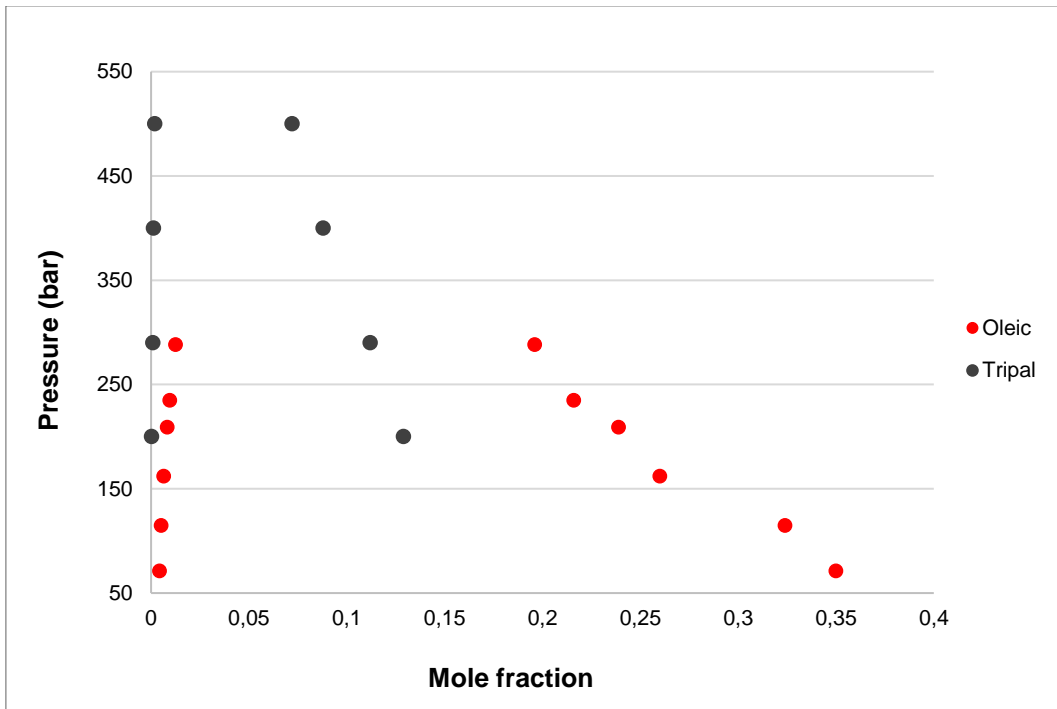


Figure 4.2-10: Tripalmitate/oleic acid at 60°C

Figure 4.2-10 demonstrates the behaviour of the binary systems of tripalmitate/oleic acid in CO_2 at 60°C. Pressures from 310 bar and above indicate that only tripalmitate can be enriched in mixture while at low pressures of 71 bar to 290 bar only oleic acid is enriched. This means that the liquid phase is poorly enriched in tripalmitate than in oleic acid. The binary systems composed of tripalmitate with CO_2 and oleic acid with CO_2 reach saturation (bubble point) at 0.239 and 0.129 respectively. And they become one vapour phase (dew point) at concentrations of CO_2 less than 0.00022 and 0.0011 respectively. The concentration ranges of the solute lying between 0.129 - 0.239 and 0.00022 and 0.0011 show that the binary system exist as two-phase systems. It can thus be deduced that, assuming no interaction between oleic acid and tripalmitate, between the concentration ranges 0.129 and 0.239, a mixture of tripalmitate and oleic acid can be separated completely caused by the dissolution of oleic acid in the CO_2 phase while triolein remains in the liquid phase.

4.2.2.4 TRIPALMITATE/ LINOLEIC ACID

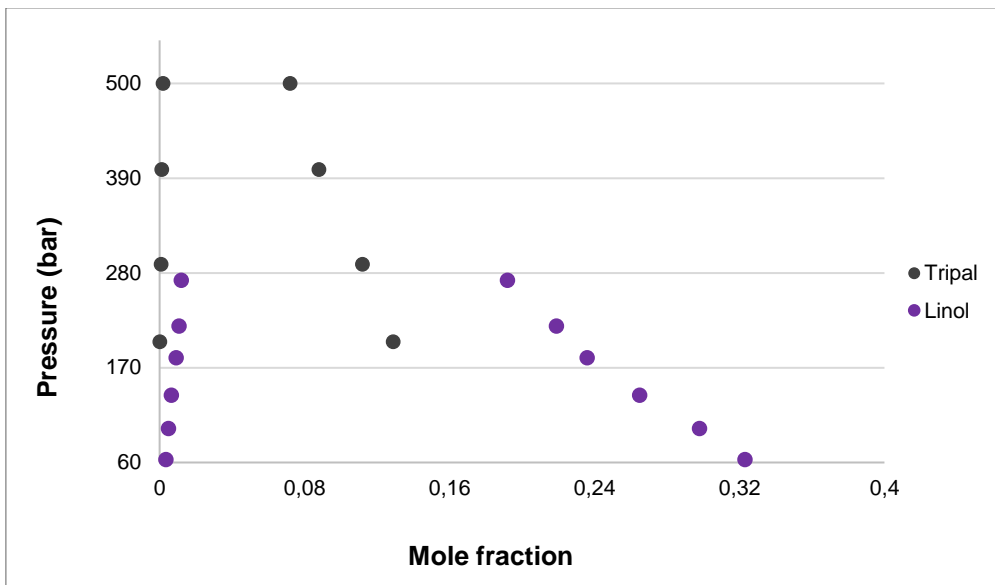


Figure 4.2-11: Tripalmitate/linoleic acid at 60°C

Figure 4.2-11 displays the behaviour of binary systems of tripalmitate/linoleic acid in carbon dioxide at 60°C. From the diagram it can then be assumed that it is possible to enrich linoleic acid more in the solvent than tripalmitate. At pressures above 290 bar up to 500 bar only tripalmitate can be enriched while at low pressure below 200 bar only linoleic acid can be enriched. At 240 bar the first drop of tripalmitate in the vessel is obtained at a concentration of 0.129 while the for linoleic acid it is obtained at 0.219. It can thus be presumed that, if no interaction between linoleic acid and tripalmitate, between the concentration ranges 0.129 and 0.219, a mixture of tripalmitate and linoleic acid can be separated completely due to the dissolution of linoleic acid in the CO₂ phase.

4.2.2.5 PALMITIC ACID /TRIPALMITATE

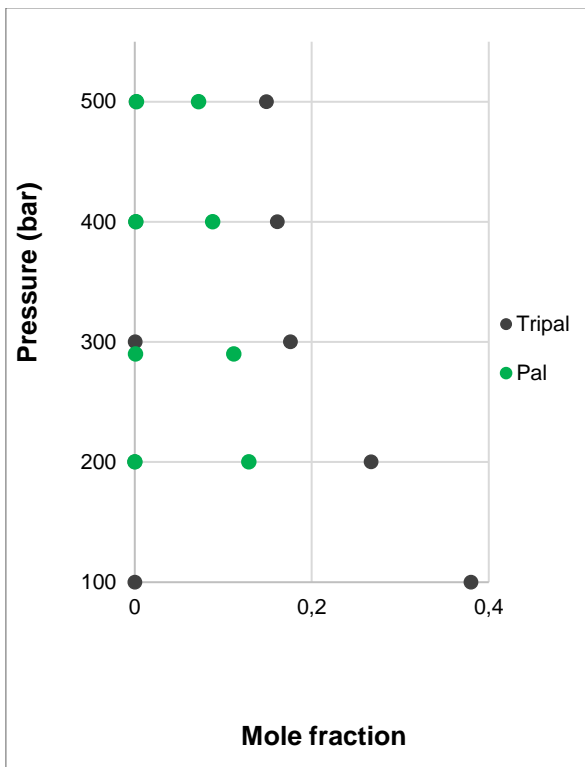


Figure 4.2-12: Palmitic acid/tripalmitate at 60°C

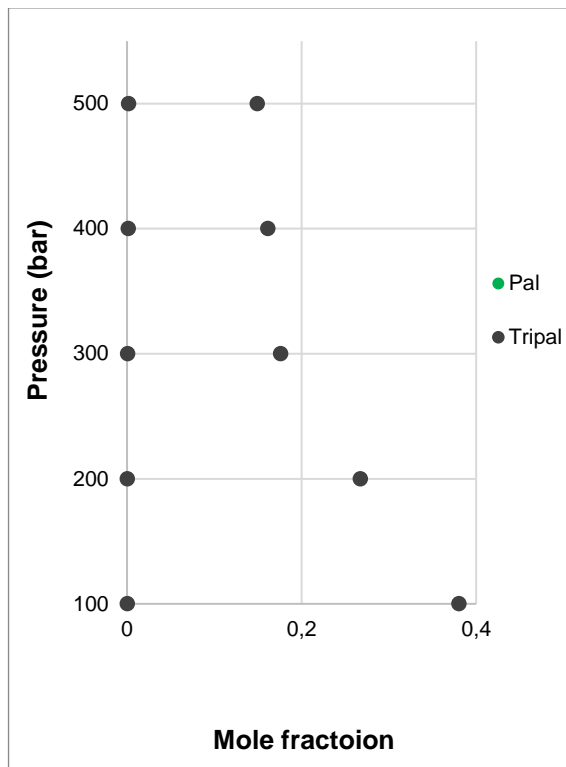


Figure 4.2-13: Palmitic acid/tripalmitate at 80°C

Figure 4.2-12 and 4.2-13 show the behaviour of the binary systems of palmitic acid/tripalmitate in carbon dioxide at 60°C and 80°C respectively. At 400 bar the binary systems composed of palmitic acid with CO₂ and tripalmitate in CO₂ reach saturation (bubble point) at 0.088 and 0.161 respectively. And they become one vapour phase (dew point) at concentrations of CO₂ less than 0.00012 for both components. If no interaction between palmitic acid and tripalmitate within the concentration ranges, then a mixture of palmitic acid and tripalmitate can be separated completely. It would be impossible to enrich one component than the other in CO₂ at 80°C due to the fact that the two graphs are on top of one another. This is can be accounted to their very similar and complex structure though one is a free fatty acid and another a triglyceride. There is no behaviour of one being enriched in the liquid or vapour phase than the other. Therefore, it can be concluded that the two should be separated as a binary mixture.

Using the information obtained from the phase behaviour binary curves, a process model was developed based on flash calculations of a single and multi-stage process to confirm the above finding and to estimate the resources required for separation.

