The Study of Parameters in Supercritical Carbon Dioxide Extraction of Oil by Response Surface Methodology

by

Fareeda Chemat

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2012

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CERTIFICATION OF APPROVAL

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Approved by,

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Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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FAREEDA CHEMAT

ABSTRACT

Response surface methodology was applied in this study to optimize the operating parameters of supercritical carbon dioxide (SC-CO_2) extraction of wheat bran oil (WBO) and rice bran oil (RBO). The effect of operating temperature, pressure and carbon dioxide (CO_2) mass on the oil yield were studied. First, the design was carried out following a Box-Behnken design of experiment for the WBO, the independent variables were the temperature (40, 50 and 60 ^oC), pressure (10, 20 and 30 MPa) and CO_2 mass (400, 1825 and 3250 g). Second, 3-level factorial design for RBO, the independent variables were the temperature (45, 65 and 85 ^oC) and pressure (20, 27.5 and 35 MPa). The study showed that the second-order polynomial model was sufficient to be used and best fit of the data. The optimal conditions predicted within these experimental ranges were at 29.4 ^oC, 60 MPa and 3250 g, the maximum oil yield was 2.97 g/12g of wheat bran for the WBO. The operating temperature, pressure and CO_2 mass proved significant effect in increasing the yield of WBO while these parameters increased. For the RBO, optimal conditions were at 45 ^oC and 35 MPa, the maximum oil yield predicted was 0.23 kg/kg of rice bran for RBO. The operating temperature increase effect in decreasing the yield of RBO while the pressure has the significant effect in increasing the RBO yield.

From the result, the extraction process has not been optimized yet because the optimal operating conditions were predicted at the maximum value of each parameter. However, the suggestion is to further conduct the additional experiments in a wider range of parameters in order to get the best result and more accurate optimum value of parameters. Lastly the economic feasibility study was conducted for the supercritical carbon dioxide extraction of RBO plant and it is economically justified.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Supercritical Fluid (SCF) technology has been examined as an alternative technique for the conventional oil and oilseed processing methods for more than two decades. Supercritical fluid extraction (SCFE) is getting wide interest for its prospective application in several sectors such as food, medicinal and petroleum [1]. Many substances have been used as SCF solvents, for instance, hydrocarbon such as hexane, pentane and butane, nitrous oxide, sulphur hexafluoride and fluorinated hydrocarbons [2] but the most generally utilize as SCF solvent is carbon dioxide (CO_2) [3].

Solvent extraction is one of the most commonly employed processes for extracting oil from vegetables, seeds flowers and other rich in oil sources. SC-CO_2 has been studied as alternative solvents for edible oil processing and has been the choice for the majority of edible oil applications. Various examples of the studies such as supercritical fluid extraction of black pepper oil [4], SC-CO_2 extraction of cuphea seed oil [5], supercritical fluid extraction of isoflavones from soybean flour [6], supercritical fluid extraction of peach (Prunus persica) seed oil using carbon dioxide and ethanol [7], the modeling of SC-CO_2 fluid extraction from herbaceous matrices [3] and etc. The exclusive benefit of SC-CO_2 is the easy removal of solvent from the extract, non-toxicity and decreased waste streams.

Wheat bran is by product from milling process and it is one of the important crops used to produce oil in various countries. Wheat bran is not only a good source of dietary fibers but also a rich source of various nutrients.

The demand of vegetables oils has been increasing. Recently rice bran oil has risen and received some attention from the public because it contains a group of chemical compounds called sterols which may be effective in lowering cholesterol. Carol Ann (2011) mentioned that “In a study conducted at the University of Rochester, Mohammad Minhajuddin, Ph.D., and researchers determined that the tocotrienol (a form of vitamin E) in rice bran oil reduced cholesterol in rats up to 42 percent while lowering LDL cholesterol up to 62 percent" [8]. Nowadays rice bran oil has been used in many Asian countries such as Japan, Thailand, Korea, China, Taiwan and Pakistan [9, 10].

Many studies have been reported regarding the rice bran oil extraction by using solvent extraction process [11, 12, 13, 14]. These studies emphasized on effects of various extraction parameters such as the use of different solvents, extraction time, temperature, and flow rates of solvent, etc., to improve the oil yield in terms of quantity and quality.

Environmental degradation is a major problem that people facing today along with finding alternate fossil fuels and vegetable oils have the potential to solve this problem. Thus, it is necessary to develop and carried out vegetable oil extraction process efficiently and effectively.

1.2 Problem Statement

1.2.1 Problem Identification

Conventionally used solvent for the vegetable oil extraction process is hexane. But, it is highly flammable, toxic, severe extraction condition and some contamination of solvent in final extracted oil. Also the use of alcohol solvent has the disadvantage of requiring a high solvent to feed ratio and alcohol tends to form an azeotrope when mixed with water. This project studies use SC-CO_2 as a solvent for extraction.

The study of effect of parameters on SC-CO_2 extraction and prediction of vegetable oil yield will involve many trial and error experiments based on previous researches. This method is time consuming and costly. Therefore, the present study is an attempt to use response surface methodology to obtain the second-order polynomial response surface equation to be a model equation for estimating the amount of oil yield. Moreover, optimizes the parameters of SC-CO_2 extraction of rice bran oil and wheat bran oil and examine the behavior of system are performed once changing the parameters of the system such as pressure and temperature, is a rational approach in process analysis and design or debottlenecking which is economical and saves time with limited risk of failures.

Also the model should be easy to understand and set up for use by analyzers or engineers controlling the process. It can significantly enhance the task of analysis, diagnosis the overall extraction process.

1.2.2 Significance of the Project

The significance of the study will be to:

- Improve literature on SC-CO_2 extraction of wheat bran and rice bran oil.
- Broaden public understanding about the effect of operating parameters such as temperature, pressure and solvent mass to the behavior of SC-CO_2 extraction of wheat bran and rice bran oil.
- Use the model estimated by response surface methodology to improve SC-CO_2 extraction yield.
- Conduct as a pilot project. In the event that the project is successful, continuation of the study to use other oilseeds will happen.

1.3 Objectives

The objectives of the project are:

1. To apply response surface methodology to optimize the operating parameters of SC-CO_2 extraction of wheat bran oil and rice bran oil.

2. To obtain the second-order polynomial response surface equation to estimate the amount of oil yield.

3. To examine the effect of temperature, pressure and solvent mass on SC-CO_2 extraction of wheat bran oil.

4. To examine the effect of temperature and pressure on SC-CO_2 extraction of rice bran oil.

5. To perform an economic feasibility study for the SC-CO_2 extraction of rice bran oil process.

1.4 Scope of Study

The project deals with $SC\text{-}CO_2$ use as a solvent for extraction of wheat bran oil and rice bran oil. This will focus primarily on applying the response surface methodology to optimize the operating parameters and to obtain the second-order polynomial response surface equation to estimate the amount of oil yield. It includes analysis and validation of the model equation. Upon the optimization, an examination of the effect of temperature, pressure and solvent mass on the extraction process will be performed.

1.5 The Relevancy of the Project

Nowadays people have more concern about clean technology, environmental and human health hazards of organic solvents and residues. Supercritical fluid has gained more attention and widely used in many industries such as industrial purification, pharmaceuticals, medical products and oil extraction processes. Supercritical technology is considered as a sustainable solution in many ways and carbon dioxide is one of the examples available in unlimited quantities, it is environmentally friendly and easy to handle.

1.6 Feasibility of the Project

The feasibility of this project highly possible to be completed within the scope and time frame, some of the reasons are as follows:

- Availability of software: STATGRAPHICS Centurion software is available.
- The project involves the experimental results that were developed by other researchers and the operating conditions were known. Therefore, model equation is possible to be generated, the use and analysis of the model would be able to complete in a given time period.
- Cost saving: unnecessary to purchase any equipment, just use existing software.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Supercritical Carbon Dioxide

Supercritical carbon dioxide (SC-CO_2) is a fluid state of carbon dioxide where it is held at or above its critical temperature (T_c) and critical pressure (T_p). The critical pressure is the highest pressure at which a liquid can be converted into a gas by an increase in temperature, while critical temperature is the highest temperature at which a gas can be converted into liquid by an increase in pressure.

SC-CO_2 is becoming an alternative solvent in many industries such as edible oil processing, biomaterial processing, medicinal and enhance oil recovery in mature oil fields. Mohamed and Mansoori (2002) and Raventos et al. (2002) reviewed applications of supercritical fluids in the food industry.

SC-CO_2 is becoming an important commercial and industrial solvent due to its role in chemical extraction in addition to its low toxicity, it is not flammable and its critical temperature and pressure are not high (31.1 ^oC and 7.38 MPa). Phase diagram for carbon dioxide is shown in Fig. 2.1 Furthermore, it is easy to remove solvent from the extract and no environmental issue.

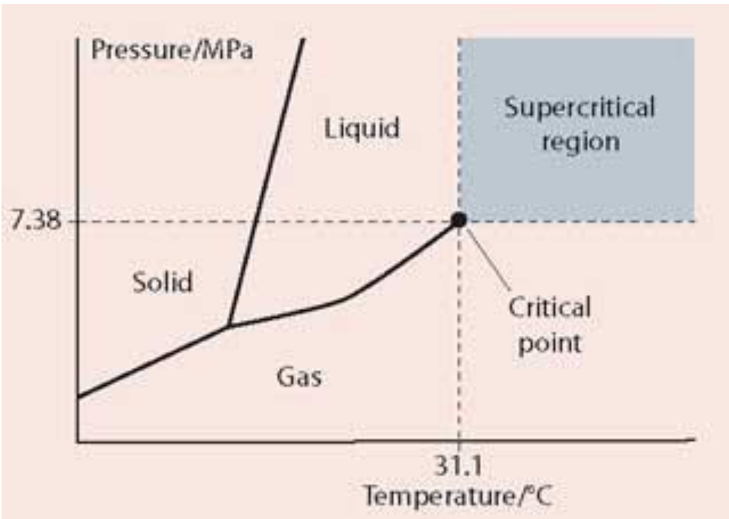


Figure 2.1**:** Phase diagram for carbon dioxide [26]

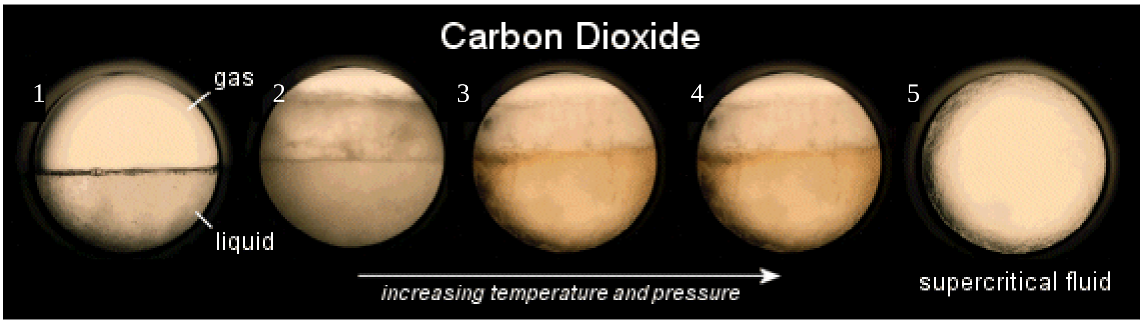


Figure 2.2: The formation of supercritical carbon dioxide [15]

Fig. 2.2 above illustrated by conducting a modern version of the Cagniard de la Tour experiment for the formation phase of SC-CO_2 and a brief description of each phase are as follows:

1. Here we can see the separate phases of carbon dioxide. A substance below its critical temperature existing as a liquid with the gas above it. The meniscus is easily observed.

