

**DEVELOPMENT OF A PREDICTIVE MODEL  
FOR A REFINED PALM OIL USING  
SUPERCRITICAL EXTRACTION.**

**BY**

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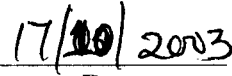
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## DECLARATION

I Abubakre F. K. declare that this project work has never been presented for the award of certificate or degree elsewhere.



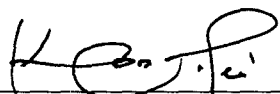
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## CERTIFICATION

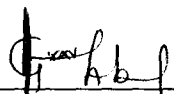
This is to certify that this project work "Predictive Model for a Refined Palm Oil using Supercritical Extraction" has been presented by Abubakre F. K. to the Department of Chemical Engineering, Federal University of Technology, Minna.



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## DEDICATION

This project work is dedicated to my late brothers and sisters including all the dead Muslims. May ALLAH forgive and have mercy on them and may He protect all the kids they left behind. “VERILY FROM ALLAH WE COME AND TO HIM WE SHALL RETURN” (Q2:156). OH ALLAH! Make the agony of death easy for us, let the grave be our peaceful abode and take our souls when you are pleased with us.

## ABSTRACT

A model equation was developed to predict the quantity of refined palm oil using supercritical extraction.

The model was obtained using multiple linear regression of statistical analysis.

Loading of the oil (kg/L) that represents the quantity of oil was used as a function of temperature (K) and density (kg/L)

The fitted model obtained was:

$$y = \exp(4037676.28 - 571555006.1X_1 - 2.13507X_2 - 7099.5688X_3)$$

where  $X_1$ ,  $X_2$  and  $X_3$  represent reciprocal of temperature, square of temperature's reciprocal and density respectively.

The  $R_2$  value obtained was 0.99 which confirms the accuracy of model.

## TABLE OF CONTENT

Title page.....	i
Declaration.....	ii
Certification.....	iii
Dedication.....	iv
Acknowledgement.....	v
Abstract.....	vi
Table of Content.....	vii

### CHAPTER ONE

1.0 Introduction.....	1
1.1 Aim and objective.....	2

### CHAPTER TWO

2.0 Literature review.....	3
2.1 Oil palm tree.....	3
2.1.1 The palm fruit.....	4
2.1.2 Palm oil processing.....	4
2.1.3 Process-flow chart.....	7
2.1.4 Composition of palm oil.....	8
2.1.4.1 Components of fatty acids of palm oil.....	9
2.1.4.2 Components of glycerides of palm oil.....	10
2.1.4.3 Average densities of palm oil.....	10
2.1.5 Economic importance.....	11
2.2 Extraction.....	11
2.2.1 Types of extraction.....	11

2.2.2	Factors affecting rate of extraction.....	12
2.3	Solvent extraction.....	13
2.3.1	Characteristics of an ideal solvent.....	13
2.3.2	Choice of solvent.....	14
2.4	Supercritical extraction.....	14
2.4.1	Advantages and disadvantages of supercritical extraction.....	15
2.4.1.1	Advantages of supercritical extraction.....	15
2.4.1.2	Disadvantages of supercritical extraction.....	16
2.4.2	Application of supercritical extraction.....	16
2.5	Carbon IV oxide (CO <sub>2</sub> ).....	16
2.5.1	Physical and chemical properties.....	17
2.5.1.1	Physical properties.....	17
2.5.1.2	Chemical properties.....	17
2.5.2	CO <sub>2</sub> as a supercritical solvent.....	18
2.5.2.1	Advantages of CO <sub>2</sub> .....	20
2.5.2.2	Disadvantages of CO <sub>2</sub> .....	21
2.5.3	CO <sub>2</sub> application.....	21
2.6	Mathematical modelling.....	21
2.6.1	Theory of modelling.....	22
2.6.2	Purpose of modelling.....	23
2.6.3	Statistical process modelling.....	23
2.6.4	Principles of data collection.....	24
2.7	Multiple regression software packages.....	25
2.7.1	MathCAD Professional.....	25
2.7.2	Microsoft Excel.....	26

### CHAPTER THREE

3.0	Methodology.....	27
3.1	Collection of experimental data.....	27
3.1.1	Equipment and apparatus used.....	27
3.1.2	Experimental procedure.....	29
3.2	Modelling.....	31
3.2.1	Development of the model.....	31
3.2.2	Manipulation of selected variables from Table 3.0.....	33
3.3	Simulation of the model.....	34

### CHAPTER FOUR

4.0	Result and discussion of result.....	35
4.1	Result .....	35
4.2	Discussion of result.....	37

### CHAPTER FIVE

5.0	Conclusion and Recommendation.....	38
5.1	Conclusion.....	38
5.2	Recommendation.....	38
	References.....	39
	Appendices.....	40



## CHAPTER ONE

### 1.0 INTRODUCTION

Chemical Engineering involves the application of the principles of physical sciences, principle of economics and human relation to field that pertain directly to processes and process equipment in which matter is treated to effect a change a state, energy content or composition ((Edoga, 2000). As a profession, it involves the production of bulky material from basic raw materials in a most economic and optimum way.

With greater demand for palm oil in industries and household, this work was carried out to predict the efficiency of a supercritical extraction of palm oil in order to improve both the quality and quantity of palm oil production.

Modelling serves as a method or means for predicting a process in various situations. It simplifies raw data and it is also the mathematical aspects of a process of interest. (Alkareem, 2000). It gives the description of the process, both chemical and physical phenomena taking place. In the process of modelling, analysis must be undertaken that enables one to predict such process and likewise helps in optimising the process. It improves understanding of some mechanism in the studies and helps in formulating models that yield reasonable accurate description, while also minimizing the programming time.

Supercritical extraction process is based on counter current flow of solvent at temperature and pressure higher than their critical temperature and pressure and oil bearing seeds in the extraction vessels. Operation of extraction in a supercritical condition gives the solvent ability to extract at high boiling point component of raw materials and penetrate more intro pores, hence gives faster and more efficient extraction (Eggers and Stein, 1987).

Palm oil is prepared or manufactured from fruit of the palm tree. Palm tree grows naturally in the West Africa and countries like Indonesia, Malaysia, Nigeria, etc. and because of its economic importance or value, it is grown in many other parts of the tropics. The fruit is about 2.5 to 5.0mm long and oval shape, it weighs about 6 to 8g in the average.

Palm oil is deep yellow to red-brown in colour and thick in consistency. The oil content ranges from 40 to 50% of the seed. It has a pH value of 4.5-6.0. Palm oil is extensively used in the manufacture of soaps, candles and lubricating greases. It is also used in process-tin plate and as a coating material for iron plates.

Oil palm is tapped for wine, which is consumed largely by the urban dwellers. The wine contains vitamin B. Crude palm oil is also a source of vitamin A to African natives who use the oil for cooking (Purseglove).