4.2.3 REGRESSION

Using a properties simulator i.e., Aspen Plus, the data was regressed using a suitable thermodynamic model, Peng Robinson. This is because of its ability to represent accuracy in the district of the critical point. The results are shown below:

4. OLEIC ACID/ CO₂

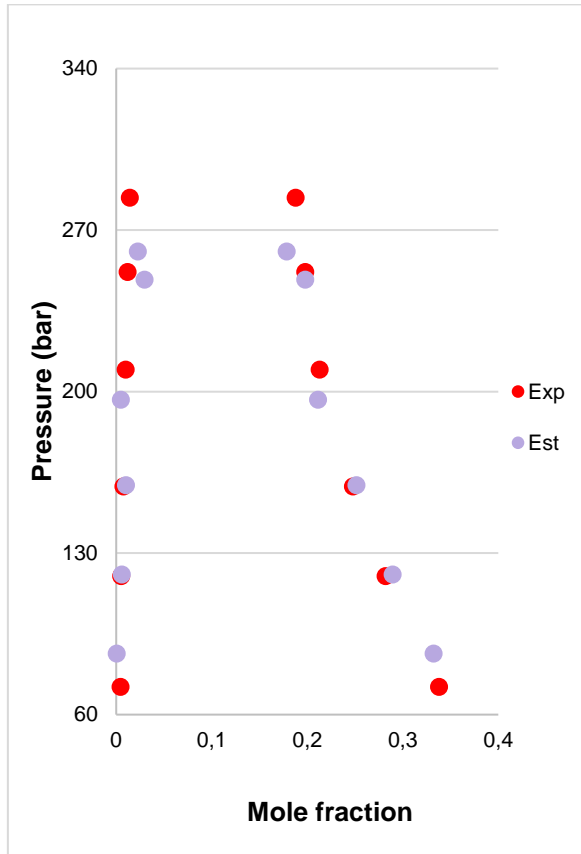


Figure 4.2-14: Oleic acid/CO₂ regressed at 40°C

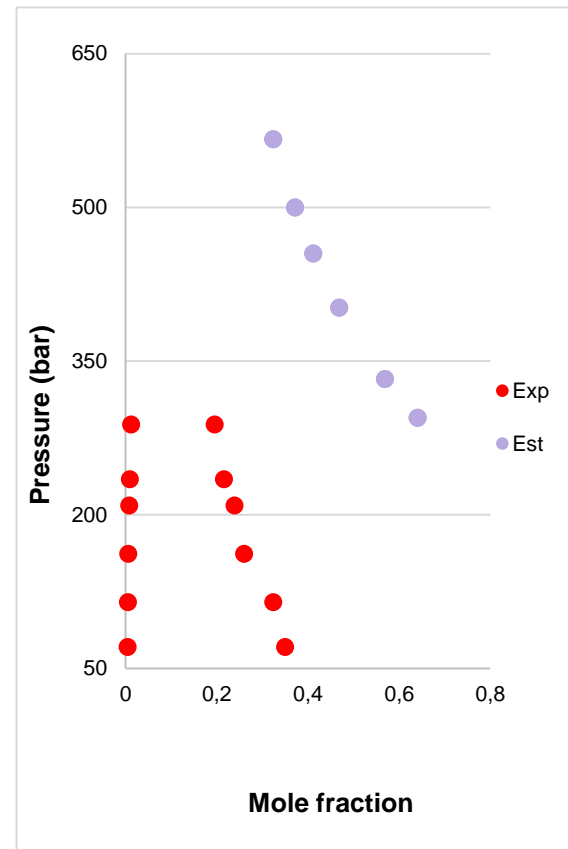


Figure 4.2-15: Oleic acid/CO₂ regressed at 60°C

Figure 4.2-14 represents the regressed VLE data for oleic acid/CO₂ at 40°C using Peng Robinson. The diagram illustrates that the thermodynamic model of choice was in agreement with the VLE data. The average standard deviation for the regression of oleic acid at 40°C is about 0.04. The thermodynamic model gives close values for the binary interaction parameters. Likewise, figure 4.2-15 shows the regressed VLE data for oleic acid/CO₂ at 60°C. It can be deduced from the diagram that the thermodynamic equation of state which was used could not perfectly fit the regressed experimental data at 60°C. The model was supposed to estimate a temperature of 60°C but it estimated data between the temperature range of 30-60 °C. A different thermodynamic equation of state would need to be used on the data.

5. LINOLEIC ACID/ CO₂

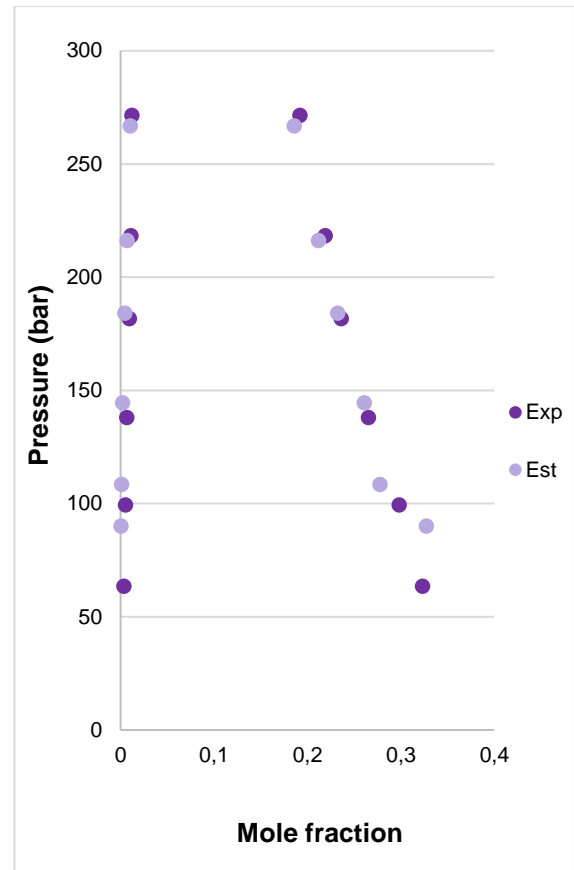
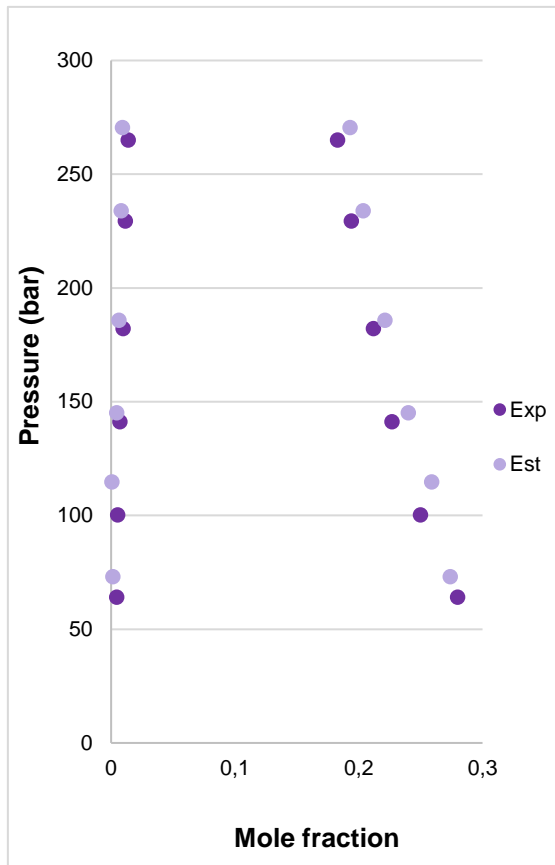


Figure 4.2-16: Linoleic acid/CO₂ regressed at 40°C Figure 4.2-17: Linoleic acid/CO₂ regressed at 60°C

Figure 4.2-16 represents the regressed VLE data for linoleic acid/CO₂ at 40°C using Peng Robinson. The diagram illustrates that the thermodynamic model gives close values for the binary interaction parameters. The average standard deviation for the regression of oleic acid at 60°C is about 0.022 which is smaller than that obtained at 40°C for oleic acid. It can then be assumed that the model predicted the binary parameters better for linoleic acid than I did for oleic acid. Similarly, figure 4.2-17 shows the regressed VLE data for linoleic acid/CO₂ at 60°C using Peng Robinson. It can be deduced from the diagram that the thermodynamic equation of state almost perfectly predicted or mimicked the VLE data.

6. PALMITIC ACID/ CO₂

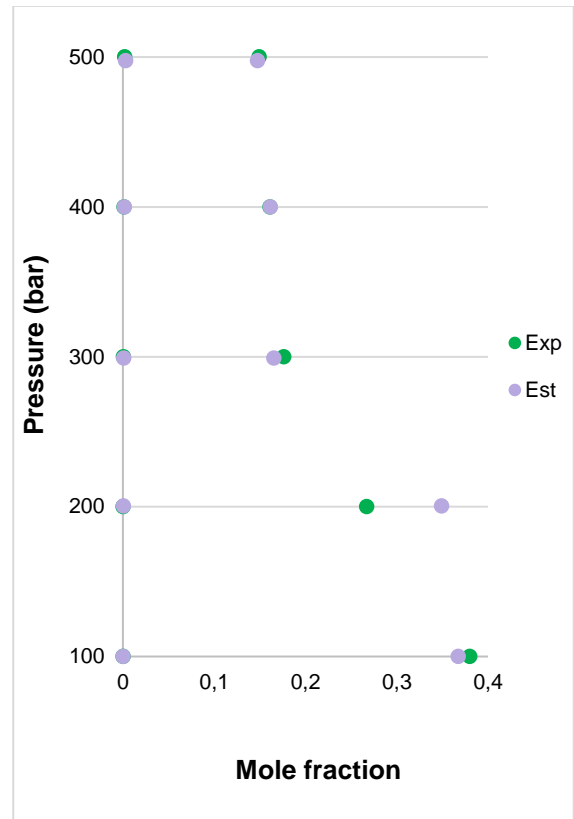
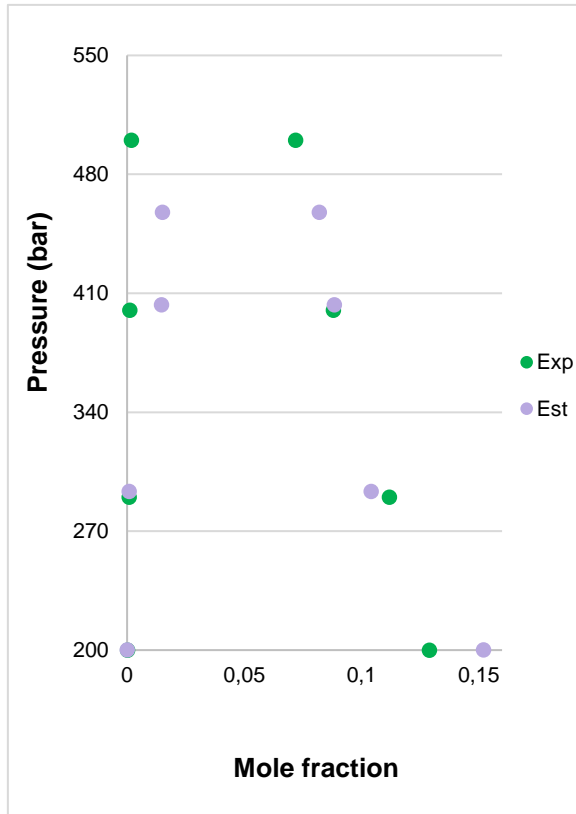


Figure 4.2-18: Palmitic acid/CO₂ regressed at 60°C Figure 4.2-19: Palmitic acid/CO₂ regressed at 80°C

Figure 4.2-18 illustrates the regressed VLE data for palmitic acid/CO₂ at 60°C using Peng Robinson. Fitting of VLE data of the palmitic acid/CO₂ systems at 60°C for the determination of optimized parameters, was performed by the simple PR model with two temperature-dependent parameters. The obtained results of all thermodynamic model show an average standard deviation of 0.033 which shows that the deviation is still within the experimental accuracy. The model predicted the VLE data more accurately on the liquid phase than the vapour phase. Figure 4.2-19 also shows the regressed VLE data for palmitic acid/CO₂ at 80°C using Peng Robinson predicted the VLE data almost perfectly with a standard deviation of 0.02