2. With an increase in temperature the liquid density falls due to expansion and the gas density rises as more of the substance evaporates. The densities approach each other and the meniscus between the two phases becomes less distinct.

3 and 4. An increase in the temperature further causes the gas and liquid densities to become more similar. The meniscus is less easily observed but still evident.

5. Once the critical temperature and pressure have been reached the two distinct phases of liquid and gas are no longer visible. The meniscus can no longer be seen. One homogenous phase called the "Supercritical fluid" phase occurs which shows properties of both liquids and gases.

SC-CO_2 have properties midway between a gas and a liquid. In Table 2.1, the critical properties of carbon dioxide are shown.

Table 2.1: Critical properties of carbon dioxide [27]

Solvent	**Molecular Weight**	**Critical Temperature**	**Critical Pressure**	**Critical Density**
	g/mol	$^oC)$	MPa (bar)	Kg/m^3
Carbon Dioxide	44.01	31.1	7.38 (73.8)	464

2.2 Introduction to Rice Bran

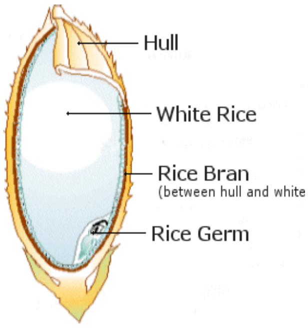


Figure 2.3: The composition of rice [28]

Rice bran is the layer between the inner white rice grain and the outer hull. As in Fig. 2.3 shows the picture of rice paddy is composed of hull at the outer layer has less nutrients but it helps to protect the insect disturbance [16, 14].

Rice bran is a useful source of protein and fat for a meals products. Composition of rice bran is including 11-15% proteins, 34-62% carbohydrates, 7-11% crude fibers, 7-10% ashes and 15-20% lipids, these consider by-product after the refining process [17]. There is an enzyme lipase in rice bran which cause fast deterioration of oil to free fatty acids and glycerol [18]. Rice bran contains 12-22% oil [19]. Rice bran oil is produced from rice bran [20]. The composition of crude rice bran oil is given in Table 2.2.

Table 2.2: Composition of crude rice bran oil [21]

Component	%
Saponifiable lipids	**90-96**
Neutral Lipids	88-89
Triglycerides	83-86
Diglycerides	3-4
Monoglycerides	6-7
Free fatty Acids	2-4
Waxes	3-4
Glycolipids	6-7
Phospholipids	4-5
Unsaponifiable lipids	**4.2**
Phytosterols	43
Sterolesters	10
Triterpene alcohols	28
Hydrocarbons	18
Tocopherols	1

2.3 Introduction to Wheat Bran

The whole kernel of wheat consists of three primary parts: the endosperm, germ and bran. The wheat bran is the outer shell, which has the duty of protecting the seed. When wheat is processed to become flour, the bran is discarded, even though it is a good source of nutrients, starch, dietary fibers [29], protein, vitamins, minerals [30] and natural antioxidants such as tocopherol, phenolic acid and etc. [31].

When they are processed, this bran layer becomes a byproduct. Bran oil can be extracted and use for industrial purposes such as in the paint industry, pharmaceuticals, food and etc.

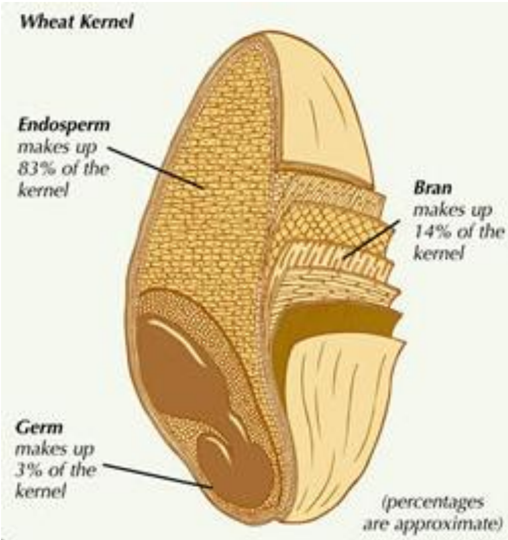


Figure 2.4: Wheat kernel

Some studies about wheat bran oil had been conducted such as Reddy et al. (2000) studied about fractions of wheat bran and it contains some bioactive compound that can prevent carcinogenesis for human colon cancer. Sung et al. (2006) studied about wheat bran oil and its fractions inhibit human colon cancer cell growth and intestinal tumorigenesis in a mouse model. The result showed that the oil fraction of wheat bran was active against the growth of human colon cancer cell lines and that 2% WB oil significantly inhibited the overall tumorigenesis by 35.7% in the mouse model.

2.4 Previous Studies on Supercritical Carbon Dioxide Extraction

One of the criteria to increase the extraction yield is by adjusting the operating parameters such as pressure, solvent flow rate and temperature. These parameters will affect the extraction yield performance of the process. Adjusted operating parameters have been studied in many researches in order to find optimal operating conditions and examine the effect of operating parameters. Zhao et al. (1987) carried out the fractional extraction of rice bran oil with supercritical fluid extraction at different pressure which are 14.7 to 34.3 MPa, and at a fixed temperature of 40 ^oC. They found the pressure affect on oil yield (18.6 to 22.0%). Kuk and Dowd (1998) conducted supercritical fluid extraction of rice bran (6% moisture, below 0.297 mm particle size) at different pressure which are 48.26 a32nd 62.05 MPa for a 1.5 hours and the result was 19.2-20.4% rice bran oil yield given better result as compared to 20.5% extraction yield using hexane in 4 hr. Kwon et al. (2010) conducted SC-CO_2 extraction of wheat bran oil in semi-batch process at temperatures ranging from 40-60 ^oC and pressure from 10-30 MPa, the result showed that the highest amount of antioxidants (phenolics and tocopherols) were found at a temperature of 60 ^oC and a pressure of 30 MPa

The table below is the summary of some previous studies on SC-CO_2 extraction and operating parameters used in the studies.

Table 2.3: Previous studies on SC-CO_2 extraction of various operating parameters

Author	Paper	Parameters
Reverchon et al. (1993)	Modeling of SCF extraction from Herbaceous Matrices	CO_2 flow rate : 1.2 kg/h Pressure : 80 - 120 bar (8 - 12 MPa) Temperature : 35 - 50 ^oC
Papamichail et al. (2000)	SCF extraction of celery seed oil	CO_2 flow rate : 1.1, 3.0 kg /h Pressure : 100, 150, 200 bar (10, 15, 20 MPa)

		Temperature : 45 and 55 ^oC
Pourmortazavi et al. (2003)	SC-CO_2 extraction of essential oils from Perovskia Atriplicifolia Benth	Pressure : 100, 200, 300 atm (10, 20, 30 MPa) Temperature : 35, 45, 55, 65 ^oC
Perakis et al. (2005)	SCF extraction of black pepper oil	CO_2 flow rate : 1.1, 2, 3 kg /h Pressure : 90, 100, 150 bar (9, 10, 15 MPa) Temperature : 40, 50 ^oC
Chen et al. (2008)	SC-CO_2 extraction of rice bran oil and column partition fractionation of γ-oryzanols	CO_2 flow rate : 5 L/min Pressure : 250 - 350 bar (25 - 35 MPa) Temperature : 313 - 333 K (40 - 60 ^oC)
Imsanguan et al. (2008)	Extraction of α-tocopherol and γ-oryzanols from rice bran	CO_2 flow rate : 0.45 mL/min Pressure : 38 and 48 MPa Temperature : 45 - 65 ^oC
Amarasinghe et al. (2009)	Effect of method of stabilization on aqueous extraction of rice bran oil	Temperature : 60 - 80 ^oC

Operating parameters presents in the above list of various experimental works and studies are conducted in laboratory scale. For this project studies is focusing on the simulation of the small scale extraction process and utilize the data of operating parameters in the range based on the literatures.

The result of most studies on SC-CO_2 extraction of various operating parameters reveals that the pressure and solvent flow rate play important roles in the process. As pressure increases lead to the extraction rate increase. Likewise, the increase of the solvent flow rate leads to the increase of extraction yield.

The table below is the summary of finding of previous studies on SC-CO_2 extraction to study the effect of pressure and solvent flow rate and temperature on the extraction yield.

Table 2.4: Finding of previous studies on SC-CO_2 extraction

Author	**Paper**	**Parameters**	**Finding**			
			Pressure (P)	**Solvent Flow Rate (Q)**	**Temperature (T)**	**Extraction Yield**
Papamichail et al. (2000)	SCF extraction of celery seed oil	CO_2 flow rate : 1.1 kg /h P : 100, 150, 200 bar (10, 15, 20 MPa) T : 45 and 55 ^oC Solute : 30 g	Increase	Increase	Decrease	Increase
Pourmortazavi et al. (2003)	SC-CO_2 extraction of essential oils from Perovskia Atriplicifolia Benth	P : 100, 200, 300 atm (10, 20, 30 MPa) T : 35, 45, 55, 65 ^oC Solute : 1.0 g			Increase	Decrease

Perakis (2005)	SCF extraction of black pepper oil	CO_2 flow rate : 1.1, 2, 3 kg /h P : 90, 100, 150 bar (9, 10, 15 MPa) T : 40, 50 ^oC Solute : 100 g	Increase	Increase	Decrease	Increase
Sarmento et al. (2006)	Supercritical fluid extraction (SFE) of rice bran oil to obtainfractions enriched with tocopherols and tocotienols	CO_2 flow rate : 0.0756 kg/h P: 150, 200, 250 bar (15 - 25 MPa) T : 25, 40, 50, 60 ^oC Solute : 40 g	Increase		Decrease	Increase
Chen et al. (2008)	SC-CO_2 extraction of rice bran oil and column partition fractionation of γ-oryzanols	CO_2 flow rate : ~ 0.59 kg/h P : 250 - 350 bar (25 - 35 MPa) T : 313 - 333 K (40 - 60 ^oC) Solute : 0.5 g	Increase		Decrease	Increase

Kwon et al. (2010)	Supercritical carbon dioxide extraction of phenolics and tocopherols enriched oil from wheat bran.	CO_2 flow rate : 26.81 g/min (1.6 kg/h) P : 10 - 30 MPa T : 40 - 60 ^{o}C Solute : 12 g	Increase			Increase

2.5 Extraction

Extraction is considered one of the separation processes that normally used to separate compounds from a mixture. The process of separating a substance can be Liquid Liquid Extraction (LLE) is a method to separate compounds from a liquid mixture based on their relative solubilities in two different immiscible liquids, Solid Liquid Extraction or generally referred to leaching for separating a substance from solid mixture, it is the separation of one or more components of a solid mixture by preferential absorption through contact with a liquid solvent, or Solid Supercritical Fluid Extraction like this study..