## **1.1 AIMS AND OBJECTIVES**

1. To obtain a Predictive model for a supercritically extracted refined palm oil.
2. To test for the accuracy of the model.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 OIL PALM TREE

Oil palm is as member of the palm family. It is botanically related to the coconut palm and because of its majestic appearance the true was called prince of plant kingdom. There are about 2000 species, mostly confined to the tropical regions. Oil palm thrive well in tropical rain forests and are natures of West Africa. When matured, oil palm tree may attain a height of nearly 30m (100ft) but generally it grows no fallen than 10m (32ft) and may live for up to 200 years. The single erect trunk has the same thickeners throughout its length and is generally rough because it is covered by persistent leaf bases.

Palm leaves produced in spiral succession at an angle of about  $138^{\circ}$ , borne in 2 spirals, 8 leaves in one direction and 13 in a steeper spiral running the other way. A mean maximum of  $30-32^{\circ}\text{C}$  and a mean minimum of  $21-24^{\circ}\text{C}$  provide the most suitable temperature and the seedling growth is arrested at temperature below  $15^{\circ}\text{C}$ . A high level of solar radiation is also essential for the growth and enrich product.

Adequate soil moisture is more important for the growth of oil palm than nutrient supply which can be provided artificially. Palm in eastern Nigerian grows mainly on acid sands which are deficient in exchangeable cautions particularly potassium and magnesium.

Palm tree can also be grown over a wide range of pH value of many of the soils used for the crop have a pH of 4-6.

### **2.1.1 THE PALM FRUIT**

The time from flowering to marketing of ripe fruits is 5-6 months. Fruit bunches in the axial of low leaves, massive, nearly spherical about 10-90kg in weight with an average of 18kg in Africa. Palm fruit which is a sensible drupe nearly spherical to ovoid or elongated, bulging some what at the top which is about 2-5cm long.

Palm fruit are classified into Deli palms, teneradina and pusifera palms, they all varied in the size of their fruit yield. The degree of loosening of ripe fruit in the bunch varies. Annual number of bunches per palm depends on the rate of leaf production, sex ratio and abortion ratio' bunch number and weight per bunch negatively correlated. Bunch number decreases rapidly until the two factors, level out at maturity and yield per palm increases until about 6 to 8 years.

The fruit branches ripe between 4-5 years after planting in case of seedling and between 3-4 years in case of transplanting, which is 12-18 months before planting.

### **2.1.2 PALM OIL PROCESSING**

The objective of palm oil processing or extraction is to produce maximum amounts of oil of a acceptable quality at minimum cost. The extraction consists of sterilization, stripping digestion, pressing, static settling and centrifugal purification.

**STERILIZATION:** The fresh fruit bunches from the palm tree is sterilized, stabilization is carried out to inactivate fruit enzymes, to also loosen fruit from the bunch and soften the fruit in preparation for its digestion. Sterilization of fresh fruit help in coagulating the mesocarp proteins, hydrolyse and decomposes

miscellaneous mucillagenous materials. It partially dehydrates the nuts in preparation for cracking.

**STRIPPING:** Stripping process is a straight forward process which could be improved through a better design of feeders to the strippers and ensuring that flow of fluid to the digestion in such that digester are kept full at all times.

**DIGESTION:** Digestion is also the oil extraction. It is done to convert the stripped fruit into a homogenous mass so that oil can be efficiently extracted in the press and efficient separation of fibre and nuts (after pressing) can be achieved.

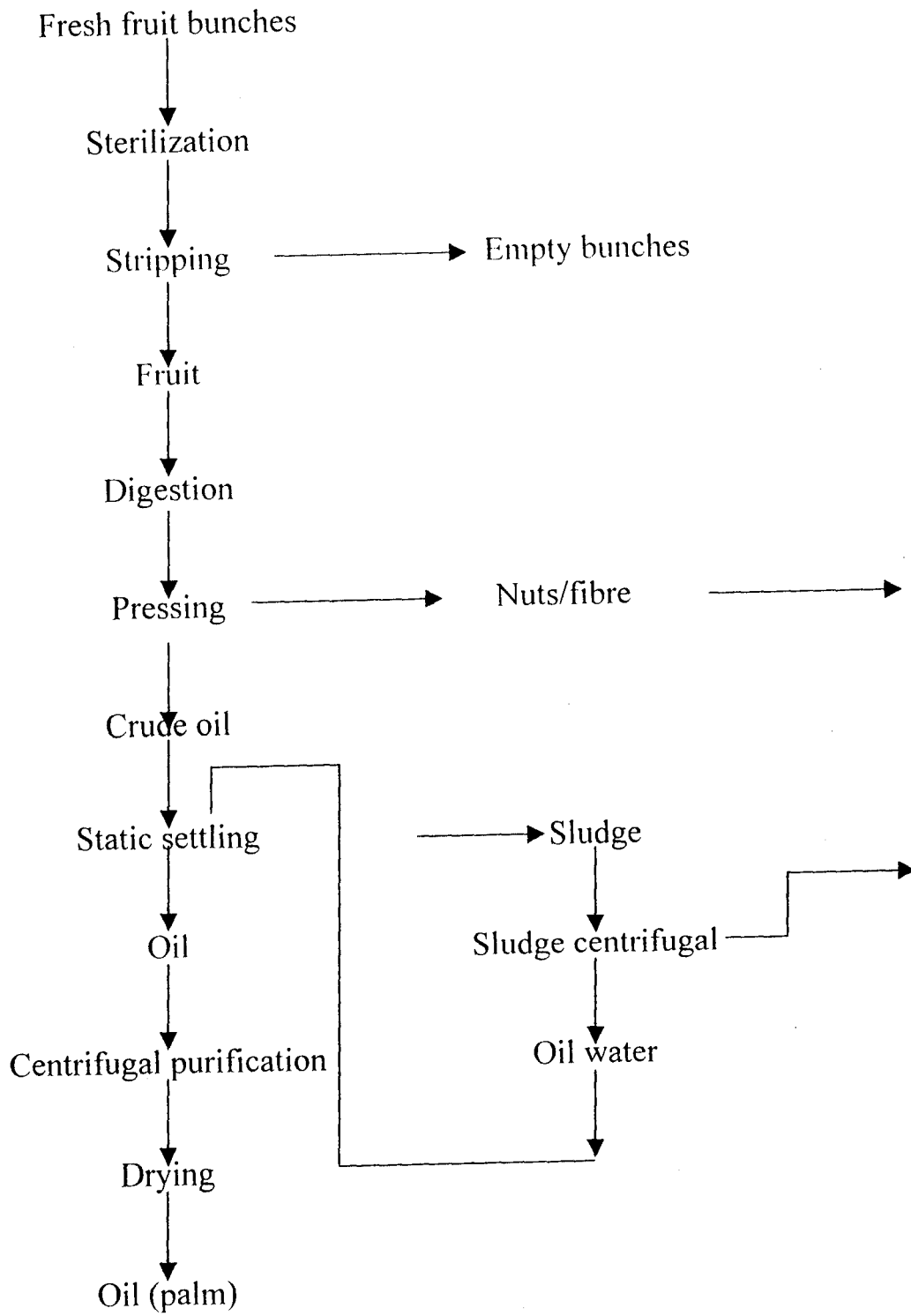
**PRESSING:** There are different types of pressing; we have hydraulic press, screw press, etc. Hydraulic pressing is widely used. It is considered for a mill of small throughput capacity or care processing fruit with a high nut fibre ratio.