7. TRIOLEIN/ CO₂

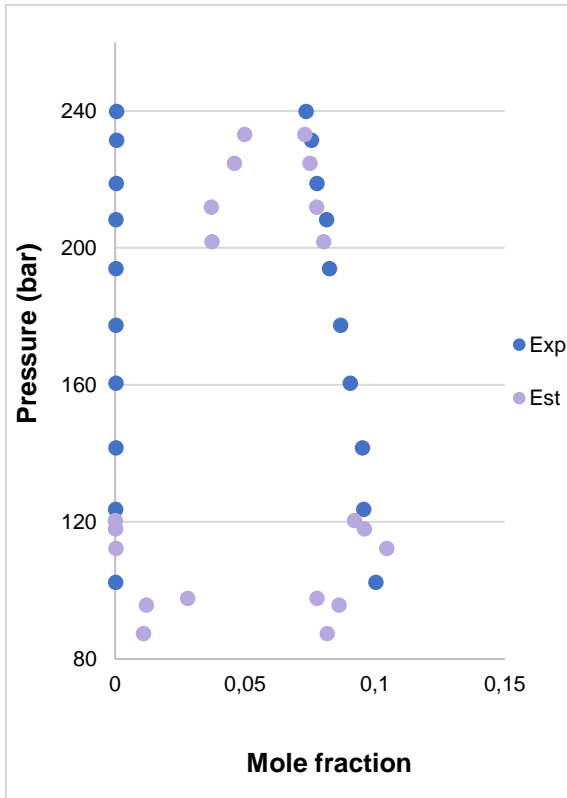


Figure 4.2-20: Triolein/CO₂ regressed at 40°C

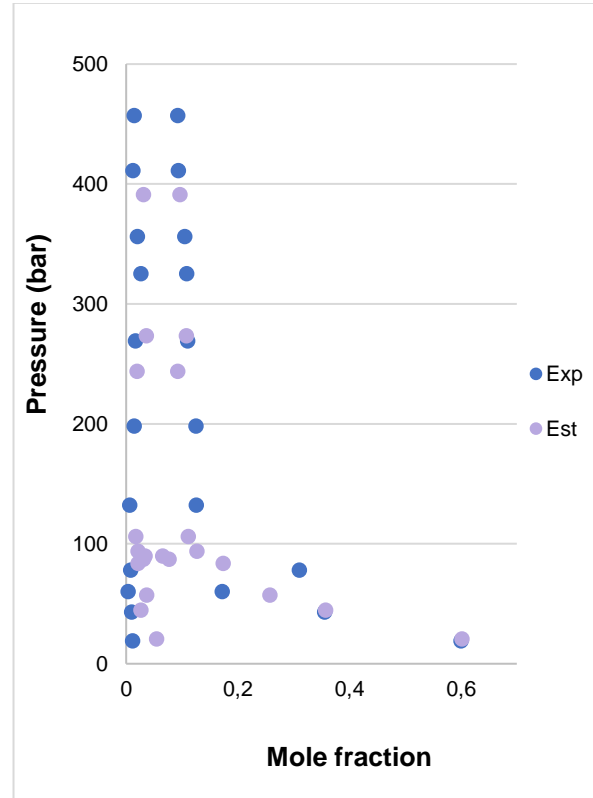


Figure 4.2-21: Triolein/CO₂ regressed at 60°C

Figure 4.2-20 above shows the regressed VLE data for triolein/CO₂ at 40°C using Peng Robinson. From the diagram it can be deduced that the equation of state chosen for this set of experimental data was not compatible. The model was able to predict the liquid phase but not the vapour. Perhaps a different thermodynamic model can accurately predict vapours should be used together with Peng Robinson for this regression. While Figure 4.2-21 that shows the regressed VLE data for triolein/CO₂ at 60°C using Peng Robinson was able to mimic the VLE data perfectly well with an average standard deviation of 0.001.

8. TRIPALMITATE/ CO₂

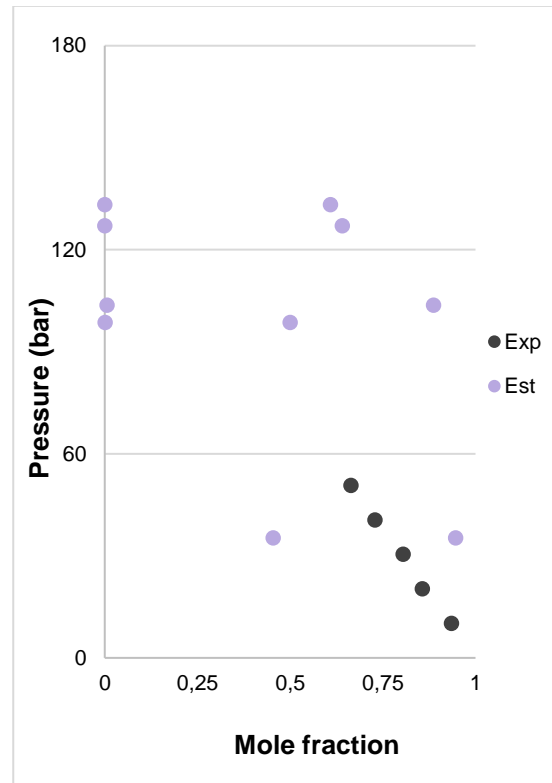
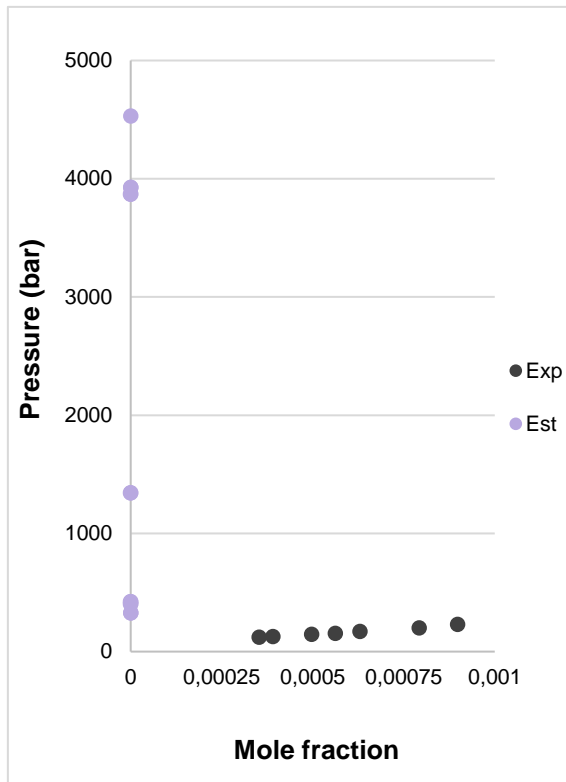


Figure 4.2-22: Tripalmitate/CO₂ regressed at 40°C Figure 4.2-23: Tripalmitate/CO₂ regressed at 100°C

Figure 4.2-22 shows regressed VLE data for tripalmitate/CO₂ at 40°C using Peng Robinson. The thermodynamic model could not estimate the experimental data. Another process model will have to be chosen or rather more data to be looked for in literature, perhaps data at a higher temperature. Likewise, figure 4.2-23 indicates the thermodynamic model was not able to estimate the investigational data for the regression of tripalmitate at 100°C.

The feasibility of separation of each class of compounds was tested from the others using a flash calculation.

4.3 SIMULATION AND OPTIMIZATION

A process model was developed based on the existing experimental set-up, and they were estimated as required for separation. A process layout was generated that could be used to achieve a separation between A, B, C, D.

4.3.1 FLASH CALCULATIONS

Literature was surveyed to find the different percentage compositions of each of the above-mentioned components in roasted peanuts. A simulation for the existing experimental set-up was done in order to estimate the process conditions required for separation.

Based on the vapour liquid equilibrium data, two phase separation diagrams were plotted and the results obtained there were used on Aspen as extraction conditions.

4.3.1.1 FRACTIONATION OF A/B/C/D

Given that: A = aromas, B= free fatty acids, C= triglycerides & D= waxes

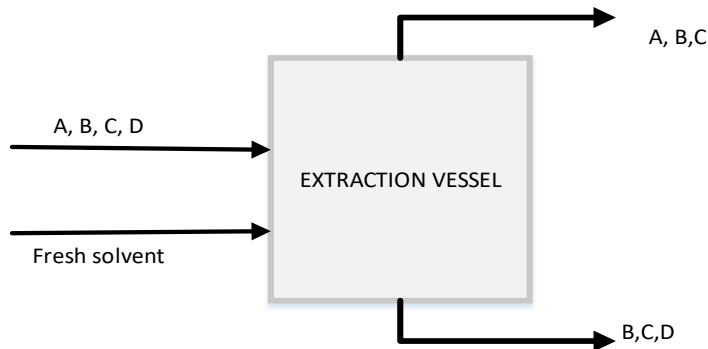


Figure 4.3-1: Process layout for separating desired components from roasted peanuts

Figure 4.3-1 represents a layout for an extraction of the different components from roasted peanuts using scCO₂ at process conditions of 40°C and 150 bar. A fresh feed of peanuts was assumed to be at 2.2 kg with a solvent a flowrate of 40 kg/hr. Different pressure ranges were varied to determine the best separation. A pressure of 140 bar gave better separation than that at 150 bar. If a lower solvent flowrate is used, then there is no separation because everything from the feed goes to the bottom however a flowrate of 40 kg/hr there is separation.

4.3.1.2 SEPARATING A&B/ C&D

This separation was done in the extraction vessel and A/B was separated in the separators S1 and S2 respectively. Where F, G & H are palmitic acid, triolein and trilinoleic acid respectively.

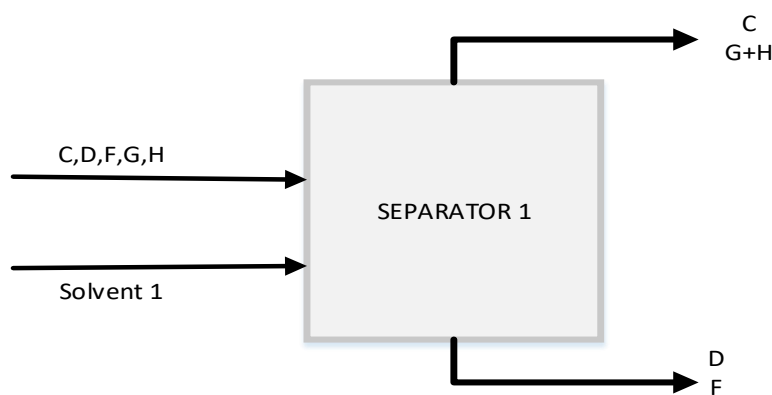


Figure 4.3-2: Top stream components separated from the extractor vessel

The products obtained from the extractor vessel showed that palmitic acid, triolein, trilinoleic acid, aroma compounds and wax fractions were separated into the top stream of the first separation. To remove the free fatty acid (palmitic) from triglycerides (triolein and trilinoleic acid), a higher temperature and pressure of 60°C and a 160 bar were used. It was noticed that the aroma compound and wax fraction could not be separated from the free fatty acid, this can be attributed to the fact that no VLE data was found in the NIST data base for them. A pressure of 100 bar gave a 50% percent separation hence the increase to 160 bar that gave a better separation of free fatty acids from triglycerides, the separation was almost perfect. A lower solvent flowrate of 15 kg/hr which is at the same conditions as the flash unit was used for a better separation. It was found that low and high solvent flows produced no separation at all. This can be accredited to the fact that low solvent flowrates might result in very long extraction times while high flowrates might mean that the solvent doesn't get enough time to be saturated in the solute inside the extractor vessel. Only the triglycerides were obtained in the bottom stream while all the light components went to the top stream.

4.3.1.3 SEPARATING A&B&C/D

This separation was performed in the extraction vessel, and A/B/C was separated in S1, S2 and S3.

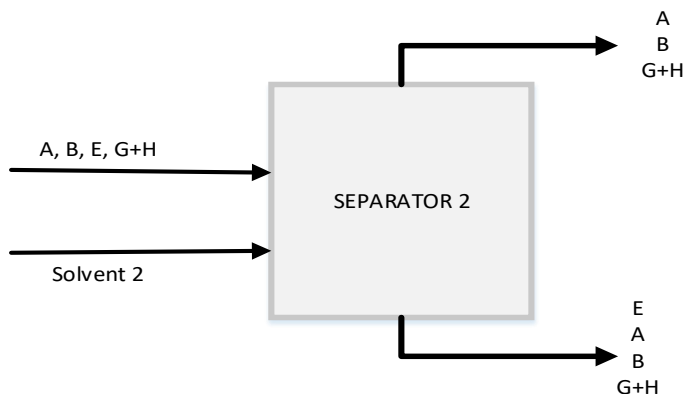


Figure 4.3-3: Bottom stream components separated from the extractor vessel

The products obtained from the extractor vessel showed that oleic acid, linoleic acid, tripalmitate and some traces of aroma compounds and wax fraction were separated into the bottom stream of the first separation. In order to remove the free fatty acid (tripalmitate) from the triglycerides (oleic acid and linoleic acid), a temperature and pressure of 60°C and 150 bar were used. It was noticed that the aroma compound and wax fraction could not be separated from the free fatty acid. 150 bar gave better separation while a higher and lower pressure below gave no separation at the solvent flowrate of 150 kg/hr. The separation in one sense

was feasible because most of the oleic acid and linoleic acid went to the top stream together with some traces of G and H.