The operation of Solid Liquid Extraction or Solid Supercritical Fluid Extraction allow soluble components to be removed from solids using a solvent. Applications of this unit operation include extraction of vegetable oils or obtaining oil from oil seeds such as extraction of rice bran oil, soy

bean oil, etc. One of the most daily encountered examples of extraction is the preparation of the coffee. Here the water is used to remove the coffee flavor from the coffee powder (extraction material).

Another conventional use is known as mechanical extraction, it uses the operation such as pressing and extrusion to extract constituent from a solid phase.

2.6 Operation Consideration

In any chemical industries, many processes undergo extraction, solvent extraction has to be operated with a specific set of operating condition for optimum efficiency. Two factors below are the key factors that ease of extraction depends on:

1. Solid phase resistance or ease of solvent penetration into a solid.
2. Solubility of the material to be extracted in the solvent.

Solid phase resistance is a quite significant factor in extraction, in most of the cases experienced low extraction efficiency because the difficulty for the solvent to reach the solute that trapped in solid’s pores. One way to reduce the solid phase resistance is to reduce the size of the solid particles by grinding or crushing them before extraction. Extraction of vegetable oils from oil seeds need to undergo a pretreatment process such as dehulling, grinding and etc.for this purpose.

Another important factor that influences the extraction is solubility. The solubility is defined as the ability of the solvent to dissolve a solute from a mixture. The higher the solubility, the more the solute will be extracted in the solvent. The temperature is the most effect parameter on solubility. Higher temperatures result in higher solubility. And thus, improve extraction efficiency.

2.7 Response Surface Methodology (RSM)

RSM is a collection of mathematical technique that helps in exploring the optimum operating conditions of the experiments. Normally, this includes conducting some experiments, and using the results of one experiment to give direction for what to do next. At the beginning, the RSM was started to model experimental responses (Box and Draper, 1987), and then migrated into the modeling of numerical experiments. RSM evaluates the effect of various parameters, single or combination to design variables and predict their behavior for different set of conditions.

The mathematical models that represent RSM model are as follows (Alexander):

1. The first-order (linear model) without interaction/cross-product terms:

$$Y(x)= \beta o \sum_{i=1}^{k} \beta ixi + e$$

2. The first-order (linear) model with interaction/cross-product terms:

$$Y(x)= \beta o \sum_{i=1}^{k} \beta iXi + \sum_{j=2}^{k} \sum_{i=1}^{j-1} \beta ijXiXj + e$$

3. The second-order (quadratic) model:

$$Y(x)= \beta o \sum_{i=1}^{k} \beta iXi + \sum_{j=2}^{k} \sum_{i=1}^{j-1} \beta ijXiXj + \sum_{i=1}^{k} \beta ii\, X^2 + e$$

2.8 Previous Studies of RSM on Supercritical Carbon Dioxide Extraction Process

Wang et al. (2008) examined the supercritical carbon dioxide extraction of oryzanols contained rice bran oil. The extraction efficiencies and concentration factors of oryzanols, free fatty acids and triglycerides in the SC-CO_2 extracts were determined. The result showed that the pressure was more effective than the temperature to enhance the extraction efficiency and concentration factor of oryzanols. A two-factor central composite scheme of response surface methodology was used to determine the optimal pressure (300 bar) and temperature (313 K) for increasing the concentration of oryzanols in the SC-CO_2 extracted oil.

Liu et al. (2009) conducted response surface methodology (RSM) to optimize the process parameters of supercritical carbon dioxide extraction of the passion fruit seed oil to investigate the effects of temperature, pressure and extraction time on the oil yield. The result showed that the data were adequately fitted into the second-order polynomial model. The prediction of optimum extraction process parameters within the experimental ranges would be at temperature of 56 °C and pressure of 26 MPa and extraction time of 4 h. The maximum oil yield was 25.83%.

Mariod et al. (2010) performed SC-CO_2 extraction of sorghum bug oil and compared with Soxhlet extraction using hexane. Response surface methodology (RSM) was used to determine the effects of pressure (200 - 400 bar) and temperature (50 - 70 ^oC) on the sorghum bug oil yield. The high extraction yield was obtained at 300 bar and 60 ^oC followed by 400 bar and 70 ^oC, while the lower yield was obtained at 159 bar and 60 ^oC. The oil yield decreased due to the reduced density of CO_2 at higher temperatures.

Yu et al. (2012) conducted the SC-CO_2 extraction extract oil from rapeseed. Extraction temperature, pressure, time and the sample particle size were selected and optimized by response surface methodology. The result showed that maximum extraction yield of 32.65 ± 1.01% was achieved at a temperature of 40 °C and a pressure of 345 bar, using an extraction time of 3 h and a 60-mesh particle size.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

1. Design research problem.

Single out the problem that student wants to study and decide the general area or subject matter of interest. At this stage student discussed with the supervisor about the problem and objective in seeking a solution.

2. Review the literature.

Proceed to review the concept or theories for the related subject matter and review previous research finding.

3. Development of working hypothesis.

Student focus, delimit the area of the project and review similar studies in the area or of studies on similar problem.

4. Preparing the research design.

- Collection of information: Obtain the experimental results of SC-CO_2 extraction of wheat bran oil and rice bran oil from the existing literature.
- Further analyze the effect of operating parameters on extraction yield by using STATGRAPHICS Centurion software.
- Use Response Surface Methodology (RSM) to analyze the experimental design response and obtain the optimum condition of the extraction process. The statistical significant is analyzed in analysis of variance approach (ANOVA).

5. Performing economic feasibility study for SC-CO_2 extraction process.

6. Preparation of the report.

3.2 Statistical Analysis Methodology

1. Create design options: Choose a response surface for the design class.

Process	Wheat bran		Rice bran	
No. of response variable	1	Oil yield	1	Oil yield
No. of experimental factor	3	Temperature	2	Temperature
		Pressure		Pressure
		CO_2 mass		

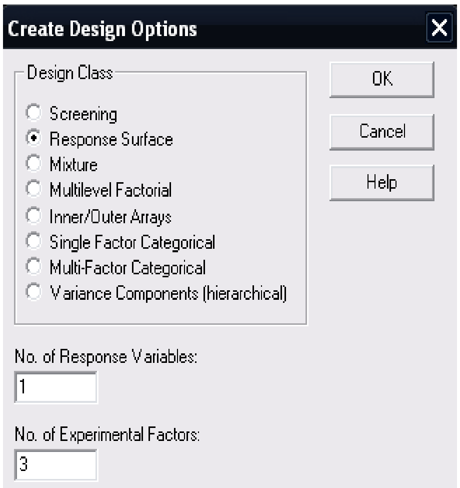


Figure 3.1: Create design options for wheat bran

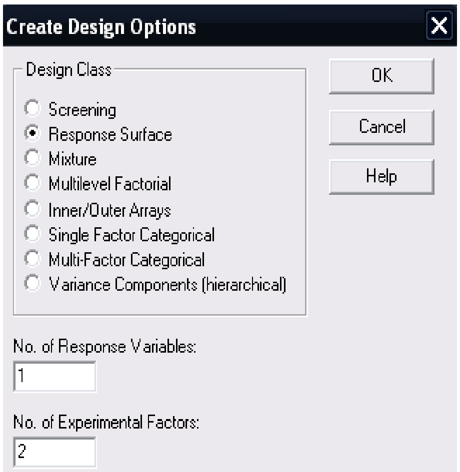


Figure 3.2: Create design options for rice bran

2. Fill the value in factor definition option.

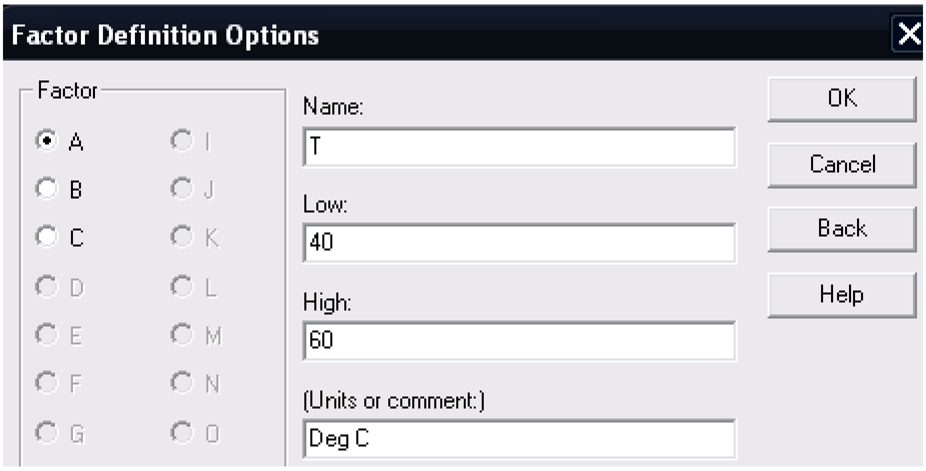


Figure 3.3: Factor definition options

Factor	Wheat bran	Min.	Max.	Rice bran	Min.	Max.	Units
A	T	40.0	60.0	T	45.0	85.0	^{o}C
B	P	10.0	30.0	P	20.0	35.0	MPa
C	M	400	3250	-	-	-	g