Screw press is also preferred in most modern mills for processing fruits with low nut fibre ratio at throughput greater than 6 tons per hour. It has low cost per unit throughput relative to hydraulic press. Screw press also has higher extraction efficiency and low maintenance cost. (Corley and Hardin)

Other steps like static setting, centrifugal purification and drying rate carried out to minimize the level of moisture or dirt present in the oil, to minimize the oil losses as well as minimizing deterioration in oil quantity and to minimise the costs.

In general, the less dilution water added to crude oil, the more easily oil separates out during stable setting and moreover without dilution sludges becomes thick, viscous and flow is difficult.

## 2.1.3 FLOW CHART OF PALM OIL PROCESS



#### 2.1.4 COMPOSITION OF PALM OIL

The oil palm gives the highest yield of oil per unit area of any crop and produces two distinct oils (palm oil and palm kernel oil). Palm oil is obtained from the fleshy mesocarp of the fruit that contained 45-55% of oil. The oil melts over a range temperature of 25°C-50 °C. It is light yellow to orange red in colour; the depth of colour depends on the amount of carotenoid present.

Palm oil contains a high proportion of saturated palmitic acid but it also contains considerable quantities of oleic acids which gives a higher unsaturated acid content.

Poorly prepared palm oil has a high free fatty acid content caused by autocatalytic action, this renders it is unsuitable for edible purposes. Palm oil is also rich sources of carotene and the richest precursor of vitamin A.



## 2.1.4.1 COMPONENT OF FATTY ACIDS OF PALM OIL

### Saturated acids

Common name	Systematic name	% of total weight
Lauric	n-dodecanoic	<1%
Myristic	n-tetradecanoic	1-6%
Palmitic	n-hexadecanoic	32-47%
Stearic	n-octosanoic	1-6%
Arachidii	n-eicosanoic	<1%

### Mono unsaturated acids

Common name	Systematic name	% of total weight
Palmitoleic	n-hexadec	<1
Oleic	n-octadec	40-52%
Gadoleic	n-eico-genoic	<1

### Poly unsaturated acids

Common name	Systematic name	% of total weight
Linoleic	n-octadec-9	5-7%

### 2.4.1.2 COMPONENT GLYCERIDES OF PALM OIL

Triglyceride	% of total triglycerides
Tripalmitin	3-5%
Dipalmitostearin	1-3%
Oleo''-myristopalmitin	0-5%
Oleo''-dipalmitin	21.43%
Oleo''-palmitostearin	10-11%
Palmito-di-''olein''	32-48%
Steano-di-''olein''	0-6%
Linoleo-diolein	3-12%

(Hilditch T. P. William, Chemical Constitution of Natural Fats)

### 2.4.1.3 AVERAGE DENSITIES OF PALM OIL

Density	Temperature (°C)
925-935	20
910-920	30
897-3	40
890.0	50
883.0	60
876.3	70
869.5	80
862.7	90
857.9	100

(Loucs H.V. & Vankede Laboratory Hardwork for Fat & Oil Analysis)

### 2.1.5 ECONOMIC IMPORTANCE

Both palm oil and other palm product such as palm kernel oil are used extensively in the manufacture of margarine, cooking oil, confectionary fat, cooking fat and soap. Palm oil is also used in the processing of tin plating and as a coating for iron plates. It is used in making candles and lubricating greases.

Palm kernel cake, the meal after the extraction of oil is a good cattle feeds. Crude palm oil is a source of vitamins A for those who use the oil for cooking. The dried leave of the oil palm are used for thatching the roofs of houses, the petioles and rachises for fencing.

## 2.2 EXTRACTION

Extraction is a process of transferring a solute from one solvent to another. It is also a process in which a component in a liquid mixture is selectively transferred to a liquid solvent in contact with the liquid mixture. Extraction process also involves liquid-liquid extraction, solvent recovery and raffinate desolventizing.

### 2.2.1 TYPES OF EXTRACTION

Extraction of oil is carried out using the following basic methods:

- (a) Extraction by lead (distillation).
- (b) Continuous mechanical pressing.
- (c) Solvent extraction.

All the three depend on the nature of constituent required.

- (a) **Distillation-extraction by heat:-** Distillation produces volatiles and as well as volatile breakdown product and is not used where materials required are

thermally unstable. It is also the standard technique by which the essential oils of many spices are obtained. The temperature applying to this route particularly is reasonably low.

- (b) **Solvent Extraction:-** This is a method of extraction with volatile solvent. It is a modern process that yields a high quality product of oil. The method requires less energy than in case of normal liquid extraction and virtually no solvent residue is left in the product.
- (c) **Continuous mechanical pressing:-** This is a process of extraction by means of pressure. The oil bearing material are squeezed through a tapering outlet and the rate of oil obtain is increased by increasing the pressure.

## 2.2.2 FACTORS AFFECTING RATE OF EXTRACTION

There are several factors influencing the rate of extraction that are responsible for limiting rate of reaction. They are:

- (a) Temperature
  - (b) Particle size
  - (c) Solvent
- (a) **Temperature:-** Temperature affects the rate of extraction because the solubility of material being extracted will increase with temperature in order to give a higher rate of extraction.
  - (b) **Particle size:-** The smaller the size of particle, the higher and greater the interfacial area between the solid and liquid and the higher will be the

transfer of material and rate of diffusion. Also the larger the size of particles, the smaller the rate of diffusion due to the low interfacial area.

- (c) **Solvent:-** Solvent chosen should be an ideal solvent. The solvent viscosity should be low in order to allow its free circulation.

## 2.3 SOLVENT EXTRACTION

Solvent extraction is a process of continuous extraction based on countercurrent flow of solvent and the material solvent extraction basically extracts the hydrophobic constituents of material depending on the choice of solvent used and also operate at low temperatures. In order to obtain a high quality product an ideal solvent must be used.

### 2.3.1 CHARACTERISTICS OF AN IDEAL SOLVENT

Properties of an ideal solvent are summarized below:

- (1) The solvent must have desirable solvent powers, i.e. the balance required for the extraction of hydrophobic substituents making up the required product.
- (2) The use of solvent must not change or damage the quantities of the extract obtained.
- (3) It must be readily removed from the extract without residues being left.
- (4) It must be non-toxic.
- (5) It must be readily available and economical.
- (6) It must be available with a high degree of purity and it has to be inert and chemically stable.

### 2.3.2 CHOICE OF SOLVENT

Choice of solvent depends on the final end product desired. Solvent to be used for extraction must possess the following summarized factors:

- a. Low toxicity, density and flammability of the solvent.
- b. Extraction must be able to stable to heat, light and water, i.e. they must be stable chemically under any of the process condition.
- c. Recoverability: The solvent must be completely recovered from the extract.
- d. The solvent must have high selectivity for the solid to be extracted and must have low viscosity and non reactive with apparatus or equipment involved.