However, a great amount of free fatty acids was still found in the bottom stream. Another separation vessel was used at higher pressure, temperature and flowrate to separate the free fatty acids from triglycerides.

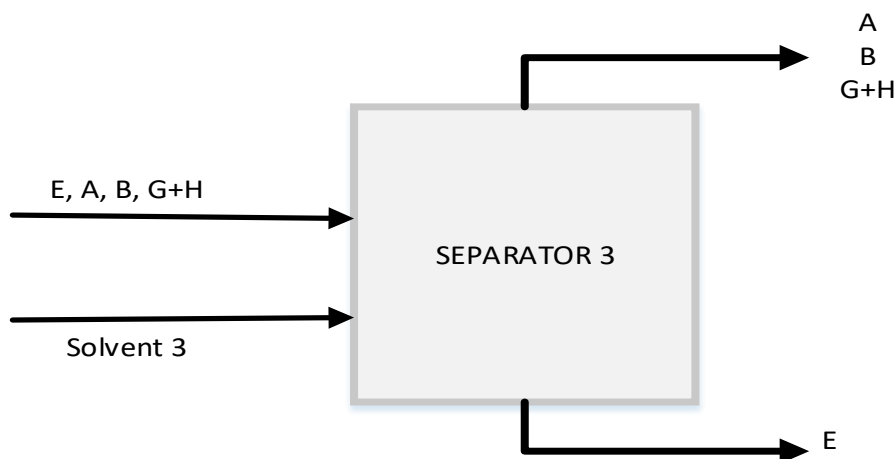


Figure 4.3-4: Bottom stream from separator 2, components separated from the extractor vessel

4.3.1.4 MODELLING BASED ON FLOWRATE

The bottom stream of separator 2 was further separated at 60°C, 150 kg/hr and 500 bar. The separation of free fatty acids from triglycerides was feasible. However, the aroma compounds and the wax fraction still cannot be separated from the free fatty acids. Beyond the fact that no vapour liquid equilibrium data was found for these components, this can be attributed to their molecular structures being similar which would make the separation complex. To test the feasibility of separation of each class of compounds from the others, a flash unit was used as the separation process using Aspen. At the same temperature of 40°C in all the feed streams and the flash unit, the flowrate of the solvent was reduced to determine the effect in the product streams.

To test the feasibility of separation of each class of compounds was also tested using a flash unit. The temperature of all the feed streams and the flash unit was set at 40°C. From the two-phase diagrams plotted above, they deduce that the best separation conditions for separating oleic acid from triolein is at 40°C which was used as the extraction temperature for this simple model. The solvent mass flowrate was set to 300 kg/hr and using an arbitrary feed ration 50/50, the separation was almost perfect. It can also be noticed that the liquid produced contains

more triolein than oleic acid which makes sense because triolein is a heavy component in comparison to oleic acid since it is a triglyceride.

Because a decrease in the solvent used resulted in an increase in the liquid product obtained, when linoleic acid was separated from triolein the lower solvent mass flowrate of 180 was used to determine the impact it would have on the produce. This model yielded results which were not expected, a decrease in the solvent flowrate resulted in the decrease of the liquid and increase in the vapour for oleic acid. Separation factors were compared with literature values for separable compounds using the same principle.

Table 4.3-1: Separation factors of peanut oil binary mixture at varying temperatures

Binary mixtures	Temperature	Process model
Triolein/oleic	40°C	0.74
Triolein/linoleic	60°C	1.0
Triolein/ palmitic acid	60°C	7.1×10^{-18}
Tripalmitate/ oleic acid	60°C	0.25
Tripalmitate/ linoleic acid	60°C	0.10

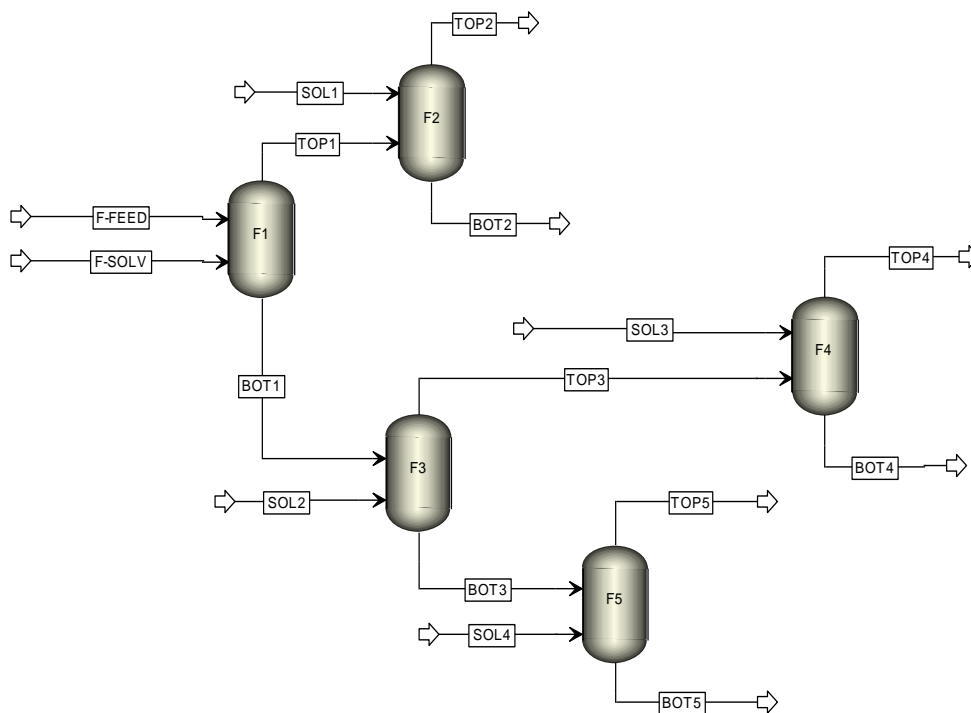


Figure 4.3-5: Entire process layout for a single pass peanut oil extraction

Different scenarios were eliminated those that appear not to be promising. Separating aroma compounds and wax fractions from free fatty acids whether from the extractor vessel or the

separators is not a promising scenario. The process model was used to adjust extraction conditions and to determine the conditions that achieves desired separations.

The results obtained are used to experimentally validate the model by examining the influence of process conditions on the yield.

4.4 VALIDATION OF SEPARATION EFFICIENCY

The pilot plant equipment was prepared prior to the running of the experiments. For each of the two experiments, a feed of approximately 1000g of roasted peanuts were grounded and sieved to a particle size of $< 80 \mu\text{m}$ and fed into the extraction basket. A headspace of about 20 cm was left to excuse for the growth of the feed when saturated with the solvent during extraction. The system and the material were purged once with CO_2 before filling the equipment with pressure to remove any air that might be in the system and in the basket. Throughout the experimental runs, the solvent flowrate, particle size were at 5 kg/hr, $< 80 \mu\text{m}$ and 60 minutes, respectively. The temperature and pressure were varied in each run. This run was at 40°C while varying the pressure at 150, 250 and 350 bar; sampling was done at 15-minute intervals.

4.4.1 SEPARATION EFFICIENCY EVALUATION

The extraction yield was calculated and represented with response to pressure over time. The effects of pressure, temperature, solvent flowrate, and particle size were studied and represented:

4.4.1.1 INFLUENCE OF EXTRACTION PRESSURE

The effect of the extraction pressure on the extraction yield of peanut oil was investigated at 150, 250 and 350 bar at 40°C for the first experiment.

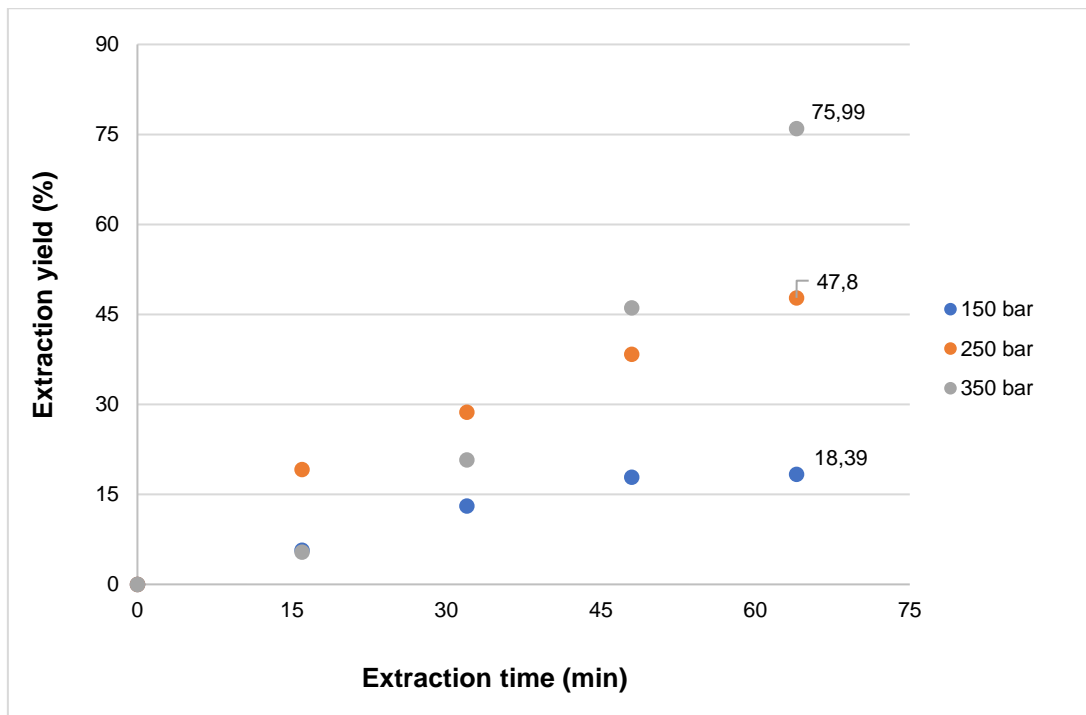


Figure 4.4-1: Effect of extraction pressure on extraction yield of peanut oil at 40°C

From the figure 4.4-1, it can be noticed that the extraction yield increases with a rise in the extraction pressure at 40°C. However, at 15 minutes of extraction at 250 bar, the yield remained the same before there was an increase to a yield of about 20.78%. This can be attributed to the fact that the solvent needed a longer time to be saturated or be enriched with the solute before there was a notable change in the mass extracted. The highest yield obtained at 150 was 18.39% while at 250 bar the yield increased to 47.8% and finally at 350 bar the highest extracted yield was 75.99%. The curves at 150 and 250 bar show a linear behaviour meaning the increase in the slopes represent a rise in solubility of the oil in solvent. The experiment at 250 and 350 bar was not ran until completion because of the slow extraction and the oil recovered was so little such that it was negligible.