3. Choose a design name in response surface design selection.

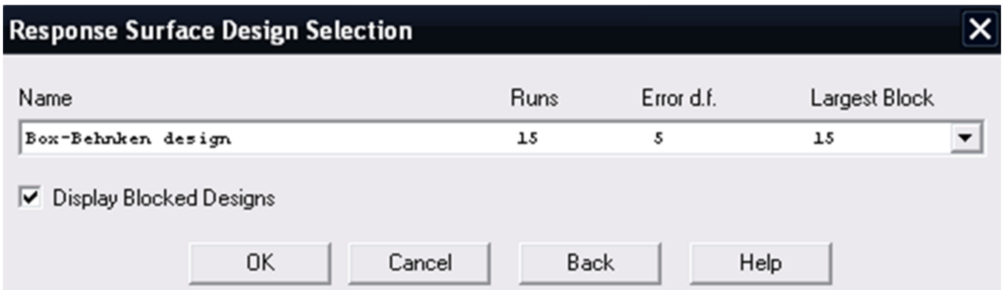


Figure 3.4: Box-Behnken design for wheat bran

Figure 3.5: 3-level factorial design: 3^2 for rice bran

4. Define center points.

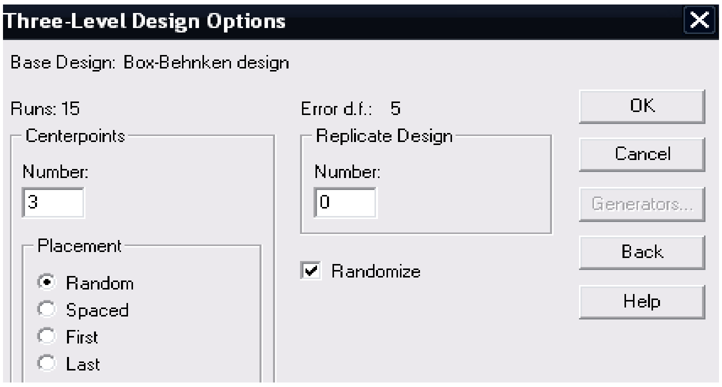


Figure 3.6: 3 center points with 15 runs for wheat bran

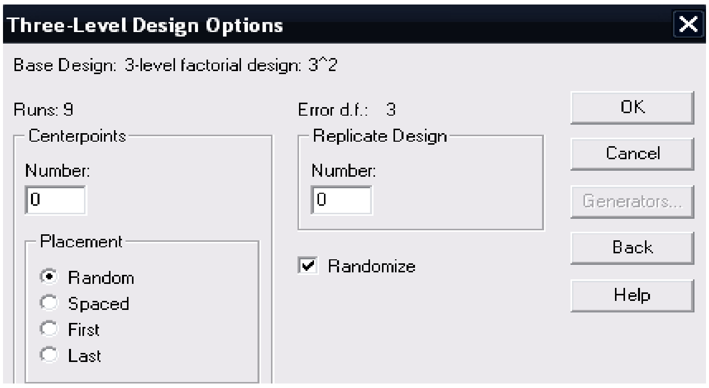


Figure 3.7: 0 center point with 9 runs for rice bran

5. After entering the data and range of parameters into software, the parameters would be placed randomly into a different row. In the oil yield column, the results of oil yield were collected first at specified parameters. The values based on experiment would be filled manually.

	BLOCK	T	P	M	Yield
		oC	MPa	g	g/12g of wheat bran
1	1	40.0	10.0	1825.0	0.48
2	1	60.0	20.0	3250.0	2.20
3	1	50.0	30.0	3250.0	2.04
4	1	50.0	10.0	400.0	0.14
5	1	50.0	20.0	1825.0	1.53
6	1	60.0	20.0	400.0	0.80
7	1	50.0	30.0	400.0	0.60
8	1	40.0	30.0	1825.0	1.20
9	1	60.0	30.0	1825.0	2.58
10	1	40.0	20.0	3250.0	1.00
11	1	50.0	20.0	1825.0	1.53
12	1	50.0	20.0	1825.0	1.53
13	1	50.0	10.0	3250.0	0.70
14	1	60.0	10.0	1825.0	0.74
15	1	40.0	20.0	400.0	0.45

Figure 3.8: Experimental results of wheat bran oil yield at different condition

	BLOCK	T	P	Yield
		Deg C	MPa	Kg Oil Extracted/Kg of Rice Bran
1	1	45	35	0.22
2	1	65	27.5	0.135
3	1	45	27.5	0.165
4	1	85	20	0.018
5	1	65	20	0.04
6	1	45	20	0.076
7	1	85	35	0.178
8	1	65	35	0.2
9	1	85	27.5	0.089

Figure 3.9: Experimental results of rice bran oil yield at different condition

6. Analyze the design.

Once the data have been loaded into the STATGRAPHICS Centurion DataBook,

- Go to command tab → choose DOE → choose Design Analysis → choose Analyze Design.

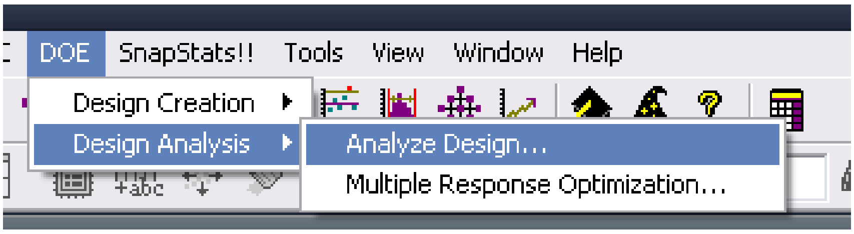


Figure 3.10: Command tab for design analysis

- This data input dialog box will appear and select Yield.

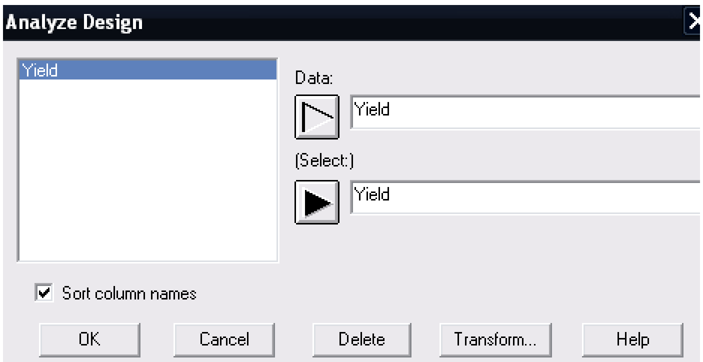
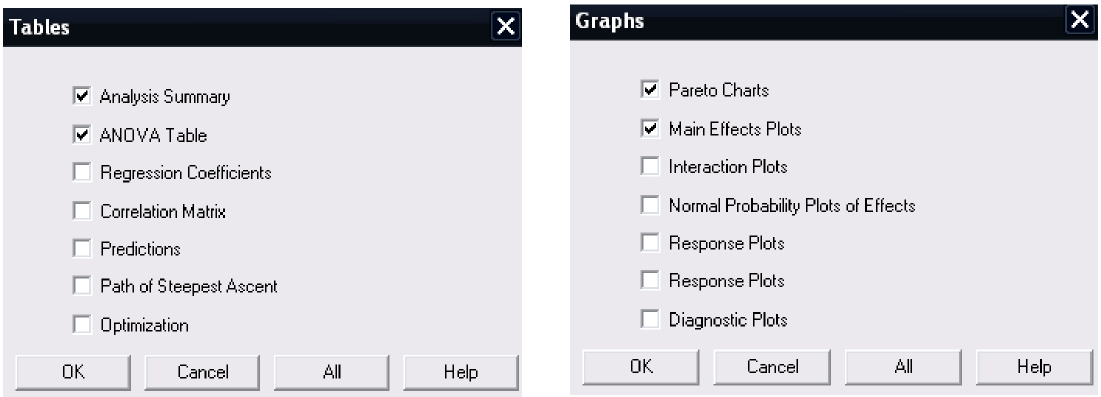
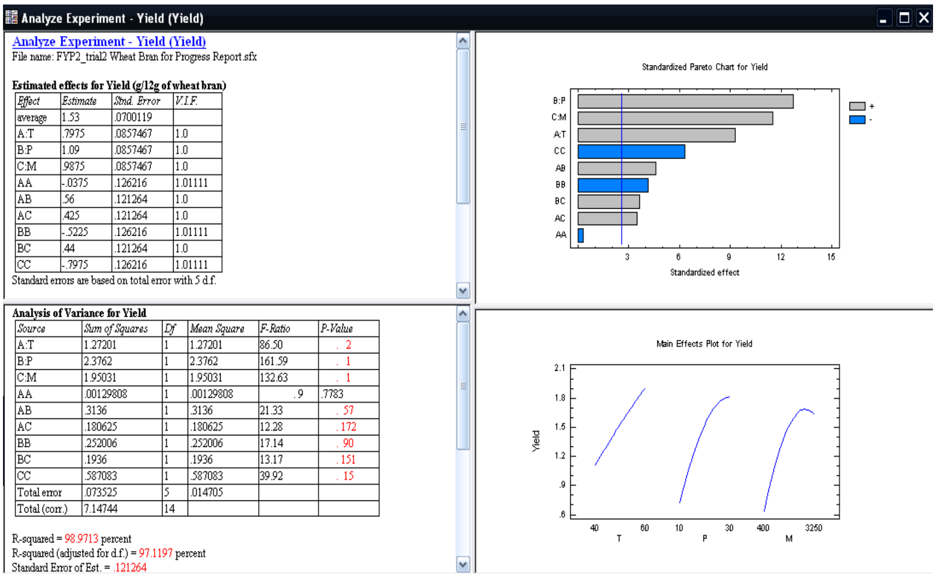


Figure 3.11: Data input dialog box for analyze design

- When OK is pressed, the tables and graphs dialog box appears. This dialog box shows the tables and graphs that are available.





Effect	Estimate	Stnd. Error	V.I.F.
average	1.53	.0700119	
A:T	.7975	.0857467	1.0
B:P	1.09	.0857467	1.0
C:M	.9875	.0857467	1.0
AA	-.0375	.126216	1.01111
AB	.56	.121264	1.0
AC	.425	.121264	1.0
BB	-.5225	.126216	1.01111
BC	.44	.121264	1.0
CC	-.7975	.126216	1.01111

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:T	1.27201	1	1.27201	86.50	. 2
B:P	2.3762	1	2.3762	161.59	. 1
C:M	1.95031	1	1.95031	132.63	. 1
AA	.00129808	1	.00129808	.9	.7783
AB	.3136	1	.3136	21.33	. 57
AC	.180625	1	.180625	12.28	.172
BB	.252006	1	.252006	17.14	. 90
BC	.1936	1	.1936	13.17	.151
CC	.587083	1	.587083	39.92	. 15
Total error	.073525	5	.014705		
Total (corr.)	7.14744	14			

Figure 3.12: Analyze Experiment- Analysis Window

7. Obtain regression equation from the software. The software computes the linear, quadratic, and interaction terms in the model. Example displays as follows:

Y = 0.370379 - 0.0245899*T - 0.00917544*P + 0.00000884888*M - 0.0001875*T^2 + 0.0028*T*P + 0.0000149123*T*M - 0.0026125*P^2 + 0.0000154386*P*M - 1.96368E-7*M^2

8. Observe the optimum parameters of the process.

9. Discuss the main effect of operating parameters on the oil yield.

- For wheat bran: Temperature, Pressure and CO_2 mass.
- For rice bran: Temperature and Pressure.