### 2.4 SUPERCRITICAL EXTRACTION

The process of extraction with a solvent above its critical point is variably described as supercritical extraction or vapour phase or supercritical distillate extraction or even a solvent free extraction. This is also typical number of separation processes operating at high pressures and making use of increased solubility effects at higher temperature and pressure. It is one of the more recent extraction and separation techniques.

The phenomenon itself had been known for about hundred years, though mainly because of the complications and interference.

Supercritical extraction is attractive despite the high pressure involved for a number of reasons:

- a. High boiling components can be gasified at relatively low temperatures. —
- b. Recovery of solute and solvent is relatively easy.

- c. At lower temperature, heat sensitive compounds are undamaged during the extraction process.
- d. Separations can be achieved which are not possible by other techniques such as distillation or extraction process.
- e. It allows the use of non-toxic solvents that leave no harmful residues.

Supercritical extraction exhibit properties intermediate between those of gases and liquid, consequently each of these two boundary conditions shed in sight into the native of the fluids. Supercritical extraction process considerable solvent strength, transport is also more favourable by the lower viscosities, and higher rate of diffusion. It ensured a minimum energy loss during the process and good selectivity.

## **2.4.1 ADVANTAGES AND DISADVANTAGES OF SUPERCRITICAL EXTRACTION**

### **2.4.1.1 ADVANTAGES OF SUPERCRITICAL EXTRACTION**

Supercritical extraction has received great interest in the recent years.

Supercritical extraction offers the following potential advantages:

- (a) Enhanced transport properties, i.e. solute diffuses more rapidly through a supercritical solvent.
- (b) Equilibrium and separation factor are generally quite high.
- (c) Solvent used can be recovered as a gas by using pressure which offers the prospect of significant energy saving.
- (d) Slight changes in temperature and pressure within the critical region gives extremely large changes in solvent density and solubility and there is

greater flexibility in the process operating parameters of temperature and pressure. Above all, it results in maximum oil yield.

#### **2.4.1.2 DISADVANTAGES OF SUPERCRITICAL EXTRACTION**

The cost of supercritical extraction equipment or plant is substantially higher than conventional extraction plant and is costly in maintenance.

#### **2.4.2 APPLICATION OF SUPERCRITICAL EXTRACTION**

Supercritical extraction process can be applied for treatment and extraction of numerous natural substances such as:

- (a) Extraction of vegetable oils for special purposes.
- (b) Production of extract and decaffeinating of coffee and tea.
- (c) Extraction and isolation of fat associated substances. In addition to this, supercritical extraction enables:
  - (1) Extraction of vegetable food fats & oils, e.g. Rapeseed.
  - (2) Refining of vegetables and animal oil and fats.
  - (3) Aromatisation of food stuffs.
  - (4) Treatment of organic substances from adsorbents and extraction of materials from waste.

### **2.5 CARBON IV OXIDE (CO<sub>2</sub>)**

Complete removal of organic solvent used for extracting seed oils is mandatory. If the oil is to be used for human consumption. Carbon IV oxide offers the advantage of being easily removable from the extracted oil.



CO<sub>2</sub> is found in the dissolved form in water. In the combined form it is mainly found as metallic trioxocarbonate IV in the earth's crust especially limestone region and coral reefs. Carbon IV oxide is prepared in the laboratory by the action of dilute acids on calcium trioxocarbonate IV (CaCO<sub>3</sub>) in form of marble chips.



## 2.5.1 PHYSICAL AND CHEMICAL PROPERTIES OF CO<sub>2</sub>

### 2.5.1.1 PHYSICAL PROPERTIES OF CO<sub>2</sub>

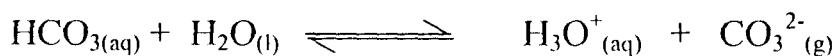
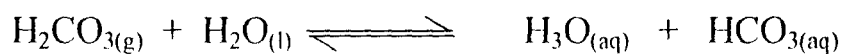
- (a) Carbon IV oxide is a colourless, odourless gas with a sharp, refreshing taste. It is about 1.5 times denser than air.
- (b) It is soluble in water and at room temperature and standard pressure; water dissolves its own volume of the gas.
- (c) It changes damp blue litmus paper to pink

CO<sub>2</sub> dissolves in water to yield tin oxo carbonate IV acids. On cooling, it readily liquefies and solidifies at (-78°C) to form a white solid.

### 2.5.1.2 CHEMICAL PROPERTIES

#### (1) REACTION WITH WATER

CO<sub>2</sub> dissolves in water to form tin oxo carbonate IV acid which is a weak acid that ionised slightly.



On cooling, tin oxo carbonate IV acid decomposes to form H<sub>2</sub>O and CO<sub>2</sub>.

### (2) REACTION WITH ALKALI

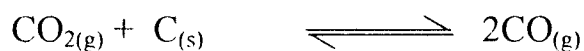
It reacts directly with alkali to yield CO<sub>2</sub>



Solutions of alkalis absorb CO<sub>2</sub> readily and are frequently used to remove it from mixtures of gases.

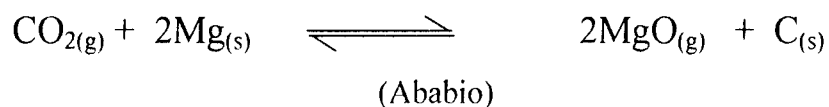
### (3) REACTION WITH RED-HOT CARBON

If the gas is passed over red-hot carbon, it is reduced to CO, i.e. carbon II oxide. The reaction is reversible and of great commercial importance.



### (4) REACTION BURNING MAGNESIUM

CO<sub>2</sub> does not burn nor does it support combustion of most substances. Intense heat decomposes CO<sub>2</sub> to release oxygen for further oxidation of magnesium



## 2.5.2 CO<sub>2</sub> AS A SUPERCRITICAL SOLVENT

The application of the technology of supercritical extraction requires a working knowledge of areas of physical chemistry and chemical engineering especially in the processing of natural products or raw materials. The extraction or separation of raw materials is increasingly an essential and important part of

food and other industries process technology which can be considered in three categories.

- (a) Separation by mechanical means.
- (b) Separation by heat.
- (c) Separation by solvent, using organic liquids as solvent.

This development of supercritical extraction has resulted in using CO<sub>2</sub> (carbon IV oxide) as a solvent. CO<sub>2</sub> has also become important for reasons of safety and economic. The extraction of solid is especially of interest for materials, which are present in small amount and yield high quality products after extraction. Generally, a solvent must possess high degree of purity and chemically stable.

CO<sub>2</sub> as a compressed gas have been know to have solvent properties that could be highly desirable for achieving separation or extraction of constituent in a large number of materials. Compressed gas have been also demonstrated to be selective solvents which can lead to very complete separation of extractable constituents of raw materials which are subsequently very readily fractionated by quite small changes in the physical condition applying to the extract entrained in the gas.