The results for the second experiment are represented at 70°C with varying pressures of 150 bar and 250 bar:

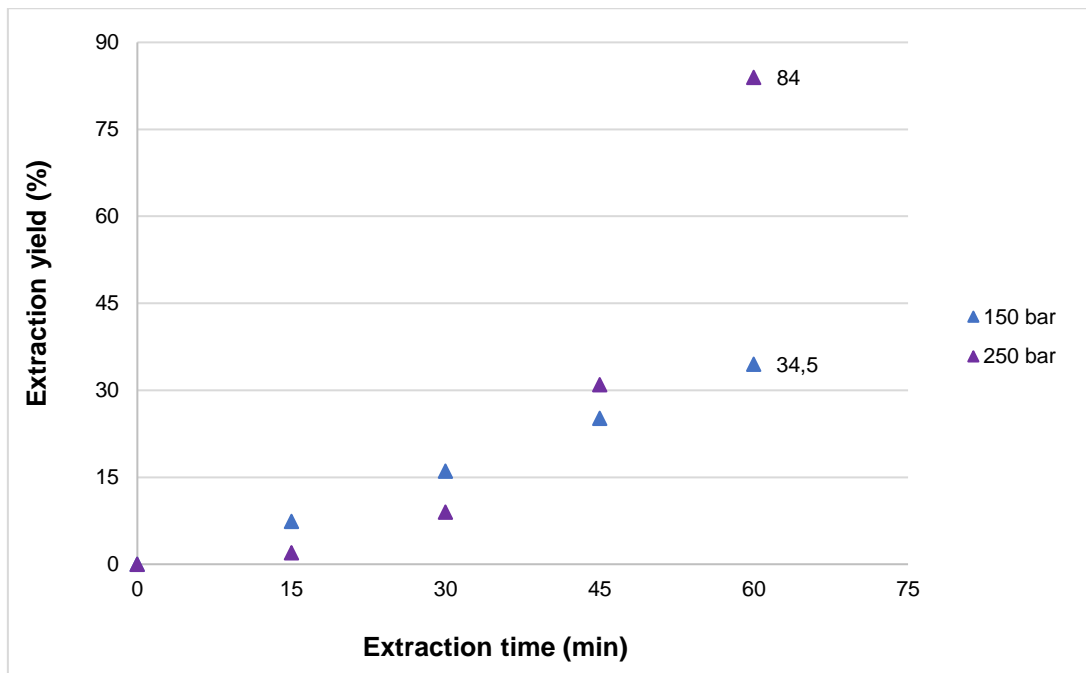


Figure 4.4-2: Influence of extraction pressure on extraction yield of peanut oil at 60°C

Figure 4.4-2 shows somewhat the same behaviour of an increase in the extraction yield as constant temperature because of a rise in pressure. Nevertheless, it can still be noticed that for the first 30 minutes of the experiment the yield at 150 bar was higher than that at 250 bar. This can be attributed to the rise in the temperature. A rise in the extraction temperature decreases the density of the solvent and thereby decreases the solubility and the affinity of the solvent. It can be noted that contrary to the effect of an increase in temperature to the solvent power, the highest yield obtained at 70°C is 84%. Comparing the results that were obtained in the preliminary results and the latter, a conclusion is drawn that smaller particle sizes produce high extraction yields. This is because for the preliminary run, the roasted peanuts were used as is within grinding. The highest extraction yield obtained in the preliminary results at 45°C and 400 bar was 38.91% while in this at 40°C and 350 bar the highest extraction yield obtained is 75.99%.

4.4.1.2 INFLUENCE OF EXTRACTION TEMPERATURE

The influence of temperature was studied at 250 bar amid the extraction temperature 40 and 70°C through the extraction at 5kg/hr solvent flowrate.

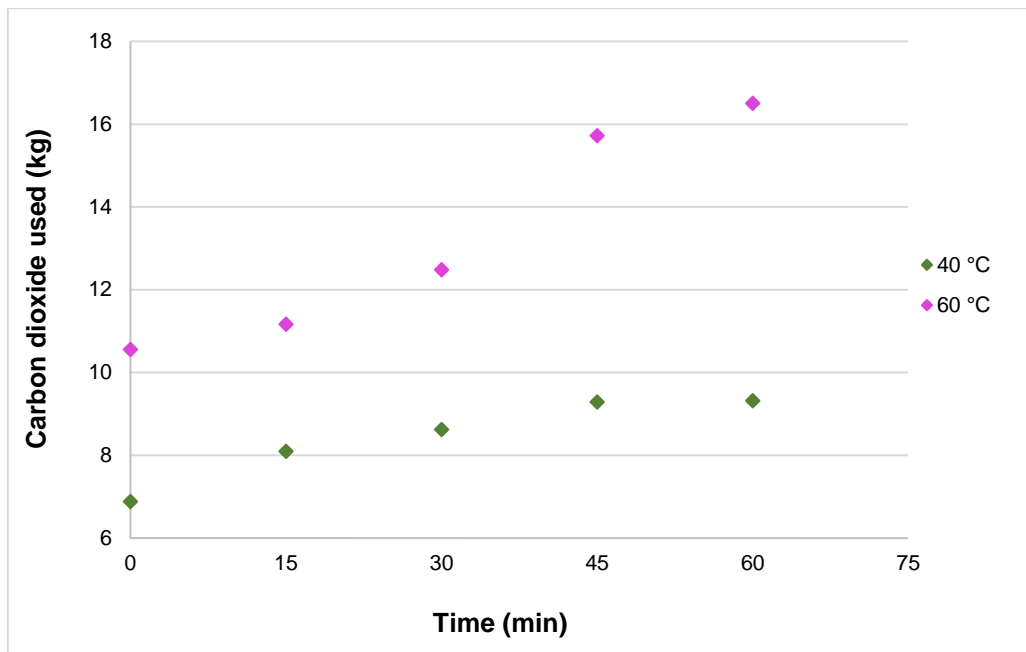


Figure 4.4-3: Influence of extraction temperature on extraction yield of peanut oil at 40 and 60°C

The carbon dioxide used starts at zero because the system was already running and the CO₂ was used to build pressure in the system and bring it to equilibrium. The graph shows that the mass of the solvent increases with a rise in temperature. This is clarified by the rise in the slopes of the extraction curves accounting to the increase in the solubility of the oil in the solvent. This was expected because the solubility increases with an increase in temperature, which indicates that the solvent will be more saturated with the solute resulting in an increase in the extraction yield.

4.4.1.3 INFLUENCE OF PARTICLE SIZE

The peanuts were roasted and ground using a conventional coffee grinder to a particle size < 80 μm. The grinding of peanuts before extraction not only intensifies the surface area but also releases oil from the intact cells of the peanuts. The results can only be compared to those of the preliminary run where the peanuts were not ground.

It is expected that a different mass transfer mechanism be noted because of the change in the particle size. The increased surface area means that the solvent has more affinity to dissolve more solute in the extract. This increases the mass extracted and the yield. The oil which is not released from the cells is extracted by a controlled flow or diffusion inside the particle hence the low solvent flowrate of 5 kg/hr. This consequently results in short extraction periods. Another step followed in the experimental validation of the process model is by means of estimating the operating costs. This section of the results describes the procedure followed in the estimation of operating cost per mass of the peanut oil extracted.

4.4.2 PROCESS ECONOMIC EVALUATION

One of the major aspects that affects the cost of SCF extraction processes is the extraction time which consequently affects the yield extracted. In the study, the process conditions were optimised by use of a process model and these affect the yield depending on the height of the extraction vessel. The operating costs were estimated by means of the solvent cycle which corresponds to the pump energy cost, heater, cooler comparative to the flow rate of CO₂ and extraction time. Aspen was used to estimate the operating costs. The research does not include a full economic analysis, instead utility costs and solvent consumption will be used as a reasonable basis for comparison of the running costs for each extraction route.

4.5 EXPERIMENTAL ANALYSIS

After the peanut oil extraction, the oil was analysed and a GC-MS analytical method was used to characterize the fatty acids.

4.5.1 CHARACTERISATION OF EXTRACTS

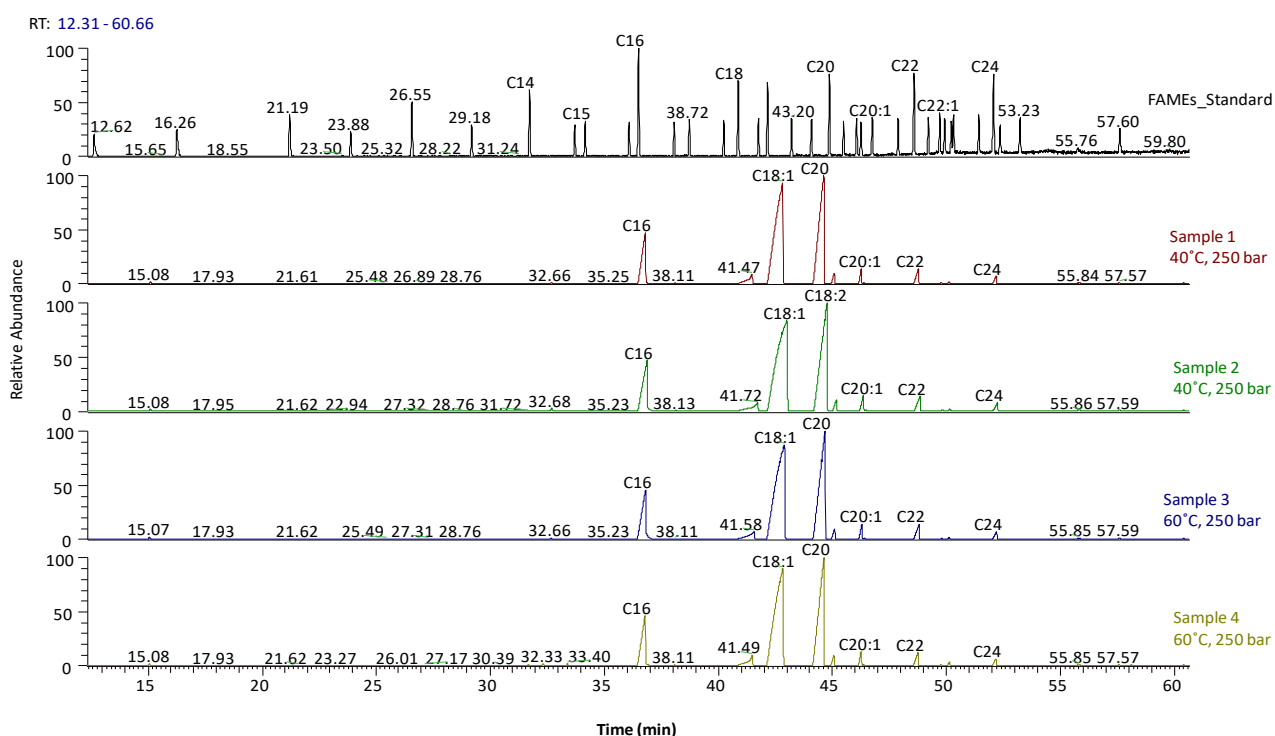


Figure 4.5-1: GC chromatogram of roasted peanut fatty acid methyl esters

The results obtained from the chromatogram of FAMES from peanut oil using a 100m long polarity capillary column indicates that the three fatty acids consisted of three classes of compounds: the saturated fatty acid, monounsaturated fatty acid and polyunsaturated fatty acids. The analysis achieved a separation with oleic acid, linoleic acid, palmitic acid, and stearic acids were found to be the major fatty acids in the extracted samples. Some of the

other high levels were noted as arachidic acid (C20) and behenic acid (C22). The fatty acid profile of peanut oil revealed that oleic acid is the main monounsaturated fatty acid. In summary, the peanut oil obtained about 48% saturated fatty acids, 7% monounsaturated fatty acids and 32% of polyunsaturated fatty acids. High levels of saturated fatty acids increase the oil oxidative stability and the levels of polysaturated and monosaturated fatty acid promote the roasted peanut oil nutritional value.

4.6 CHAPTER OUTCOMES

The results obtained during experimental work and analysis are presented to answer the research objectives:

- ✓ For objective one and two, the theoretical prediction of separation feasibility resulted in the development of a thermodynamic model with relevant systems of peanut oil. The data obtained during this simulation focused on the behaviour of the volatile compounds in supercritical carbon dioxide. Flash calculations were used to determine the feasible conditions of extraction.
- ✓ The results obtained were used to answer objective three, the highest yield obtained at 150 was 18.39% while at 250 bar the yield increased to 47.8% and finally at 350 bar the highest extracted yield was 75.99%. A high temperature of 60°C produced the highest extraction yield by increasing the mass of the carbon dioxide used. The best separation would be obtained at 40°C and varying pressures for different classes of compounds: 150, 250 and 350 bar for aroma compounds, free fatty acids and triglycerides respectively.
- ✓ These samples were sent for HPLC and GC-MS analysis to fulfil objective four. The analysis data was used to characterise the different peanut oil extracts.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This chapter gives conclusions on the overall research. The study focussed on the multi-product fractionation of roasted peanuts using scCO₂ by evaluation of process alternatives. The separation technique suitable for the extraction and optimization of peanut oil from roasted peanuts was identified as Supercritical Fluid extraction. Carbon dioxide was identified as an alternative solvent to the conventional ones because of its 100% oil recovery without solvent residues in the final product. Extraction parameters were optimised for the simultaneous determination of multiple products from food grade oil in a single step fractionation process.