10. Compare the result of wheat bran oil yield between the result from the experiment and result from second order polynomial model. And do the same for rice bran oil yield.

11. Validate the equation of response surface modeling for wheat bran and rice bran oil yield.

3.3 Conduct economic feasibility study for SC-CO_2 extraction process.

3.4 Gantt Chart

Table 3.1: Final Year Project I (May 2012) Gantt Chart

Detail Work \ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
Selection of Project Topic								Mid-semester break							
Preliminary Research Work - Literature Review: Simulations of SC-CO_2 extraction of Rice Bran Oil															
Submission of Extended Proposal Defense															
Proposal Defense															
Project Work Continues															
Submission of Interim Draft Report															
Submission of Interim Report															

Suggested milestone

Process

Table 3.2: Final Year Project II (September 2012) Gantt Chart

Detail Work \ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	17
Project work continues	■	■	■	■	■	■	■								
Progress report submission								●							
Pre-EDX Poster presentation											●				
Submission of Draft Report												●			
Submission of Dissertation (Soft Bound)													●		
Submission of Technical Paper													●		
Submission of Dissertation (Hard Bound)															●

3.5 Key Milestone

Table 3.3: Final Year Project I (May 2012) Summary of Activities

Week	FYP1 Activities	*Date	*Time	Venue	Remarks
1	FYP Briefing- 'Supervision'	23rd May	3.00- 4.00 pm	05-02-16	Briefing on FYP Supervisor.
2-14	Regular Meeting with Supervisor	-	-	-	
3	Literature Search & LFSU Briefing	6th June	2.30- 5.00 pm	Auditorium, IRC	All Students
5	FYP Requisition Form submission deadline	20th June	by 5pm	FYP1 pigeon hole, Block 4, Level 3	Students who performed experiments and need to buy chemical through Chem. Eng. Department
6	Submission of Extended Proposal	25th June	by 5pm	-	All students submit to individual supervisors
7	IRC Training- Citation	-	-	-	
11	Proposal Defense	30th	10.00	05-02-09	All Students-Supervisor-Internal

	(Oral Presentation)	August	am		Examiner
13	Submission of draft Interim Report	17th August	by 5 pm	-	All students to prepare 2 copies and distribute to Supervisor and Internal Examiner for assessment.
14	Submission of Interim Report to Coordinator	27th August	by 5 pm	Chemical Eng. Office. (Pn Hafizah/ Pn Suhana) 04-03-02	All students to prepare 2 copies. Coordinator to distribute to Supervisor and Internal Examiner for assessment.

Table 3.4: Final Year Project II (September 2012) Summary of Activities

Week	FYP1 Activities	*Date	*Time	Venue	Remarks
1	FYP II Briefing- 'Supervision'	26th September	3.00-4.00 pm	21-02-12	Briefing on FYP Supervisor.
6	Briefing How to Write Dissertation	24th October	3.00-4.00 pm	05-02-16	All students
11	Pre-EDX Poster presentation	26th & 28th November	2.30-5.00 pm	Block 5	All Students
12	Submission of Draft Report	3rd December	by 5pm	-	All students submit to individual supervisors
13	Submission of Dissertation (Soft Bound)	10th December	by 5pm	Block 5	All students submit to the coordinator
13	Submission of Technical Paper	10th December	by 5 pm	Block 5	All students submit to the coordinator
17	Submission of Dissertation (Hard Bound)	11th January	by 5 pm	Block 5	All students submit to the coordinator

3.6 Software Required

- STATGRAPHICS Centurion software

CHAPTER 4

RESULTS AND DISCUSSION

4.1 RSM for SC-CO_2 Extraction of Wheat Bran Oil

4.1.1 Experimental Design for Wheat Bran Oil Yield

Box-Behnken design has been created which will study the effects of 3 factors in 15 runs. The order of the experiments has been fully randomized. The ranges of parameters are as follows:

Factor	Low	High	Units	Continuous	Response	Unit
T	40.0	60.0	^oC	Yes	Oil Yield	g/12g of wheat bran
P	10.0	30.0	MPa	Yes		
M	400	3250	g	Yes		

After entering the data and range of parameters into the software (refer to steps in methodology), the parameters would be placed randomly in a different row. In the oil yield column, the results of oil yield were collected first at specified temperature, pressure and CO_2 mass. The values based on experiment would be filled manually. Table 1 shows the experimental design and results derived from each run.

Table 4.1: Experimental design for wheat bran oil yield

Run	Temperature (^oC)	Pressure (MPa)	CO_2 Mass (g)	Oil yield (g/12g of wheat bran)
1	40	10	1825	0.48
2	40	20	3250	1.00
3	40	20	400	0.45
4	40	30	1825	1.20
5	50	10	400	0.14
6	50	10	3250	0.70
7	50	20	1825	1.53
8	50	20	1825	1.53
9	50	20	1825	1.53
10	50	30	3250	2.04
11	50	30	400	0.60
12	60	10	1825	0.74
13	60	20	3250	2.20
14	60	20	400	0.80
15	60	30	1825	2.58

4.1.2 Pareto Chart of the Standardized Effect for Wheat Bran Oil Yield

In the Pareto chart in Fig. 4.1 shows the statistically significant factors. In the interpretation of this chart, it should be noted that the lengths of the bar are proportional to the absolute value of the estimated effects. A bar crossing this vertical line corresponds to a factor or a combination of factors that have a significant influence on response. The maximal effect was presented in the upper part and then progressed down to the minimal effect. Result directly shows that the most important factors or main factors determining oil yield were pressure (P), CO_2 mass (M), and temperature (T). This chart demonstrates that all of the factors were significant at 95% confidence level except interaction of temperature with temperature (AA).

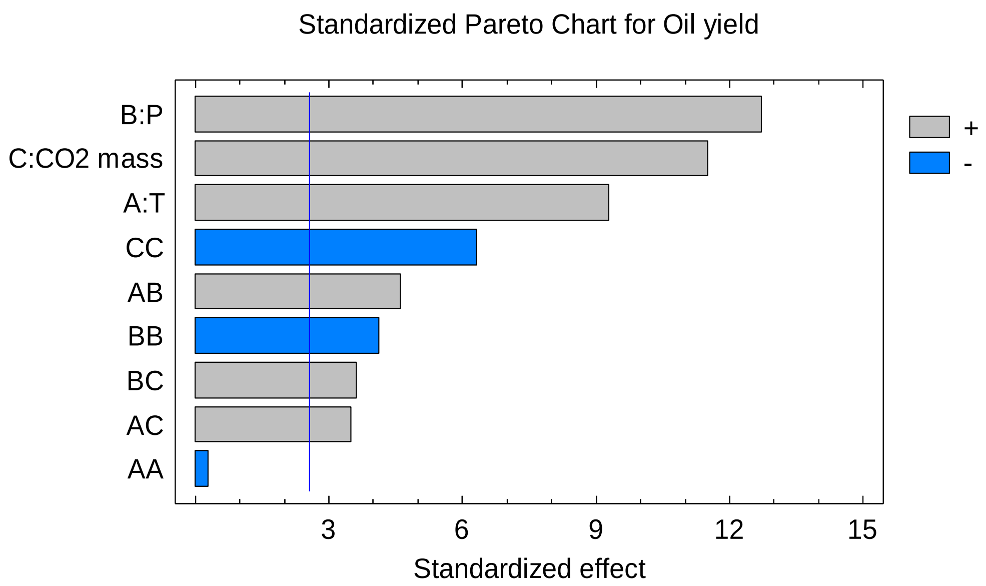


Figure 4.1: Pareto chart of the standardized effect for wheat bran oil yield

4.1.3 ANOVA Table for Wheat Bran Oil Yield

Table 4.2: Analysis of variance of the regression coefficients of the fitted quadratic equation for wheat bran oil yield

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:T	1.27201	1	1.27201	86.50	0.0002*
B:P	2.3762	1	2.3762	161.59	0.0001*
C:CO_2 mass	1.95031	1	1.95031	132.63	0.0001*
AA	0.00129808	1	0.00129808	0.9	0.7783

AB	0.3136	1	0.3136	21.33	0.0057*
AC	0.180625	1	0.180625	12.28	0.0172*
BB	0.252006	1	0.252006	17.14	0.0090*
BC	0.1936	1	0.1936	13.17	0.0151*
CC	0.587083	1	0.587083	39.92	0.0015*
Total error	0.073525	5	0.014705		
Total (corr.)	7.14744	14			

R-squared = 98.9713 percent

R-squared (adjusted for d.f.) = 97.1197 percent

Standard Error of Est. = 0.121264

Mean absolute error = 0.0536667

Durbin-Watson statistic = 2.20405 (P = 0.4471)

Lag 1 residual autocorrelation = -0.255568

Star (*) numbers indicate significant factors as identified by the analysis of variance (ANOVA) at the 95% confidence level.

The ANOVA table partitions the variability in oil yield into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 8 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level. The 8 significant effects correspond to the Pareto chart.

How well the estimated model fits the data can be measured by the value of R^2. The R^2 lies in the interval [0,1]. When R^2 is closer to the 1, the better the estimation of the regression equation fits the sample data. In general, the R^2 measures the percentage of the variation of y around y that is explained by the regression equation. However, adding a variable to the model always increased R^2, regardless of whether or not that variable statistically significant. Thus, some experimenter rather using adjusted- R^2. When variables are added to the model, the adjusted- R^2 will not necessarily increase. In actual fact, if unnecessary variables are added, the value of adjusted - R^2 will often decrease. From the result, R^2 is 98.9713 % showing the good estimation of the regression equation fits the sample data.

4.1.4 Main Effect Plot for Wheat Bran Oil Yield

The lines indicate the estimated change in oil yield as each factor is moved from its low level to its high level, with all other factors held constant at a value midway between their lows and their highs. Note that the three factors with significant main effects have a bigger impact on the response than the others.