Carbon IV oxide as a supercritical solvent is more far penetrating in their ability to bring into solution even difficult constituents under the right conditions thus it extracts the high boiling point components of the raw material. In considering the various compressed gases that are available in term of their solvent power, it is very easy to realise why CO<sub>2</sub> stands out as an ideal solvent with wide potential for replacing conventional organic solvent and its following characteristics would seem to cover this point.

- (1) Carbon IV oxide is inert, i.e. it is non flammable, non toxic and non reactive in most conditions.
- (2) It is also safe and economical to use.
- (3) It can be removed from the extracts without causing damage to them.
- (4) Its standard of purity is extremely high and it has a critical temperature of 31.3°C and critical pressure of 73 bar.

Also, the solvent power of compressed gases have been known since the second half of last century, with the development of high pressure processes, however, this solvent power often proved difficult. Compressed gases are an example of relatively cheap solvent as have earlier been mentioned and when sued at high pressure, they enable separation to be achieved in both liquid and vapour phase. Likewise the compression of supercritical gas over a mixture of compounds, it selectively dissolves one or more components enabling the component to be removed from the mixture.

The components can be separated from the supercritical gas by reducing the pressure, making possible simultaneous regeneration of the solvent.

### **2.5.3 ADVANTAGES AND DISADVANTAGES OF CO<sub>2</sub> AS A SUPERCRITICAL SOLVENT**

#### **2.5.3.1 ADVANTAGES OF CO<sub>2</sub>**

- 1) It exhibits solubility variation which is achieved by simply increasing or lowering extraction pressure and temperature.
- 2) It diffuses fast because of its low viscosity and easy solvent recovery due to its high volatility.

- 3) It is environmental friendly and leads to no explosion or fire hazards.
- 4) It is cheap compared to conventional solvents.

### **2.5.3.2 DISADVANTAGES OF CO<sub>2</sub>**

- 1) Its critical pressure is substantially higher than that of most alternative solvents. For this reason, the extraction pressure required when using carbon IV oxide tends to be higher.
- 2) It has an inconveniently high triple point pressure. The dissolving power of this solvent tends to be lower than conventional solvents although this disadvantage may be overcome in many instances by using entrainers.

### **2.5.4 CO<sub>2</sub> APPLICATION**

- a) Production of active ingredients for pharmaceuticals and cosmetics.
- b) Extraction of undesired components from liquid and solid products.
- c) Recovery of mineral oils from rock, sand and slate.
- d) Production of essential oils from blossoms, leaf, roots, etc.

## **2.6 MATHEMATICAL MODELLING**

Mathematic modelling represents the mathematical aspects of a process of interest. Model helps in providing the simplest possible description of a process and at the same time retaining its physical character (Williams, 1995).

## 2.6.1 THEORY OF MATHEMATICAL MODELLING

A model is a simplified representation of a system intended to promote our ability to understand, predict and possibly control the behaviour of a system (Alkareem, 2000). Model gives the description of the process both physical and chemical phenomena taking place, thus modelling is the process of establishing interrelationship between important entities of a system. Model is represented in terms of goals, performance criteria and constraints (James et al, 1981). Also, it can be used to predict the effect of changing conditions and capacity on mass and energy balance and to optimise operation easily and quickly (William, 1995).

In the process of model building, system analysis must initially be undertaken. A lot of decision must be made for further development and these include finding solution to following observations (James et al, 1981)

- a) Model aims must be stated clearly and unambiguously as possible.
- b) Various kinds of constraints and omissions must be taken into account.
- c) General assumption and omission must be carefully argued.
- d) The possibilities of measurement and experimentation on the system being studied must be investigated.
- e) The solution strategy must be chosen. This way include methods of collection and analysis of data, estimation of parameters, type of model, available computational facilities, generality of solution, possibilities of model extension and so on.

## 2.6.2 PURPOSE OF MODELLING

In this recent time, modelling has become increasingly unavoidable for solving differential kinds of practical problem such as prediction of efficiency of a particular process.

The purpose of modelling is to achieve different goals without actually operating the real process which includes the following (James et al, 1981)

- (1) To improve the understanding of some mechanisms in the studied process.
- (2) To predict system behaviours in different situation where any level of predictive ability represent a benefit.
- (3) To establish the process variables which are not directly measurable.
- (4) To enable the design and evaluation of synthesized control system.
- (5) To optimise the behaviour and efficient fault diagnose.
- (6) To test the sensitivity of system parameters.

## 2.6.3 STATISTICAL PROCESS MODELLING

Statistical process modelling is simply the concise description of total variation in one quantity (Y) by partitioning it to a determination component given by a mathematic function of one or more often quantities ( $x_1, x_2, x_3, \dots, x_n$ ) plus a random component that follows a particular probability distribution.

Basically, there are different components parts of model which includes:

- a) Response variable.
  - b) Mathematical function.
- a) Response Variable is usually denoted as Y and also known as dependent variable. It is also a quantity that varies in a way which could be

response variable is systematically related to the values of one or more other variables before the model process and verifying this is also part of modelling process.

- b) **Mathematical function:** Mathematical function usually denoted as  $F(x_1, x_2, x_3, \dots, x_n)$  is also known as regression function which consist of two parts, i.e.
- i. The predictor variables and
  - ii. The parameters.
- i. Predictor variables are also known as the independent predictor or regression variable, they are the quantities previously described as inputs to the mathematical function and are normally observed along with the response variables.
- ii. Parameters are estimated quantities during the modelling process and usually constant coefficient of the predictor variables. Both the predictor variables and parameter are used to describe deterministic variation in response variable, which are combined in different forms to give the function for the variation.

#### **2.6.4 PRINCIPLE OF COLLECTING DATA**

Employing well-planned data collection procedures often determine the success or accuracy of the result. Nist-Sematech (2001), advises to produce upon question that would allow analyst to do an optimal job of modelling a particular process such as “what can the analyst do even prior to collecting the data”. The following techniques could be considered.

- 1) Randomisation.
- 2) Replication



- 3) Orthogonality and blocking.
  - 4) Blocking
- 1) **Randomisation:** The more freely one can randomise experimental runs, the more guarantee one has against extraneous factors creeping into the design and wasting of experimental time and effort. Randomisation involves selecting the order in which experiments are to be performed at random and it also gives unbiased estimate of the parameters such as error and mean.
  - 2) **Replication:** Replication allows the calculation of random errors and standard deviation. One of the analysis assumptions is that the response dispersion is uniform across the experimental space, hence replication enables us to check this assumption and probably find the setting combinations that give inconsistent yields therefore allowing to avoid that area of factor space.
  - 3) **Orthogonality:** Orthogonality is one of the features in experimental design that ensures the different factors in an experimental design are capable of direct and separate estimation.
  - 4) **Blocking:** Blocking is a process where precision is increased and it enhances replication since the variations among units in a block is less than that within units in different blocks. Blocking is also the process of grouping of experimental units into groups such that each groups contains all treatments.