5.1 CONCLUSIONS

The data suggest that temperature had no significant effect on the solubility of triglycerides, free fatty acids and waxes in scCO₂ but much effect of the temperature was observed on the aroma compounds. A significant difference in solubility between oleic acid and TAGs was found. Within the temperature and pressure range examined, density rather than temperature was the most important factor regarding solubility. It can thus be concluded that process parameters (pressure, temperature and particle size) had a significant influence on the roasted peanut oil yield. A highest yield of 75.99% was obtained at 350 bar for a constant temperature of 40°C. While at 60°C, a highest yield of 84% was obtained at 250 bar.

Triglycerides and free fatty acids can be enriched in CO₂ allowing a possible separation. This is due to the dissolution of component in vapour while the other remains in the liquid phase. The chosen equation of state Pen Robinson was in agreement with a variety of the relevant systems. The average standard deviation for the regression of oleic acid at 40°C was obtained

to be 0.04 while for linoleic acid was 0.323. It is clear that the thermodynamic model gives close values for the binary interaction parameters. For components such as tripalmitate, the thermodynamic model could not estimate the experimental data for the regression of tripalmitate at 100°C.

Using flash calculations, best separation was obtained at 40°C by varying pressures for different classes of compounds at 150, 250 and 350 bar for aroma compounds, free fatty acids and triglycerides respectively. The aim of the study which was to extract four classes of compounds into four product streams in a single process pass using supercritical CO₂ was achieved. Additionally, the research objectives were met and the hypothesis was proven correct.

The process proved that simultaneous single pass separation of multiple compounds is possible. Although the particle size was not studied, it can be concluded that show extraction times and high extraction yield. The data suggest that temperature did not significantly influence the solubility of triglycerides, free fatty acids and waxes in scCO₂ but much effect of the temperature was observed on the aroma compounds. A duplicate analysis of sample was taken for analysis. The characterization procedure choice was feasible in determining the different peanut oil FAMEs. Oleic acid and linoleic acid were identified as the main fatty acids in the extracted samples. Other fatty acids such as palmitic acid and stearic acids were in in smaller proportion.

5.2 RECOMMENDATIONS

While this study was focussed on the optimization of peanut oil by SCF extraction using scCO₂, Supplementary study areas were recommended.

5.2.1 FEED PREPARATION

Pre-processing of the feed material is important, and it is recommended that instead of roasting peanuts for an hour at 140°C, the feed can be roasted for 30 minutes in order to obtain a residue that is white. In the study, the peanuts were roasted for long resulting in a brown residue even after peanut oil extraction.

5.2.2 PARTICLE SIZE

Studies indicated short extraction times and high extraction yields due to decreased particle size of the feed. During the grinding process, the ground feed became sticky due to some of the oil being exposed. It is recommended therefore that the feed be frozen by means of

nitrogen use in order to accurately study the effect of particle size. This is to avoid the oil being sticky and affecting the investigation.

5.2.3 RESIDUE AND OIL

The product residue can be made into a product of high value i.e., high protein powder, soaps and even add it as a baking agent. And the oil obtained from peanuts does not have solvent traces, this oil can be classified as organic.

5.3 CHAPTER OUTCOME

- ✓ Conclusions, limitations, and recommendations on future research

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CHAPTER 6

APPENDICES

This section of the work is aimed at providing additional data and information to the thesis. The following steps were taken into consideration for the pilot plant start before every extraction:

6.1 APPENDIX A: START-UP PROCEDURE

1. The list below must be used in preparation for the start-up:
2. Ensure that the air (nitrogen) and CO₂ supply are available by inspecting the supply tanks outside the laboratory
3. Make sure the bottle and shutoff valves are open
4. Switch on the HMI and open the Labview application for the extraction operation
5. Reset the alarms shown at the bottom of the screen
6. Switch the machine on by clicking on the green button on the green top of the screen
7. Have a flash drive handy for storage and logging in of data during experiment
8. Turn on the High Voltage power supply to the machine, both on the wall and on the machine
9. Ensure that the chiller is plugged onto the main frame of the machine and that it is set ON
10. The chiller should turn on; the over-temperature alarm will remain activated
11. Set all the thermal equipment to their required settings

12. Wait until the chiller and heaters reach the set temperature before filing the machine with CO₂

13. Make sure that all the draining and venting valves are closed

Vent valve	Checked	Drain valve	Checked
VMR400		DMR201	
VMR410		DMR401	
VMR420		DMR410	
VMR500		DMRV500	
VMR510		DMRV510	
VMR520		DMRV520	
		DMRV530	

14. Check if the following manual valves are closed:

Valve	Checked	Valve	Checked
MV400		MV421	
MV401		MV422	
MV402		MV423	
MV403		MV424	
MV211		MV425	
MV420		MV500	

15. When both the chiller and the machine have reached steady state temperature

16. Open CO₂ supply valve MV100 to fill P200 pump

17. Select the valves responding to your process

After the start-up, the following step by step method is followed for the extraction of peanut oil from roasted peanuts. The methods are intended to crystallize the steps involved in the experiment and to question the steps ahead of time. It should be possible to repeat the steps and get the same results hence, all possible variations of the steps are considered and that the steps are written clearly:

6.2 APPENDIX B: PEANUT OIL EXTRACTION

1. Roasted peanuts must be dried in an oven in order to maintain constant moisture content

2. Peanuts must then be weighed and then loaded into the extraction vessel
3. Before pressurization, the system must be allowed to reach different steady states, specifically the present operating temperature
4. In order to ensure a liquid feed to the piston pump, the subcooled solvent (scCO₂) stored in the cylindrical vessel must be drawn from the cylinder's outside
5. It must then be passed through the chiller, where it will be cooled to a temperature of -5 to 3 °C
6. The chilled CO₂ must be discharged from the pump
7. The pressure must be adjusted to the desired operating pressure
8. From the pump, this liquid must be sent to a heater (which uses a coil to maximize heat transfer) where it is heated to a temperature above its critical temperature (31 °C) turning it into a vapor
9. After pressurizing the vessel, the peanuts must be statically soaked for a period of about 10 minutes
10. This solvent must then be fed at the bottom of extractor vessel to begin the experiment
11. After the ten minutes, the static/dynamic valve must be opened.
12. The CO₂ containing the extracted oil will exist through the top of the vessel and passed through the static/dynamic valve
13. The unit is equipped with a restrictor valve, which is a valve that regulates the flowrate of CO₂
14. Due to the decrease in pressure from the inside of the vessel to the bottle pressure, the restrictor valve is heated to prevent the valve from freezing
15. The static interval allows the peanuts to soak so that the CO₂ can penetrate the matrix and extract the oil from the peanuts.
16. During the dynamic interval, CO₂ carrying the peanut oil will flow out of the unit and into a pre-weighed collection flask in the separator, where the CO₂ will be vented or recycled.
17. Samples will be collected in the separators.
18. Samples are taken at intervals of 30 minutes until the next process condition
19. Samples will have to be labelled and stored in the fridge until the day of analysis
20. Different analytical methods both qualitative and quantitative will be used e.g., NMR, FTIR and HPLC

Once the extraction is complete, the following general procedure to depressurize the system until shutdown. The procedure can be applied likewise for A40, A41, or the column C42.

6.3 APPENDIX C: START-UP PROCEDURE

Reduce the flow rate of the CO₂ pump to a low value (5 kg/h for extractors, 1-2 kg/h for column)

Depressurize the system down to the separator pressure by stepwise changing the set point of ARV 400, or by using the ramp function on the ARV400 control box on the screen.

Watch the pressure in the separators. The pressure will raise with the amount of CO₂ released from the Extractor / Column. If the pressure in the separator gets too high (e.g. > 70 bar in S52) open VMV520 to bring the pressure in S52 back to ~ 55 bar.

In the course of depressurization open ARV500 and ARV510 fully to attain the same pressure level in all three Separators

When the pressure in the extractor has reached the pressure level in the separators the CO₂ pump is stopped.

Close MV/VMV100 (middle position)

Close MV400 / MV410 / MV420

Set ARV400 to 0 bar

Open VMV520, VMV510, VMV500 gently to lower the pressure by venting the separators

When the pressure is getting close to zero open all other vent valves (VMRV400, VMRV410, VMRV420)

Before opening the extractors also open DMV400 and DMV410 to release any possible pressure build up underneath the basket.

Open extractors and separators to recover materials and extracts

In order to theoretically determine the feasibility of separation of the four fractions, phase behaviour data was collected from literature and is represented below:

6.4 APPENDIX D: SUMMARY OF PHASE EQUILIBRIA DATA

Table 6.4-1: Summary of phase equilibria data

Components in roasted peanuts			References
1	FFA/ CO ₂	Oleic acid/CO ₂ at 40°C Oleic acid/CO ₂ at 60°C	• Zou, M.; Yu, Z. R.; Kashulines, P.; Rizvi, S. S. H.; Zollweg, J. A. J. Supercrit. Fluids, 1990, 3, 23-8 Fluid-liquid phase equilibria of fatty acids and fatty acid methyl esters in supercritical carbon dioxide.
		Linoleic acid/CO ₂ at 40°C Linoleic acid/CO ₂ at 60°C	• Zou, M.; Yu, Z. R.; Kashulines, P.; Rizvi, S. S. H.; Zollweg, J. A. J. Supercrit. Fluids, 1990, 3, 23-8 Fluid-liquid phase equilibria of fatty acids and fatty acid methyl esters in supercritical carbon dioxide
		Palmitic acid/CO ₂ at 60°C Palmitic acid/CO ₂ at 80°C	• Weber, W.; Petkov, S.; Brunner, G. Fluid Phase Equilib., 1999, 158, 695
2	TG/CO ₂	Triolein acid/CO ₂ at 40°C	• Chen, C. -C.; Chang, C. J.; Yang, P. Fluid Phase Equilib., 2000, 175, 107-115 Vapor-liquid equilibria of carbon dioxide with linoleic acid, alpha -tocopherol and triolein at elevated pressures
		Triolein acid/CO ₂ at 60°C	• Perko, T.; Knez, Z.; Skerget, M. J. Chem. Eng. Data, 2012, 57(12), 3604-3610 Phase Equilibria of Glycerol Tristearate and Glycerol Trioleate in Carbon Dioxide and Sulfur Hexafluoride
		Tripalmitic acid/CO ₂ at 60°C Tripalmitic acid/CO ₂ at 80°C	• Weber, W.; Petkov, S.; Brunner, G. Fluid Phase Equilib., 1999, 158, 695
		Trilinolein at 40C	No data
		Trilinolein at 60C	No data

6.5 APPENDIX E: PHASE EQUILIBRIA RAW DATA

Table 6.5-1: VLE data for oleic acid at 40°C

No.	Liquid mole fraction oleic acid	Temperature (K)	Vapor mole fraction oleic acid	Total pressure (N/sqm)
1	0.188	313.15	0.0142	28410000
2	0.198	313.15	0.012	25190000
3	0.213	313.15	0.0099	20950000
4	0.248	313.15	0.0077	15890000
5	0.282	313.15	0.0053	12010000
6	0.338	313.15	0.0045	7210000