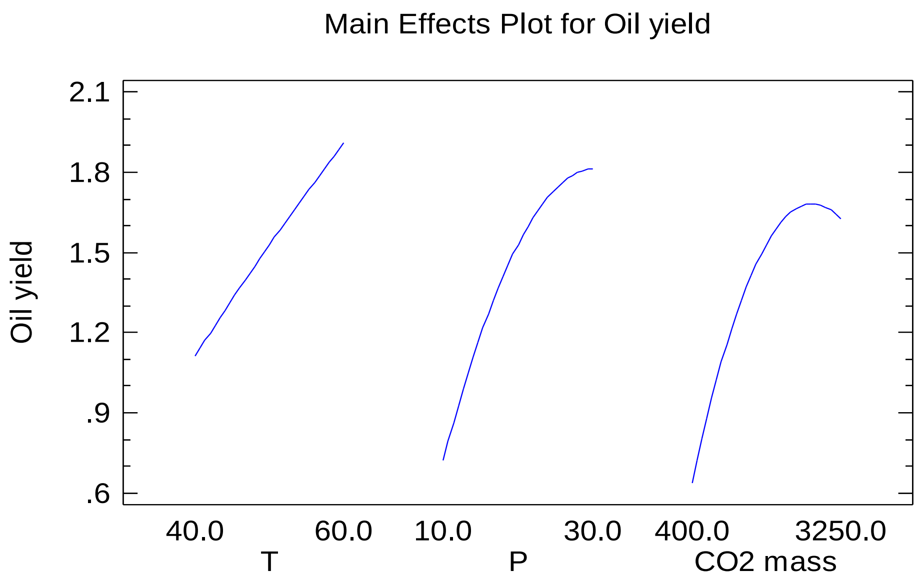


Figure 4.2: Main effects plot for wheat bran oil yield

4.1.5 Interaction Plot for Wheat Bran Oil Yield

This interaction plot confirms the significance of AB, AC, and BC interactions as stated earlier. Interaction occurs when one factor does not produce the same effect on the response at different levels of another factor. Therefore, if the lines of two factors are parallel, there is no interaction. On the contrary, when the lines are far from being parallel, the two factors are interacting. In each case of AB, AC, and BC interactions, the response oil yield increases when the line moves from the low level to high level.

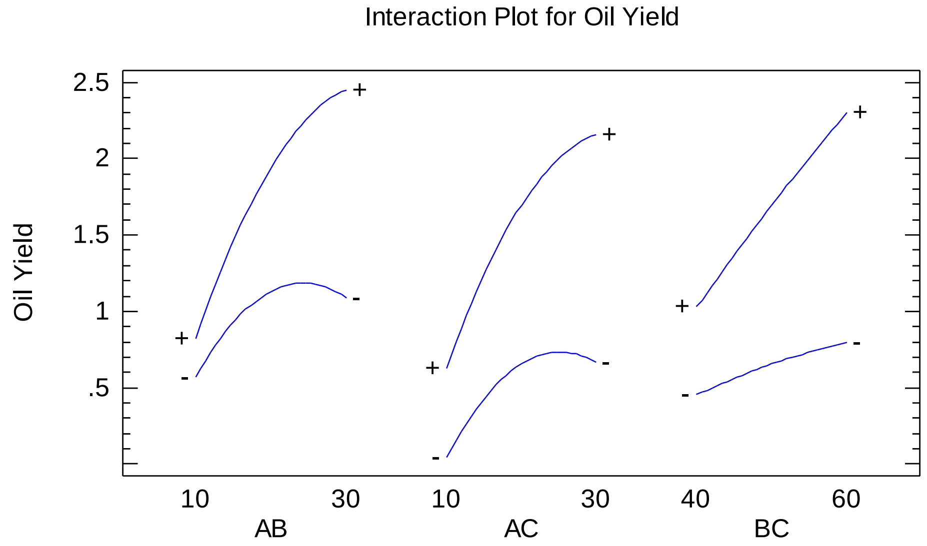


Figure 4.3: Interaction plot for wheat bran oil yield

4.1.6 Normal Probability Plot for Wheat Bran Oil Yield

If the standardized effects plot approximately along a straight line, then the normality assumption is satisfied. In this study, the standardized effects can be judged as normally distributed; therefore normality assumptions for both of the responses are satisfied. The error term is the difference between the observed value y_i and the corresponding fitted value $y^{\wedge i}$, that is, $e_i = y_i - y^{\wedge i}$. As a result of this assumption, observations y_i are also normally and independently distributed. Therefore, the test for the significance of the regression can be applied to determine if the relationship between the dependent variable Y and independent variables P, T, CO_2 Mass, exists.

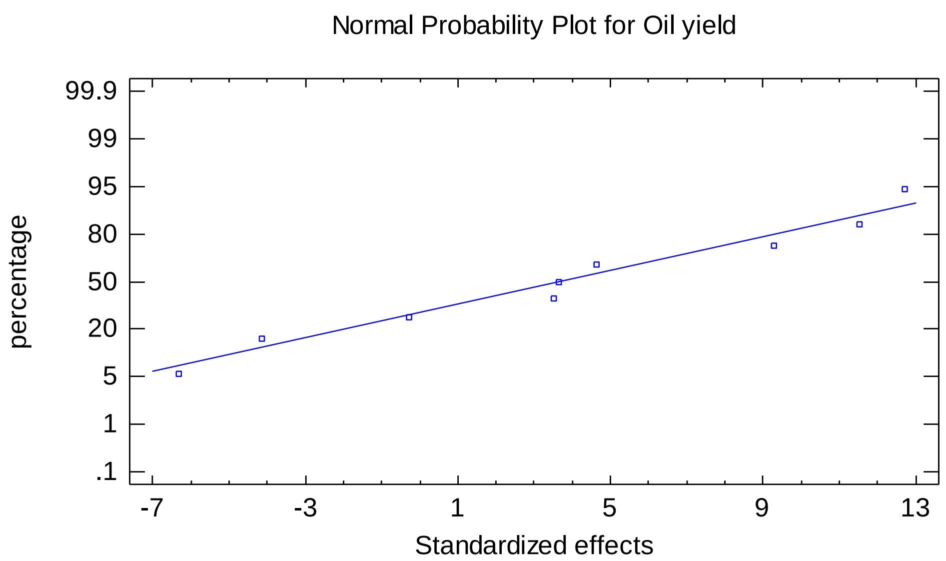


Figure 4.4: Normal probability plot for wheat bran oil yield

4.1.7 Regression Equation for Wheat Bran Oil Yield

The software computes the linear, quadratic, and interaction terms in the model. The analysis of variance indicates that there are significant interactions between the factors. The small p-values for linear and square terms also point out that their contribution is significant to the model. Small p-values for the interactions and the squared terms suggest there is curvature in the response surface. Moreover, the main effects can be referred to as significant at an individual 0.05 significant level as mentioned earlier. The quadratic terms, B^2, C^2 and interaction terms AB, AC, and BC, significantly contribute to the response model at a = 0.05. As a result, the final model for the response variable oil yield (Y) is concluded as follows:

Y = 0.370379 - 0.0245899*T - 0.00917544*P + 0.00000884888*M - 0.0001875*T^2 + 0.0028*T*P + 0.0000149123*T*M - 0.0026125*P^2 + 0.0000154386*P*M - 1.96368E-7*M^2

Where Y is the oil yield, T is the temperature, P is the pressure and M is the CO_2 mass

The regression coefficients of intercept, linear, quadratic, and interaction terms of the model are represented in the Table 4.3.

Table 4.3: Regression coefficients of predicted second order polynomial model for the response variable for wheat bran oil

Coefficient	Estimate
Constant	0.370379
A:T	-0.0245899
B:P	-0.00917544
C:CO_2 mass	0.00000884888
AA	-0.0001875
AB	0.0028
AC	0.0000149123
BB	-0.0026125
BC	0.0000154386
CC	-1.96368E-7

Since the response surface is explained by the second-order model, it is necessary to analyze the optimum setting. The graphical visualization is very helpful in understanding the second-order response surface. Specifically, contour plots can help characterize the shape of the surface and locate the optimum response approximately. The contour plot of oil yields are shown in Fig. 4.5-4.6.

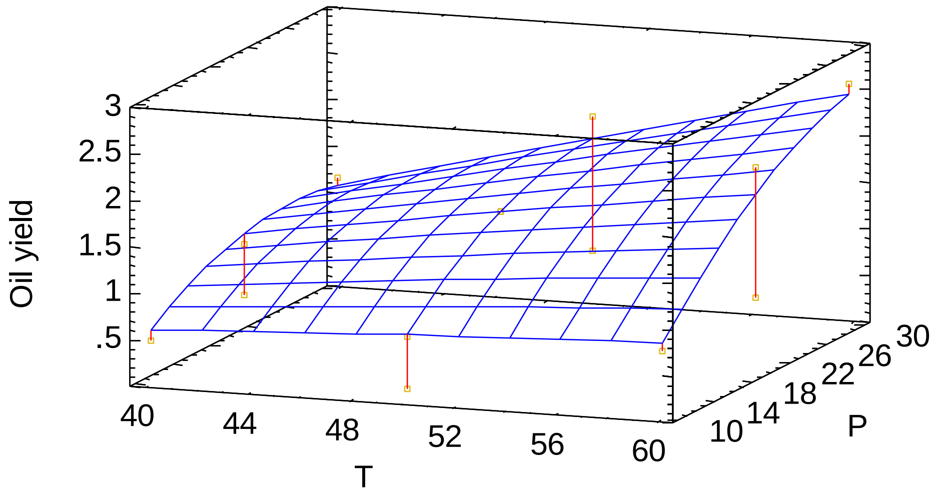


Figure 4.5: 3D contour plot of wheat bran oil yield

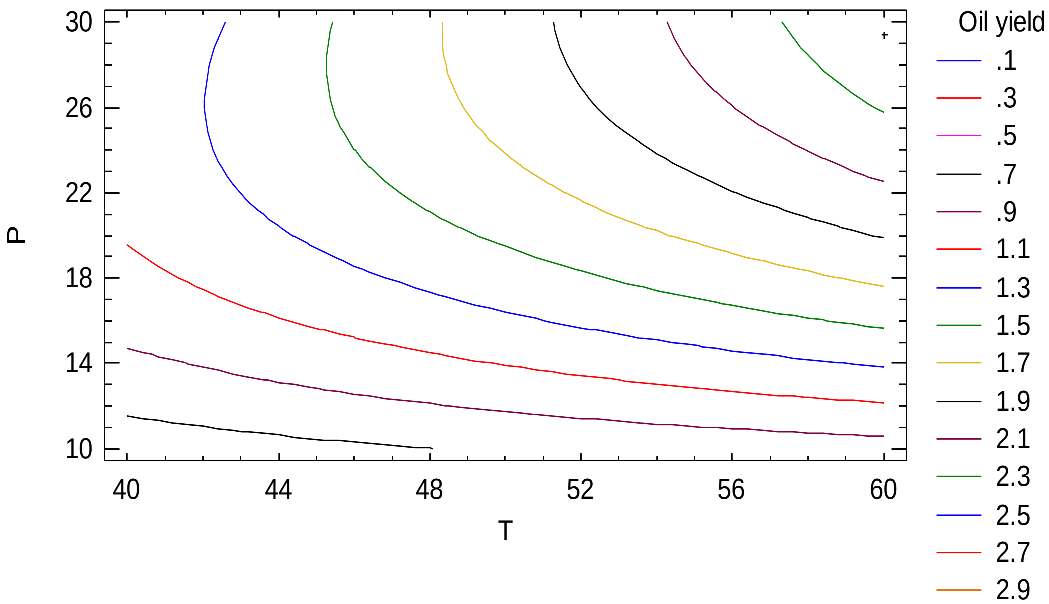


Figure 4.6: Contour plot of wheat bran oil yield

4.1.8 Optimize Response for Wheat Bran Oil Yield

This table shows the combination of factor levels which maximizes oil yield over the indicated region. The optimum conditions of the oil extraction process indicated by the software are summarized in the table below:

Optimum value = 2.96856

Table 4.4: Optimum conditions for wheat bran oil yield

Factor	Low	High	Optimum	Unit
T	40.0	60.0	60.0	^{o}C
P	10.0	30.0	29.3927	MPa
CO_2 mass	400.0	3250.0	3250.0	g/12g of wheat bran

4.1.9 Main Effect of Pressure, CO_2 Mass and Temperature to The Wheat Bran Oil Yield

At constant temperature 50 ^{o}C, the amount of oil extracted from wheat bran was increased with increasing pressure. This happened due to the increase in solvent density and hence the solvating power of SC-CO_2. Because the supercritical solvent density increased when the pressure increased, this leads to the increase in the solvent power to dissolve the substance. The increased solvating power and the strength of intermolecular physical interactions considered as belonging to the effect of pressure. The similar pressure effect was reported in SC-CO_2 extraction of celery seed oil [36].

As expected, at constant temperature 40 ^{o}C and constant pressure 30 MPa the oil yield was increased with the increasing of CO_2 mass used. A similar trend has been reported by [37] in the SC-CO_2 extraction of palm kernel oil from palm kernel.

At a constant pressure 30 MPa, the oil yield increased with the temperature increase from 40 to 60 ^{o}C. The solvent density was decreased with the increasing temperature. However, despite of the decreasing of solvent density, the oil yield was increased with the temperature which can be attributed to the increase of the oil component vapor pressure. In this case, the increase of solute vapor pressure was dominated over solvent density. Azevedo et al. [38] reported the similar effect of vapor pressure on SC-CO_2 extraction of green coffee oil.

Table 5 below shows the main effect of pressure, CO_2 mass and temperature to the oil yield at some conditions within the experimental range.

Table 4.5: Main effect of pressure, CO_2 mass and temperature to the oil yield

No.	Temperature (^oC)	Pressure (MPa)	CO_2 Mass (g)	Oil yield (g/12g of wheat bran)
Effect of pressure				
1	50	10	2811.9	0.722
2	50	20	2811.9	1.681
3	50	30	2811.9	2.117
Effect of CO_2 mass				
4	40	30	1206.4	0.824
5	40	30	2009.2	1.174
6	40	30	2811.9	1.272
Effect of temperature				
7	40	30	2811.9	1.272
8	50	30	2811.9	2.117
9	60	30	2811.9	2.924

4.1.10 Comparison of Wheat Bran Oil Yields between the Result from Experiment and from Second Order Polynomial model

The results of oil yield from the experiment and from second order polynomial model were compared here at different three main variables on SC-CO_2 extraction. From the result in Table 6 shows that the second order polynomial model was sufficient to be used and best fit of the data.

Table 4.6: Comparison of wheat bran oil yield between the result from experiment and from second order polynomial model

Run	Temperature (^oC)	Pressure (MPa)	CO_2 Mass (g)	Oil yield (g/12g of wheat bran)	
				Experiment	Model equation
1	40	10	1825	0.48	0.59
2	50	10	400	0.14	0.05
3	50	10	3250	0.70	0.60
4	60	10	1825	0.74	0.82
5	40	20	3250	1.00	1.00

6	40	20	400	0.45	0.43
7	50	20	1825	1.53	1.53
8	50	20	1825	1.53	1.53
9	50	20	1825	1.53	1.53
10	60	20	3250	2.20	2.22
11	60	20	400	0.80	0.81
12	40	30	1825	1.20	1.12
13	50	30	3250	2.04	2.13
14	50	30	400	0.60	0.70
15	60	30	1825	2.58	2.47

4.1.11 Validation of the Response Surface Modeling for Wheat Bran Oil Yield

Method validation is used to confirm that the second order polynomial model from response surface modeling employed for wheat bran oil extraction is suitable. Model from this software can be used to find the oil yield at different operating conditions within the specified range. The results of oil yield estimated by using this model must give the same or similar results to the experiment. Table 7 shows the validation of the response surface modeling at various parameter testing points and it gives the satisfactory results.

Table 4.7: Validation of response surface modeling for wheat bran oil

<table>
<tr><td colspan="2">Parameter</td><td>Range</td><td colspan="4">Value in the model</td></tr>
<tr><td colspan="2" rowspan="3">M (g)</td><td>Max</td><td colspan="4">3250.00</td></tr>
<tr><td>Medium</td><td colspan="4">1825.00</td></tr>
<tr><td>Min</td><td colspan="4">400.00</td></tr>
<tr><td colspan="2" rowspan="3">T (^oC)</td><td>Max</td><td colspan="4">60.00</td></tr>
<tr><td>Medium</td><td colspan="4">50.00</td></tr>
<tr><td>Min</td><td colspan="4">40.00</td></tr>
<tr><td colspan="2" rowspan="3">P (MPa)</td><td>Max</td><td colspan="4">30.00</td></tr>
<tr><td>Medium</td><td colspan="4">20.00</td></tr>
<tr><td>Min</td><td colspan="4">10.00</td></tr>
<tr><td colspan="2">R^2 (%)</td><td></td><td colspan="4">98.97</td></tr>
<tr><td colspan="2">Max yield
(g/12g of wheat bran)</td><td>2.69</td><td colspan="4">2.97</td></tr>
<tr><td colspan="2">Max yield error (%)</td><td colspan="5">10.36</td></tr>
<tr><td>Pressure (MPa)</td><td>Temperature (^oC)</td><td>CO_2 mass (g)</td><td>Testing point</td><td>Exp. yield (g/12g of wheat bran)</td><td>Estimated yield (g/12g of wheat bran)</td><td>Yield error (%)</td></tr>
<tr><td rowspan="2">10</td><td>60</td><td>1206.4</td><td>1</td><td>0.634</td><td>0.538</td><td>15.26</td></tr>
<tr><td>50</td><td>1206.4</td><td>2</td><td>0.449</td><td>0.530</td><td>18.06</td></tr>
</table>

	40	1206.4	3	0.319	0.485	52.10
	60	2009.2	4	0.753	0.880	16.79
	50	2009.2	5	0.609	0.752	23.47
	40	2009.2	6	0.515	0.588	14.03
	60	2811.9	7	0.825	0.969	17.42
	50	2811.9	8	0.701	0.722	3.03
	40	2811.9	9	0.640	0.437	31.64
15	60	1206.4	10	0.999	1.098	9.89
	50	1206.4	11	0.904	0.950	5.08
	40	1206.4	12	0.767	0.765	0.21
	60	2009.2	13	1.198	1.503	25.48
	50	2009.2	14	1.094	1.235	12.95
	40	2009.2	15	0.971	0.930	4.21
	60	2811.9	16	1.313	1.654	25.96
	50	2811.9	17	1.136	1.267	11.54
	40	2811.9	18	1.044	0.842	19.33
20	60	1206.4	19	1.903	1.528	19.69
	50	1206.4	20	1.306	1.241	5.00
	40	1206.4	21	0.859	0.915	6.52
	60	2009.2	22	2.126	1.995	6.19
	50	2009.2	23	1.583	1.587	0.29
	40	2009.2	24	0.961	1.142	18.83
	60	2811.9	25	2.233	2.208	1.13
	50	2811.9	26	1.772	1.681	5.14
	40	2811.9	27	1.005	1.116	11.06
25	60	1206.4	28	2.163	1.828	15.49
	50	1206.4	29	1.302	1.400	7.50
	40	1206.4	30	0.965	0.935	3.15
	60	2009.2	31	2.459	2.356	4.20
	50	2009.2	32	1.785	1.809	1.33
	40	2009.2	33	1.023	1.224	19.57
	60	2811.9	34	2.500	2.631	5.25
	50	2811.9	35	1.866	1.964	5.24
	40	2811.9	36	1.035	1.259	21.69
30	60	1206.4	37	2.298	1.997	13.10
	50	1206.4	38	1.440	1.429	0.75
	40	1206.4	39	1.100	0.824	25.12
	60	2009.2	40	2.568	2.587	0.73
	50	2009.2	41	1.831	1.899	3.73
	40	2009.2	42	1.163	1.174	0.97
	60	2811.9	43	2.643	2.924	10.63
	50	2811.9	44	2.004	2.117	5.64
	40	2811.9	45	1.198	1.272	6.22

4.2 RSM FOR $SC\text{-}CO_2$ EXTRACTION OF RICE BRAN OIL

For this experiment, only two parameters have been tested which are temperature and pressure and the results from the software display as follows:

4.2.1 Experimental Design for Rice Bran Oil Yield

In this case, 3-level factorial design has been created which will study the effects of 2 factors in 9 runs. The order of the experiments has been fully randomized. The ranges of parameters are as follows:

Factors	Low	High	Units	Continuous	Responses	Units
T	45.0	85.0	^oC	Yes	Oil Yield	kg/kg of rice bran
P	20.0	35.0	MPa	Yes		

After entering the data and range of parameters into the software (refer to steps in methodology), the parameters would be placed randomly in a different row. In the oil yield column, the results of oil yield were collected first at specified temperature and pressure. The values based on experiment would be filled manually. Table 1 shows the experimental design and results derived from each run.

Table 4.8: Experimental design for rice bran oil yield

Run	Temperature (^oC)	Pressure (MPa)	Oil yield (kg/kg of rice bran)
1	45.00	35.00	0.23
2	65.00	27.50	0.13
3	45.00	27.50	0.17
4	85.00	20.00	0.02
5	65.00	20.00	0.05
6	45.00	20.00	0.08
7	85.00	35.00	0.18
8	65.00	35.00	0.21
9	85.00	27.50	0.09

4.2.2 Pareto Chart of the Standardized Effect for Rice Bran Oil Yield

In the Pareto chart in Fig. 7 shows the statistically significant factors. In the interpretation of this chart, it should be noted that the lengths of the bar are proportional to the absolute value of the estimated effects. A bar crossing this vertical line corresponds to a factor or a combination of factors that have a significant influence on response. The maximal effect was presented in the upper part and then progressed down to the minimal effect. Result directly shows that the most important factors or main factors determining oil yield were pressure (P) which giving positive impact, meaning that as the pressure is increased the oil yield is also increased and temperature (T) on the other hand, giving the negative impact, meaning that as the temperature is increased the oil yield is decreased. This chart demonstrates that only pressure and temperature factors were significant at 95% confidence level. While the interaction of AB, BB and AA were not significant.