## 2.7 MULTIPLE REGRESSION SOFTWARE PACKAGES

### 2.7.1 MATHCAD PROFESSIONAL

MathCAD professional software is the industry standard calculation software for technical professionals. It is a versatile and powerful programming

language and also easy to learn as spreadsheet. It can expand one's research capabilities by providing a powerful means of analysing and evaluating data.

MathCAD simplifies and streamlines documentations, critical to communicating and to quality assurance standards. By combining equation, text and graphics in a single worksheet, it makes it easy to keep track of the most complex calculation and it is available in two versions:

- (a) MathCAD professional
- (b) MathCAD standard

Both of which are the industry standard for applied math in technical fields delivering complete calculation and reporting functionality for professional results, as well s ideal application for everyday technical calculations.

### **2.7.2 MICROSOFT EXCEL**

Microsoft excel is another software. It increases or decreases value by a constant value, that is, based on the difference between the selected starting values. It helps in solving series of calculation via so many functions such as regression analysis, polynomial regression, etc.

## CHAPTER THREE

### 3.0 METHODOLOGY

#### 3.1 COLLECTION OF EXPERIMENTAL DATA

The experimental data used was collected from an experiment performed to improve the quality of palm oil using supercritical extraction method (Onifade, 1989).

##### 3.1.1 EQUIPMENT AND APPARATUS USED

The equipment used is shown below in figure 3.1.

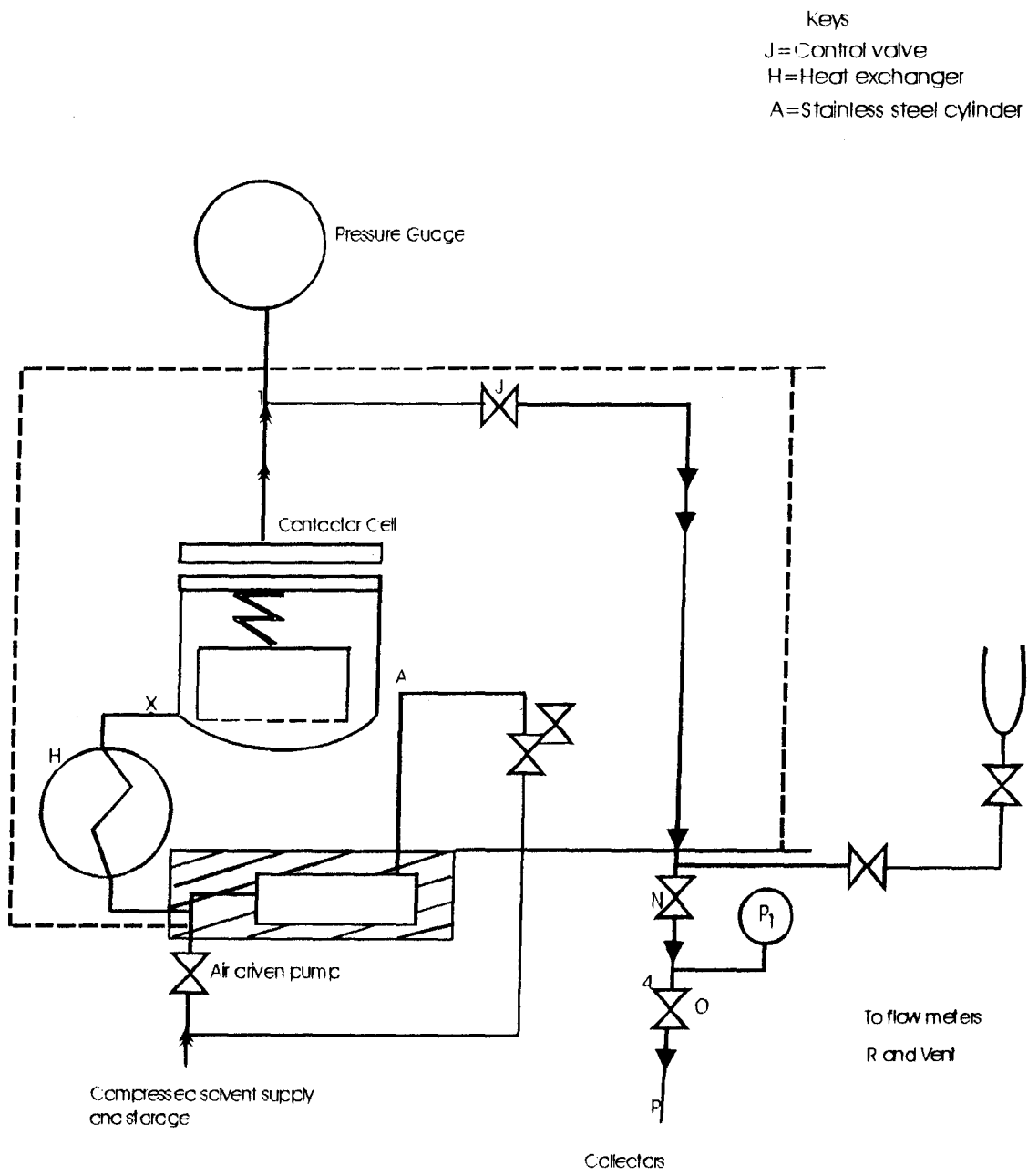


Figure 3.1: Equipment set-up

### 3.1.2 EXPERIMENTAL PROCEDURE

The rectangular region shown the broken lines on figure 3.1 is contained within an aim bath control of the temperature of the solvent stream as it enters the contractor is provided by heat exchanger H. This consists of refrigerated water with an immersed coil through which the solvent stream passes.

The bath temperature is set to give the desired extraction temperature at point X, the temperature at this point measured by a thermocouple encased in a flowing stream. Similarly, sensors are located within the contactor cell and at points 1 and 4 in the solvent stream.

Provision is also made for heating the piping between values N and O and it is usually desirable to maintain the pressure in this section above the inconveniently high triple-point pressure of carbon IV oxide. To avoid irregularities in flow, sufficient heat is applied thus preventing the formation of solid CO<sub>2</sub> at the expansion values. When determining the loading for a given bed height and set values of solvent flow rate, temperature and pressure, liquid carbon IV oxide is continuously injected at point X, passes through the contactor cell and flows down the line MNOPR.

Pressure letdown takes place at valves N and O. The product collects in the collectors below O and is weighted at intervals. The efficiency of collection was arrested by mass balance between the total extract collected and the weight loss of the contents of the extractor.

### 3.1.3 EXPERIMENTAL RESULT

The experimental results obtained are shown in table 3.2 below.