Table 6.5-2: VLE data for oleic acid at 60°C

No.	Vapor mole fraction oleic acid	Temperature (K)	Vapor mole fraction oleic acid	Total pressure (N/sqm)
1	0.196	333.15	0.0125	28810000
2	0.216	333.15	0.0096	23460000
3	0.239	333.15	0.0082	20900000
4	0.26	333.15	0.0064	16200000
5	0.324	333.15	0.0051	11480000
6	0.35	333.15	0.0044	7100000

Table 6.5-3: VLE data for linoleic acid at 40°C

PRESSURE N/sqm	X	X	Y	Y
	LINOLEIC	CO2	LINOLEIC	CO2
0.10%	0.10%	0%	1%	0%
26500000	0.183	0.817	0.0138	0.9862
22930000	0.194	0.806	0.0115	0.9885
18210000	0.212	0.788	0.0098	0.9902
14120000	0.227	0.773	0.0072	0.9928
10020000	0.25	0.75	0.0054	0.9946
6400000	0.28	0.72	0.0045	0.9955

Table 6.5-4: VLE data for linoleic acid at 60°C

PRESSURE N/sqm	X	X	Y	Y
	LINOLEIC	CO2	LINOLEIC	CO2
0.10%	0.10%	0%	1%	0%
27140000	0.192	0.808	0.012	0.988
21830000	0.219	0.781	0.0108	0.9892
18160000	0.236	0.764	0.0092	0.9908
13800000	0.265	0.735	0.0065	0.9935
9940000	0.298	0.702	0.005	0.995
6340000	0.323	0.677	0.0035	0.9965

Table 6.5-5: VLE data for tripalmitate at 60°C

PRESSURE	X	X	Y	Y
N/sqm	TRIPALM	CO2	TRIPALM	CO2
0.10%	0.10%	0%	1%	0%
50000000	0.072	0.928	0.00188	0.99812
40000000	0.088	0.912	0.0012	0.9988
29000000	0.112	0.888	0.00092	0.99908
20000000	0.129	0.871	0.00022	0.99978

Table 6.5-6: VLE data for tripalmitate at 80°C

PRESSURE	X	X	Y	Y
N/sqm	TRIPALM	CO2	TRIPALM	CO2
0.10%	0.10%	0%	1%	0%
50000000	0.149	0.851	0.00169	0.99831
40000000	0.161	0.839	0.00117	0.99883
30000000	0.176	0.824	0.0005	0.9995
20000000	0.267	0.733	4.00E-05	0.99996
10000000	0.38	0.62	1.00E-05	0.99999

Table 6.5-7: VLE data for tripalmitate at 40°C

No.	Liquid mole fraction triolein	Temperature (K)	Vapor mole fraction triolein	Total pressure (N/sqm)
1	0.0735	313	0.0006	23990000
2	0.0756	313	0.0006	23140000
3	0.0777	313	0.0005	21880000
4	0.0814	313	0.0004	20830000
5	0.0825	313	0.0004	19400000
6	0.0869	313	0.0004	17740000
7	0.0906	313	0.0003	16050000
8	0.0952	313	0.0003	14160000
9	0.0957	313	0.0002	12370000

10	0.1004	313	0.0002	10240000
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Table 6.5-8: VLE data for tripalmitate at 60°C

No.	Liquid mole fraction triolein	Temperature (K)	Vapor mole fraction triolein	Total pressure (N/sqm)
1	0.0925	333	0.014	45700000
2	0.0934	333	0.0118	41100000
3	0.1047	333	0.0202	35600000
4	0.1082	333	0.0262	32500000
5	0.1101	333	0.0165	26900000
6	0.1247	333	0.014	19800000
7	0.1255	333	0.0059	13200000
8	0.1719	333	0.0033	6000000
9	0.3102	333	0.008	7800000
10	0.3557	333	0.0094	4300000
11	0.6	333	0.0113	1900000

Table 6.5-9: VLE data for palmitic acid at 60°C

PRESSURE N/sqm	X	X	Y	Y
	PALMITIC	CO2	PALMITIC	CO2
0.10%	0.10%	0%	1%	0%
5070000	0.664	0.336	0.0002	0.9998
4050000	0.728	0.272	0.0002	0.9998
3040000	0.804	0.196	0.0001	0.9999
2030000	0.856	0.144	0.0001	0.9999
1010000	0.9348	0.0652	0.0001	0.9999

Table 6.5-10: VLE data for palmitic acid at 80°C

PRESSURE N/sqm	X	X	Y	Y
	PALMITIC	CO2	PALMITIC	CO2
0.10%	0.10%	0%	1%	0%
5070000	0.736	0.264	0.0002	0.9998
4050000	0.784	0.216	0.0002	0.9998
3040000	0.835	0.165	0.0001	0.9999
2030000	0.89	0.11	0.0001	0.9999
1010000	0.9418	0.0582	0.0001	0.9999

Using a property simulator, the phase equilibria data was regressed using a suitable thermodynamic mode and the data is represented below:

6.6 APPENDIX F: REGRESSED DATA

Table 6.6-1: Regressed data for linoleic acid at 40°C

Exp temp (°C)	Exp Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X linoleic acid	Est mol frac X linoleic acid	Exp mol frac Y linoleic acid	Est mol frac Y linoleic acid
40	43.1818	265	270.414	0.183	0.193063	0.0138	0.009229
40	41.792	229.3	233.833	0.194	0.203725	0.0115	0.008179
40	39.9847	182.1	185.734	0.212	0.221105	0.0098	0.006451
40	37.6927	141.2	145.055	0.227	0.240027	0.0072	0.004629
40	43.305	100.2	114.669	0.25	0.259096	0.0054	0.000735
40	26.318	64	73.0748	0.28	0.273878	0.0045	0.001497

Table 6.6-2: Regressed data for linoleic acid at 60°C

Exp temp (°C)	Exp Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X linoleic acid	Est mol frac X linoleic acid	Exp mol frac Y linoleic acid	Est mol frac Y linoleic acid
60	59.8252	271.4	266.715	0.192	0.185716	0.012	0.010211
60	60.2732	218.3	216.145	0.219	0.211718	0.0108	0.006765
60	58.5081	181.6	184.047	0.236	0.232433	0.0092	0.004511
60	53.5552	138	144.478	0.265	0.260577	0.0065	0.002162
60	42.7908	99.4	108.366	0.298	0.277456	0.005	0.001118
60	40.5586	63.4	90.0798	0.323	0.327167	0.0035	0.000221

Table 6.6-3: Regressed data for oleic acid at 40°C

Exp temp (°C)	Exp Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X oleic acid	Est mol frac X oleic acid	Exp mol frac Y oleic acid	Est mol frac Y oleic acid
40	38.9096	284.1	260.767	0.188	0.178666	0.0142	0.022553
40	41.3657	251.9	248.45	0.198	0.198117	0.012	0.029616
40	50.7981	209.5	196.512	0.213	0.211348	0.0099	0.004915
40	39.8384	158.9	159.386	0.248	0.251496	0.0077	0.010364
40	39.1153	120.1	120.751	0.282	0.289494	0.0053	0.00584
40	35.68	72.1	86.5257	0.338	0.332237	0.0045	0.000688

Table 6.6-4: Regressed data for oleic acid at 60°C

Exp temp (°C)	Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X oleic acid	Est mol frac X oleic acid	Exp mol frac Y oleic acid	Est mol frac Y oleic acid
3060	3058.25	288.1	566.623	0.196	0.323957	0.0125	0.323957
3060	3058.14	234.6	500.05	0.216	0.372102	0.0096	0.372102
3060	3058.17	209	455.016	0.239	0.411838	0.0082	0.411838
3060	3058.02	162	402.338	0.26	0.468536	0.0064	0.468536
3060	3058.09	114.8	332.598	0.324	0.569333	0.0051	0.569333
3060	3057.8	71	294.885	0.35	0.640571	0.0044	0.640572

Table 6.6-5: Regressed data for palmitic acid at 60°C

Exp temp (°C)	Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X palmitic acid	Est mol frac X palmitic acid	Exp mol frac Y palmitic acid	Est mol frac Y palmitic acid
59.85	70.7419	500	457.583	0.072	0.082055	0.00188	0.01513
59.85	58.9137	400	403.193	0.088	0.088494	0.0012	0.01467
59.85	58.4946	290	293.312	0.112	0.104201	0.00092	0.000933
59.85	59.7409	200	200.128	0.129	0.152076	0.00022	7.80E-05

Table 6.6-6: Regressed data for palmitic acid at 80°C

Exp temp (°C)	Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X palmitic acid	Est mol frac X palmitic acid	Exp mol frac Y palmitic acid	Est mol frac Y palmitic acid
79.85	80.4324	500	497.611	0.149	0.14748	0.00169	0.002794
79.85	79.8471	400	400.015	0.161	0.161357	0.00117	0.001353
79.85	80.2468	300	299.101	0.176	0.165252	0.0005	0.000621
79.85	79.5703	200	200.456	0.267	0.348844	4.00E-05	0.000292
79.85	79.8432	100	100.012	0.38	0.367361	1.00E-05	8.14E-06

Table 6.6-7: Regressed data for triolein at 40°C

Exp temp (°C)	Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X triolein	Est mol frac X triolein	Exp mol frac Y triolein	Est mol frac Y triolein
39.85	50.6125	239.9	233.119	0.0735	0.073057	0.0006	0.049924
39.85	50.6993	231.4	224.697	0.0756	0.075083	0.0006	0.045953
39.85	51.4222	218.8	211.905	0.0777	0.077626	0.0005	0.037038
39.85	50.4842	208.3	201.842	0.0814	0.080377	0.0004	0.037314
39.85	45.1019	194	87.4404	0.0825	0.081643	0.0004	0.010982
39.85	39.9088	177.4	95.7547	0.0869	0.086258	0.0004	0.012035
39.85	18.8484	160.5	97.7247	0.0906	0.077782	0.0003	0.027903
39.85	52.895	141.6	120.414	0.0952	0.092129	0.0003	0.000149
39.85	52.2134	123.7	117.998	0.0957	0.095934	0.0002	0.000175
39.85	50.7686	102.4	112.316	0.1004	0.104593	0.0002	0.000303

Table 6.6-8: Regressed data for triolein at 60°C

Exp temp (°C)	Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X triolein	Est mol frac X triolein	Exp mol frac Y triolein	Est mol frac Y triolein
59.85	74.9311	457	243.835	0.0925	0.092308	0.014	0.019486
59.85	71.642	411	391.045	0.0934	0.096003	0.0118	0.030633
59.85	105.368	356	87.0398	0.1047	0.076927	0.0202	0.030891
59.85	83.4321	325	89.7143	0.1082	0.06498	0.0262	0.03391
59.85	53.6726	269	273.361	0.1101	0.107711	0.0165	0.035752
59.85	131.341	198	93.5683	0.1247	0.126418	0.014	0.021151
59.85	32.2713	132	106.081	0.1255	0.111146	0.0059	0.017348
59.85	69.1934	60	83.4886	0.1719	0.173898	0.0033	0.021089

59.85	46.5044	78	57.1934	0.3102	0.257575	0.008	0.03656
59.85	57.3877	43	44.4731	0.3557	0.35718	0.0094	0.026239
59.85	63.5345	19	20.6345	0.6	0.601771	0.0113	0.054615

Table 6.6-9: Regressed data for triolein at 40°C

Exp temp (°C)	Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X tripalmitate	Est mol frac X tripalmitate	Exp mol frac Y tripalmitate	Est mol frac Y tripalmitate
39.85	107.495	121.1	423.354	1	1	0.0003534	5.79E-10
39.85	95.3325	128.8	403.018	1	1	0.0003912	4.26E-09
39.85	129.478	145.7	1343.39	1	1	0.0004968	8.12E-13
39.85	-15.5082	155.2	3868.79	1	1	0.0005624	5.21E-12
39.85	-13.3906	170.7	3927.5	1	1	0.0006302	4.32E-07
39.85	48.6693	201.5	327.736	1	1	0.0007923	1.78E-07
39.85	23.8153	229.3	4530.85	1	1	0.0008981	1.33E-05