Table 3.1: EXPERIMENTAL RESULT FOR QUALITY IMPROVEMENT EXPERIMENT

Experiment code	Weight of the sample (g)	Coolant flowrate (g/min)	Pressure (lb/in2)	Temperature (oC)	Duration of expt (t) (hours)	Mass of extract (g)	Heat of vapourisation (j/mol)	Temp. Across the cold finger (oc) ( $\Delta t$ )	Corrected $\Delta t$ (oC)	Mass flow rate of CO2 (mol/min)	Total amount of CO2 condensed over t (m0l) (s)	Loading (G/mol)	Loading (G/kg)
QIE 1	3.542	1174.8	720	14.6	10	0.642	7861.80	1.30	0.80	0.1195	71.7	$8.95 \times 10^{-3}$	0.20
QIE 2	4.043	1174.8	720	14.0	8	1.379	7969.64	1.70	1.20	0.1769	84.91	$16.4 \times 10^{-3}$	0.37
QIE 3	4.152	1174.8	720	14.0	8	2.379	7969.64	1.20	1.20	0.1769	84.91	$16.5 \times 10^{-3}$	0.37
QIE 4	4.711	783.2	700	12.8	8	1.202	8185.45	1.40	1.40	0.1340	64.32	$18.7 \times 10^{-3}$	0.42
QIE 5	6.695	391.6	650	9.8	8	1.070	8705.04	0.50	0.50	0.05398	25.91	$41.3 \times 10^{-3}$	0.94
QIE 6	3.095	391.6	670	11.0	8	0.413	8499.08	0.50	0.50	0.02304	11.06	$37.3 \times 10^{-3}$	0.85
QIE 7	3.396	783.2	630	8.6	8	0.661	8909.68	0.40	0.40	0.03516	16.88	$39.2 \times 10^{-3}$	0.89

QIE means Quality Improvement Experiment

Table 3.2: FINAL DATA USED FOR THE MODEL

S/N	Loading y (kg/L)	Density (kg/L)	Temperature (K)
1	2.0048	687680	287.15
2	3.6769	678270	287.15
3	3.6960	678270	287.15
4	4.1888	882980	285.95
5	9.2512	806230	282.95
6	8.3550	831034	284.15
7	7.7808	808360	281.75

### 3.2 MODELLING

#### 3.2.1 DEVELOPMENT OF THE MODEL

The modelling equation was developed from the data presented above using an improved equation of Chrastil's (1982) related the solubility of the solute to the density ( $\rho$ , g/mL) and absolute temperature (T, K) of gas by the following equation based on the physiochemical model where one molecule of A associates with K molecules of B to form a solvato complex which is in equilibrium with the gas.

$$\ln(c) = q - \frac{\ln(1000M_B)}{(M_A + kM_B)} + \frac{\Delta H}{RT} + k \ln \rho \quad \text{-----equation 3.1}$$

Where  $M_A$  and  $M_B$  are the molecular weights, K is an association number.  $\Delta H$  is the total reaction heat (heat of solvation plus the heat of vapourisation of the solute), and q is a constant.

Chrastil also stated that according to equation 3.1, a plot of  $\ln c$  versus  $\ln p$  for isothermal conditions should give a straight line with slope  $K$  and an intercept  $I$  for  $\rho = 1\text{g/mL}$ . Furthermore, if  $I$  values (i.e. the natural logarithm of the solubility  $c$  for  $\rho = 1\text{g/mL}$ ) for different isotherms are plotted against  $1/T$ , a straight line with a slope  $M$  and an intercept  $b$  would be obtained, i.e.

$$I = b + m/T \quad \text{----- (3.2)}$$

Where

$$b = q - \ln\{[1000M_B]^k/[M_A + kM_B]\} \quad \text{----- (3.3)}$$

$$M = \Delta H/R \quad \text{----- (3.4)}$$

Introducing empirical modification to equation 3.1 to compensate for the variation of  $\Delta H_{\text{vap}}$  with temperature:

$$I = b' + m'/T + n'/T^2 \quad \text{----- (3.5)}$$

Local  $\Delta H(T)$  value were evaluated as

$$H + R dI/d(1/T) = R(m' + 2n'/T) \quad \text{----- (3.6)}$$

Therefore, the equation becomes

$$I = b' + m'/T + n'/T^2 + k \ln p \quad \text{----- (3.7)}$$

Where the density was evaluated by double square interpolation in tables for the compressibility factor of  $\text{CO}_2$  as a function of pressure ( $P$ , atm) and reciprocal of the temperature ( $T^{-1}$ ,  $\text{K}^{-1}$ ) (Pickering, 1928).

$$\rho = 0.5362 [P/z(P, T^{-1})T] \quad \text{----- (3.8)}$$

therefore, Chrastil equation (1982), i.e. equation 3.7 which in form of

$$\ln y = \alpha + \beta/T + \gamma/T^2 + \sigma \ln p \quad \text{----- (3.9)}$$

was used to obtain predictive model for quantity improvement of refined palm oil using supercritical extraction method.

Where



y represent the loading of oil in (kg/L)

$\alpha$ ,  $\beta$ ,  $\gamma$  and  $\sigma$  are constants of the model

$1/T$  represent the reciprocal of temperature ( $K^{-1}$ )

$1/T^2$  represent the square of reciprocal of the temperature and ( $K^{-2}$ )

$\rho$  represent the density (kg/L)

The equation related the loading (kg/L) of oil (the quantity of refined palm oil) (y) directly to the density of the supercritical of solutes in supercritical carbon IV oxide over a range of pressures and temperatures.

Constants of the model, i.e.  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\sigma$  were estimated by using multivariable regression analysis of  $\ln y$  as a function of  $\ln \rho$ ,  $1/T$  and  $1/T^2$ .

### 3.2.2 MANIPULATION OF SELECTED VARIABLES FROM TABLE 3.0

#### DENSITY OF CARBON IV OXIDE

The density used for the development of the model was calculated from the formula below

$$\rho = \frac{PM}{RT} \text{-----(4.0)}$$

Where  $\rho$  is density ( $kg/m^3$ )

P is the pressure ( $lb/in^2$ )

R represent the rate constant and

T is the temperature (K)

#### LOADING

The loading was calculated from table 3.1 using the formula below.

$$\text{Loading (g/mol)} = \frac{M(g)}{S(mol)} \text{-----(4.1)}$$

Where M is the mass of extract in (g)

S is the total amount of  $CO_2$  condensed over t (mole)

Both the density and the loading obtained are converted from  $\text{kg/m}^3$  and  $\text{g/mol}$  respectively to  $(\text{kg/L})$  and  $(\text{kg/L})$  for better compatibility. And the data used in the regression analysis after the above manipulation is shown in table 3.2.

### **3.3 SIMULATION OF THE MODEL**

Two softwares, namely MathCAD and Microsoft Excel were used in simulating the model equation 3.9. They were chosen for comparison of results.

The modelling was further carried out under regression analysis of MathCAD software in order to compare the model result as well as validating or testing the accuracy of the result and variables used. The result obtained is as follows:

$R^2$  value - 0.989597 approximately 0.99

Table 4.2:

S/N	Experimental y values	Simulated y values
1	2.0048	2.19068
2	3.6736	3.5115
3	3.6960	3.5115
4	4.1880	4.0581
5	9.2512	9.9296
6	8.3522	8.4799
7	8.7808	8.3811

Table 4.3: %ERROR

OBSERVATIONS	% ERROR
1	9.2696
2	4.41132
3	4.9906
4	3.1202
5	-7.3330
6	-1.5290
7	4.5513

## 4.2 DISCUSSION OF RESULT

The effect of temperature on extraction of substances with higher molecular weight in the supercritical gas is more complex. Increase in temperature decreases the yield and its solubility, whereas at higher pressures, increasing the temperature will definitely increase the yield and solubility of the extractions.

The fitted model equation obtained was

$$y = \exp(4037676.27 - 571555006.2/T - 2.135528/T^2 - 7099.5688 \ln p)$$

with  $r^2$  value = 0.99.

From the regression analysis result, the effect of temperature and density on the loading ( $y$ ) is statistically significant at a confidence level of 95% and all the coefficient constants are significantly different.

All the independent variables show negative effects on the loading due to the negative sign of their coefficients in the model derived. The result at least confirms the observation in the experimental result where increase in temperature leads to increase in the loading.

The mean effect is the constant term which has no significance except of being the average of the data. The factor with largest effect on the loading is the reciprocal of the temperature with its value of  $-571555006$ , next is the density with its value of  $-7099.568$  and the variable with least effect has  $-2.1355$ .

Also, comparing the simulated  $y$  results and experimental  $y$  data, it shows that there is good agreement between the variables used in deriving the model since the least percentage error is 1.53%.

The  $R^2$  value obtained indicates better accuracy of variables and a fitted model because the closer the  $R^2$  value to 1.0, the more accurate and fit the model.

## CHAPTER FIVE

### 5.0 CONCLUSION AND RECOMMENDATION

#### 5.1 CONCLUSION

A model obtained for predicting the quantities of refined palm oil using supercritical method employing carbon dioxide gas where the mass of refined palm oil or the loading ( $y$ ) was expressed as a function of temperature and density ( $X_1$ ,  $X_2$  and  $X_3$ ).

The model derived was

$$y = \exp(4037676.27 - 571555006.2/T - 2.135528/T^2 - 7099.5688 \ln p)$$

In the derived model, all the independent variables give negative effects. Two softwares were used to carry out the regression analysis for confirmation. Both give similar results with regression coefficient of 0.99, which shows that the model is accurate.

#### 5.2 RECOMMENDATION

- 1) Other software such as polymath, matLAB, e.t.c should also be used to develop the model in order to compare the accuracy of the model and discussing variation in the output.
- 2) Solvents other than carbon IV oxide ( $CO_2$ ) should be used in repeating the experiment.
- 3) Manual calculation should also be used for better comparism.
- 4) Given students data without the knowledge or experience on how the experiment was carried out should be discouraged.

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$$M = 44.01 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mol}}$$

$$R = 8.314 \quad T = 39.5$$

$$\rho_1 = \frac{730 \cdot 7029.493 \cdot 44.01 \cdot 10^{-3}}{8.314 \cdot 39.5}$$

$$\rho_1 = 687.6 \frac{\text{kg}}{\text{m}^3}$$

(2) For QIE 2

$$P = 720 \frac{\text{lb}}{\text{in}^2} \quad T = 39.5^\circ\text{C}$$

$$\rho_2 = \frac{720 \cdot 7029.493 \cdot 44.01 \cdot 10^{-3}}{8.314 \cdot 39.5}$$

$$\rho_2 = 678.26 \frac{\text{kg}}{\text{m}^3}$$

(3) For QIE 3

$$P = 720 \frac{\text{lb}}{\text{in}^2} \quad T = 39.5^\circ\text{C}$$

$$\rho_3 = \frac{720 \cdot 7029.493 \cdot 44.01 \cdot 10^{-3}}{8.314 \cdot 39.5}$$

$$\rho_3 = 678.26 \frac{\text{kg}}{\text{m}^3}$$

(4) For QIE 4

$$P = 700 \frac{\text{lb}}{\text{in}^2} \quad T = 29.5^\circ\text{C}$$

$$\rho_4 = \frac{700 \cdot 7029.493 \cdot 44.01 \cdot 10^{-3}}{8.314 \cdot 29.5}$$

$$\rho_4 = 882.96 \frac{\text{kg}}{\text{m}^3}$$

(5) For QIE 5

$$P = 650 \frac{\text{lb}}{\text{in}^2} \quad T = 30^\circ\text{C}$$

$$\rho_5 = \frac{650 \cdot 7029.493 \cdot 44.01 \cdot 10^{-3}}{8.314 \cdot 30}$$

$$\rho_5 = 678.26 \frac{\text{kg}}{\text{m}^3}$$

(6) For QIE 6

$$P = 670 \frac{\text{lb}}{\text{in}^2} \quad T = 30^\circ\text{C}$$

$$\rho_6 = \frac{670 \cdot 7029.493 \cdot 44.01 \cdot 10^{-3}}{8.314 \cdot 30}$$

$$\rho_6 = 831.034 \frac{\text{kg}}{\text{m}^3}$$

(7) For QIE 7

$$P = 630 \frac{\text{lb}}{\text{in}^2} \quad T = 29^\circ\text{C}$$

$$\rho_7 = \frac{630 \cdot 7029.493 \cdot 44.01 \cdot 10^{-3}}{8.314 \cdot 29}$$

$$\rho_7 = 818.365 \frac{\text{kg}}{\text{m}^3}$$



(b) From g/mol to kg/L

g to kg

$$g \times 1000 = 1kg$$

$$22.4dm^3 = 1mol$$

$$1 dm^3 = 10^3 cm^3$$

$$cm = m \times 100$$

$$8.95 \cdot 10^{-3} \frac{g}{mol} \equiv \frac{kg}{L}$$

$$1000g = 1kg$$

$$\begin{aligned} 8.95 \times 10^{-3}g &= x \\ &= \frac{8.95 \cdot 10^{-3} \cdot 1}{1000} \end{aligned}$$

$$8.95 \cdot 10^{-3} \frac{g}{mol} = 8.95 \cdot 10^{-6} \frac{kg}{mol}$$

$$8.95 \cdot 10^{-6} mol \text{ is thus}$$

$$1mol = 22.4dm^3$$

$$8.95 \cdot 10^{-6} mol = 2.0048 \cdot 10^{-4} dm^3$$

$$2.0048 \cdot 10^{-4} dm^3$$

$$1dm^3 = 10^3 cm^3 \equiv 1000cm^3$$

$$3.0048 \cdot 10^{-4} dm^3 = 0.20048cm^3$$

$$100cm = 1m$$

$$0.20048cm = \frac{0.20048cm}{100} = 0.0020048m$$

(2) For density

$$\frac{\text{kg}}{\text{m}^3} \Rightarrow \frac{\text{kg}}{\text{L}}$$

$$687.68 \frac{\text{kg}}{\text{m}^3} \Rightarrow$$

$$\text{m}^3 \Rightarrow$$

$$1\text{L} \Rightarrow 0.001\text{m}^3$$

$$\text{m}^3 = \frac{\text{L}}{0.001}$$

$$\text{m}^3 = 1000\text{L}$$

$$687.68\text{m}^3 = 687680\text{L}$$

$$687.68 \frac{\text{kg}}{\text{m}^3} = 687680 \frac{\text{kg}}{\text{L}}$$