Table 6.6-10: Regressed data for triolein at 100°C

Exp temp (°C)	Est temp (°C)	Exp pres (bar)	Est pres (bar)	Exp mol frac X tripalmitate	Est mol frac X tripalmitate	Exp mol frac Y tripalmitate	Est mol frac Y tripalmitate
99.85	236.371	50.7	133.247	0.664	0.608168		7.70E-06
99.85	244.869	40.5	127.016	0.728	0.64008		3.94E-05
99.85	228.743	30.4	98.6032	0.804	0.5		0.0002621
99.85	256.297	20.3	103.626	0.856	0.886054		0.005549
99.85	315.176	10.1	35.2083	0.9348	0.945583		0.453754

6.7 APPENDIX G: PRELIMINARY RESULTS

Table 6.7-1: Peanut oil data at 70°C, 200 bar and 13 kg/hr

Time (min)	CO ₂ mass (kg)	Separator Mass (kg)			Separator Mass (kg)			Extract mass (kg)
		S1	S2	S3	S1	S2	S3	
15	4.852	248.71	245.57	244.38	0.249	0.246	0.244	0.7387
30	7.675	251.25	245.66	244.36	0.251	0.246	0.244	0.7413
45	10.915	252.24	246.48	244.46	0.252	0.246	0.244	0.7432
60	13.971	252.47	246.36	244.48	0.252	0.246	0.244	0.7433
75	16.924	253.49	246.71	244.58	0.253	0.247	0.245	0.7448

90	20.063	254.06	247	244.58	0.254	0.247	0.245	0.7456
105	23.258	254.57	247.23	244.57	0.255	0.247	0.245	0.7464
120	26.363	255.53	248.16	244.55	0.256	0.248	0.245	0.7482
								5.9515

Table 6.7-2: Peanut oil data at 70°C, 300 bar and 13 kg/hr

Time (min)	CO ₂ mass (kg)	Separator mass (g)			Separator mass (kg)			Extract mass (kg)
		S1	S2	S3	S1	S2	S3	
15	31.77	255.25	0	0	0.255	0.238	0.187	0.6803
30	34.922	268.26	244.8	0	0.268	0.245	0.214	0.7271
45	38.062	280.73	244.9	0	0.281	0.245	0.226	0.7517
60	41.205	300.04	246	239	0.300	0.246	0.239	0.7850
75	44.376	305.82	247.9	244.5	0.306	0.248	0.245	0.7983
90	46.854	319.61	249.2	244.5	0.320	0.249	0.245	0.8133
105	49.841	330.87	249.4	244.5	0.331	0.249	0.245	0.8249
120	52.997	342.14	250.8	244.9	0.342	0.251	0.245	0.8378
135	56.106	351.75	250.6	244.5	0.352	0.251	0.245	0.8469
								7.0651

Table 6.7-3: Peanut oil data at 70°C, 400 bar and 13 kg/hr

Time (min)	CO ₂ mass (kg)	Separator mass (kg)			Separator mass (kg)			Extract mass (kg)
		S1	S2	S3	S1	S2	S3	
0	56.106	242.86	242.8	241.14	0.0276	0.0038	0.0014	0.03288
15	60.053	271.07	247.46	242.46	0.0486	0.0047	0.00132	0.05458
30	63.091	297.13	248.56	242.67	0.0543	0.0058	0.00153	0.06156
45	67.552	316.15	248.64	243.01	0.0733	0.0058	0.00187	0.081
60	69.53	335.05	249.84	244.05	0.0922	0.007	0.00291	0.10214
75	72.195	346.27	250.82	244.4	0.1034	0.008	0.00326	0.11469
90	75.218	359.13	253.58	244.62	0.1163	0.0108	0.00348	0.13053
105	77.77	366.9	253.74	244.67	0.124	0.0109	0.00353	0.13851

6.8 APPENDIX H: RAW EXPERIMENTAL DATA

Table 6.8-1: Peanut oil experimental data at 40°C and varying pressures of 150, 250 and 350 bar

Pressure (bar)	Temperature (°C)	solvent flowrate (kg/hr)	Time (m)	Bottle mass (g)	Bottle + oil (g)
150	40	5	0	0	0
150	40	5	16	226.5	227.07
150	40	5	32	242	243.25
150	40	5	48	243.35	243.76
150	40	5	64	243.35	243.76
250	40	5	0	233.4	0
250	40	5	16	233.4	238.78
250	40	5	32	233.4	248.8
250	40	5	48	233.4	258.75
250	40	5	64	233.4	263.26
350	40	5	0	237.98	0
350	40	5	16	237.98	257.14
350	40	5	32	237.98	264.8
350	40	5	48	237.98	273.5
350	40	5	64	237.98	281.9

Table 6.8-2: Peanut oil experimental data at 60°C and varying pressures of 150, 250 and 350 bar

Pressure (bar)	Temperature (°C)	solvent flowrate (kg/hr)	Time (m)	Bottle mass (g)	Bottle + oil (g)
150	60	5	0	244.5	0
150	60	5	15	244.5	251.9
150	60	5	30	244.5	253.2
150	60	5	45	244.5	253.6
150	60	5	60	244.5	253.8
250	60	5	0	243.7	0
250	60	5	15	243.7	243.9
250	60	5	30	243.7	244.4
250	60	5	45	243.7	245.9

6.9 APPENDIX I: GC-MS RAW DATA

Table 6.9-1: GC-MS data

Component	Sample Name	Area	Calculated amount	Retention time
c14	FAMEs_S1	48274	16,664	31,72
c14	FAMEs_S2	74401	24,587	31,72
c14	FAMEs_S3	60652	20,418	31,71
c14	FAMEs_S4	145357	46,106	31,70
c15	FAMEs_S1	16214	6,889	34,16
c15	FAMEs_S2	22788	8,865	34,17
c15	FAMEs_S3	19278	7,810	34,16
c15	FAMEs_S4	17437	7,257	34,16
c16	FAMEs_S1	204220	61,508	36,51
c16	FAMEs_S2	201771	60,798	36,50
c16	FAMEs_S3	175792	53,264	36,49
c16	FAMEs_S4	160326	48,779	36,49
c18	FAMEs_S1	48173	15,342	40,87
c18	FAMEs_S2	47940	15,275	40,87
c18	FAMEs_S3	42395	13,674	40,86
c18	FAMEs_S4	40778	13,208	40,87
c18:1	FAMEs_S1	843311	253,423	42,19
c18:1	FAMEs_S2	827895	248,847	42,20
c18:1	FAMEs_S3	730442	219,918	42,19
c18:1	FAMEs_S4	632638	190,884	42,19
c18:2	FAMEs_S1	551269	180,703	44,11
c18:2	FAMEs_S2	530899	174,119	44,11
c18:2	FAMEs_S3	470294	154,530	44,11
c18:2	FAMEs_S4	399134	131,530	44,11
c20	FAMEs_S1	15104	5,508	44,85
c20	FAMEs_S2	18642	6,515	44,85
c20	FAMEs_S3	15790	5,704	44,85
c20	FAMEs_S4	12462	4,756	44,85
c20:1	FAMEs_S1	17259	7,704	46,07
c20:1	FAMEs_S2	17801	7,865	46,07
c20:1	FAMEs_S3	18309	8,016	46,07
c20:1	FAMEs_S4	12938	6,422	46,07
c22	FAMEs_S1	36459	11,737	48,56
c22	FAMEs_S2	37088	11,911	48,56
c22	FAMEs_S3	36330	11,701	48,55

c22	FAMEs_S4	24257	8,358	48,55
c22:1	FAMEs_S1	118707	40,762	48,54
c22:1	FAMEs_S2	182200	61,621	49,82
c22:1	FAMEs_S3	144036	49,083	49,79
c22:1	FAMEs_S4	121229	41,590	49,78
c23	FAMEs_S1	24445	7,856	50,33
c23	FAMEs_S2	38723	12,245	50,35
c23	FAMEs_S3	31626	10,063	50,35
c23	FAMEs_S4	19826	6,437	50,32
c24	FAMEs_S1	14852	6,077	52,04
c24	FAMEs_S2	11804	5,201	52,03
c24	FAMEs_S3	13329	5,640	52,03
c24	FAMEs_S4	8849	4,352	52,01

RT:12.31 - 60.66

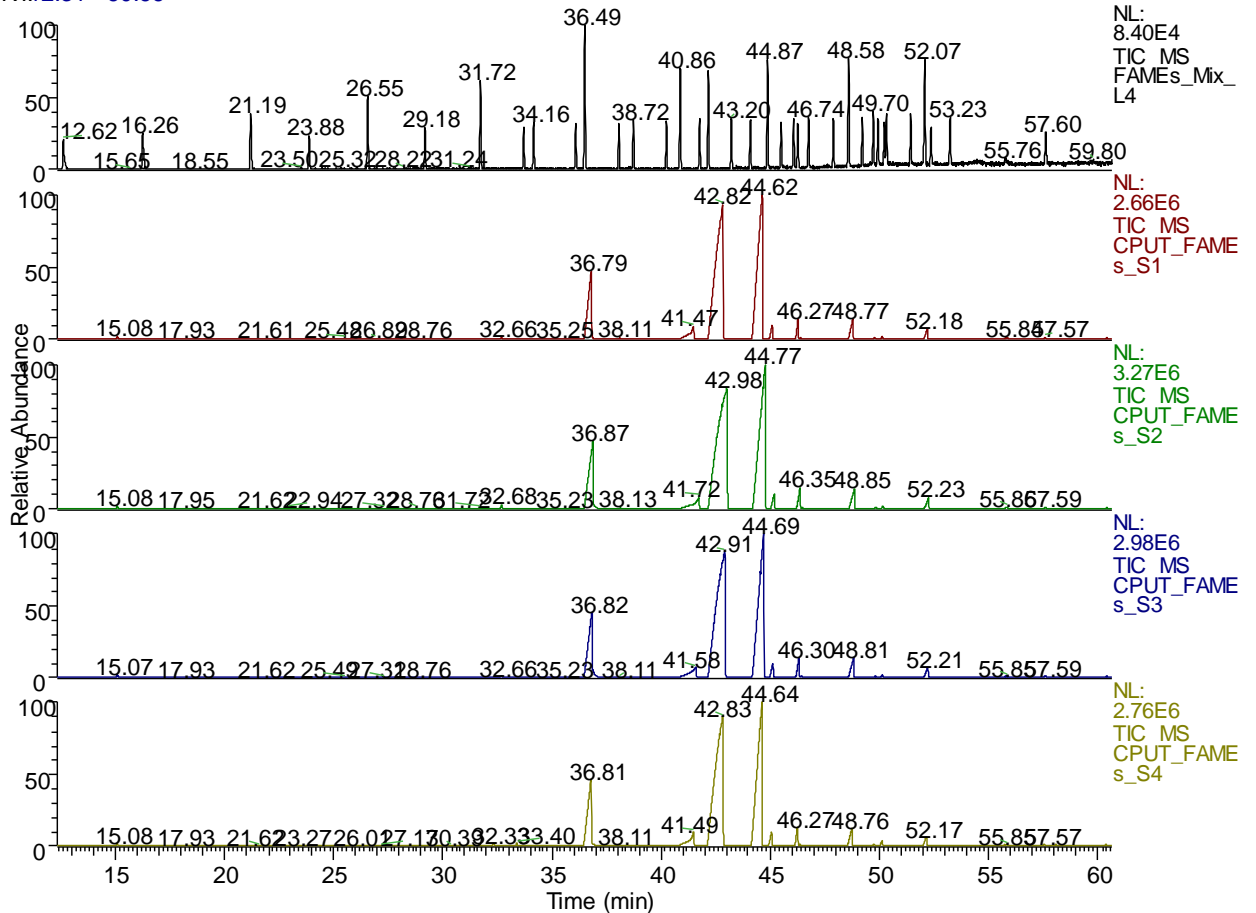


Figure 6.9-1: GC-MS Chromatogram