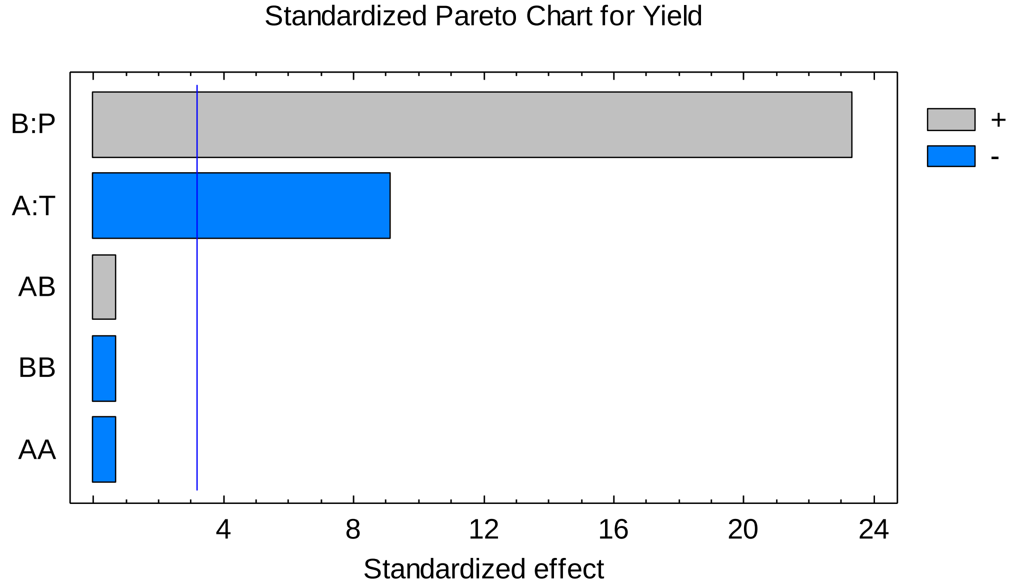


Figure 4.7: Pareto chart of the standardized effect for rice bran oil yield

4.2.3 ANOVA Table for Rice Bran Oil Yield

Table 4.9: Analysis of variance of the regression coefficients of the fitted quadratic equation for rice bran oil yield

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:T	0.00562367	1	0.00562367	83.20	0.0028*
B:P	0.0368776	1	0.0368776	545.59	0.0002*
AA	0.0000319733	1	0.0000319733	0.47	0.5410
AB	0.000034451	1	0.000034451	0.51	0.5268
BB	0.0000337486	1	0.0000337486	0.50	0.5307
Total error	0.000202775	3	0.0000675916		
Total (corr.)	0.0428043	8			
Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value

A:T	0.00562367	1	0.00562367	83.20	0.0028*
B:P	0.0368776	1	0.0368776	545.59	0.0002*
AA	0.0000319733	1	0.0000319733	0.47	0.5410
AB	0.000034451	1	0.000034451	0.51	0.5268
BB	0.0000337486	1	0.0000337486	0.50	0.5307
Total error	0.000202775	3	0.0000675916		
Total (corr.)	0.0428043	8			

R-squared (adjusted for d.f.) = 98.7367 percent

Standard Error of Est. = 0.00822141

Mean absolute error = 0.00394351

Durbin-Watson statistic = 2.81956 (P = 0.9400)

Lag 1 residual autocorrelation = -0.464617

Star (*) numbers indicate significant factors as identified by the analysis of variance (ANOVA) at the 95% confidence level.

The ANOVA table partitions the variability in oil yield into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level. The 2 significant effects correspond to the Pareto chart.

How well the estimated model fits the data can be measured by the value of R^2. And the importance of R^2 value has been explained earlier. From the result, R^2 is 99.5263 % showing the good estimation of the regression equation fits the sample data.

4.2.4 Main Effect Plot for Rice Bran Oil Yield

The lines indicate the estimated change in oil yield as each factor is moved from its low level to its high level, with all other factors held constant at a value midway between their lows and their highs. Note that the two factors with significant main effects have a bigger impact on the response than the others.

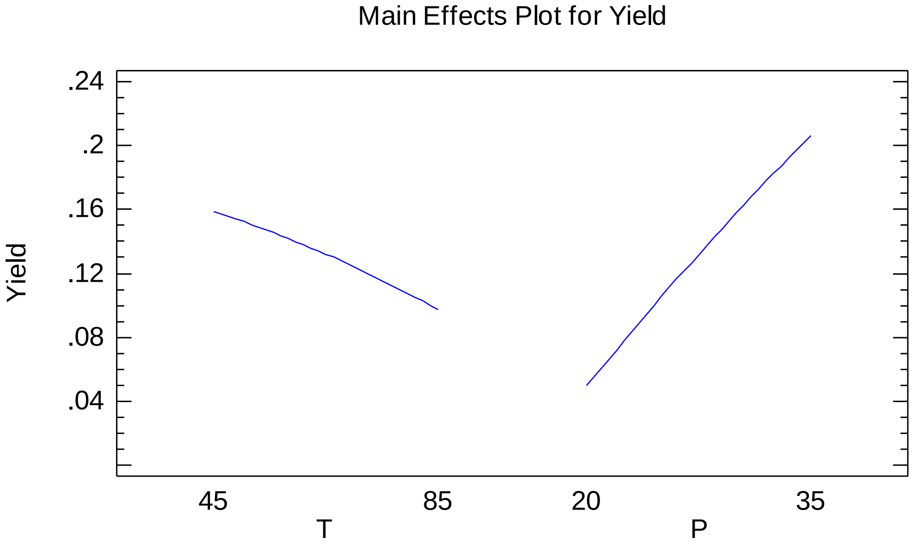


Figure 4.8: Main effects plot for rice bran oil yield

4.2.5 Interaction Plot for Rice Bran Oil Yield

This interaction plot was not showing the lines for AB, BB, and AA interactions. It confirms that the interactions were not significance as stated earlier. Only pressure and temperature factors present in this plot. As the pressure constant the response oil yield increases when the line moves from the high level to low level of temperature.

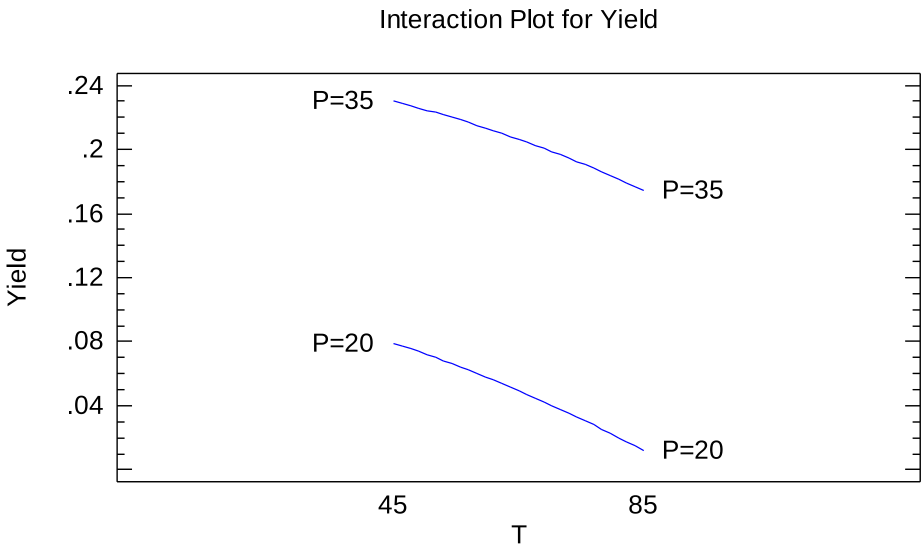


Figure 4.9: Interaction plot for rice bran oil yield

4.2.6 Normal Probability Plot for Rice Bran Oil Yield

If the standardized effects plot approximately along a straight line, then the normality assumption is satisfied. In this study, the standardized effects can be judged as normally distributed; even though some points place far along a straight line but it is acceptable, therefore normality assumptions for both of the responses are satisfied. The error term is the difference between the observed value y_i and the corresponding fitted value $y^{\wedge i}$, that is, $e_i = y_i - y^{\wedge i}$. As a result of this assumption, observations y_i are also normally and independently distributed. Therefore, the test for the significance of the regression can be applied to determine if the relationship between the dependent variable Y and independent variables P and T exists.

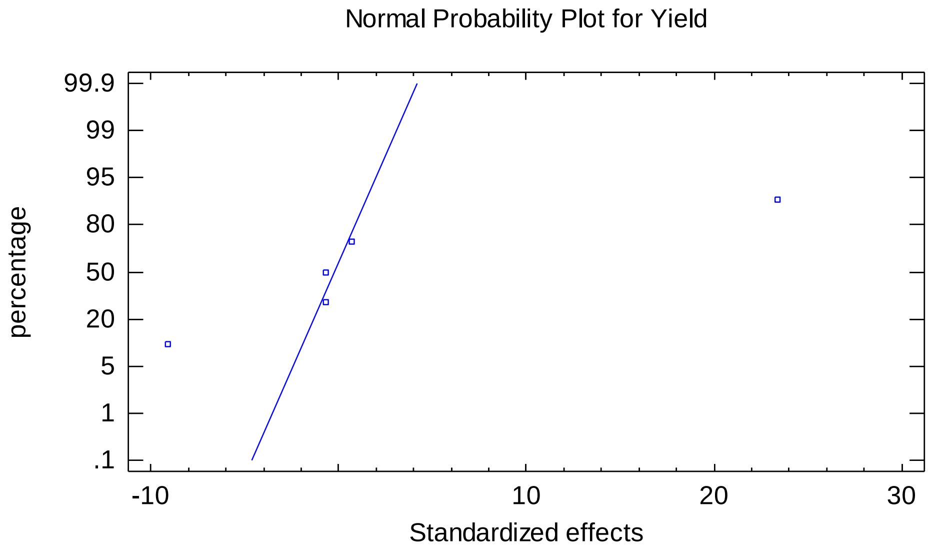


Figure 4.10: Normal probability plot for rice bran oil yield

4.2.7 Regression Equation for Rice Bran Oil Yield

The software computes the linear, quadratic, and interaction terms in the model. The analysis of variance indicates that there are no significant interactions between the factors. The small p-values for square terms also point out that their contribution is not significant to the model. Small p-values suggest there is curvature in the response surface. Moreover, the main effects can be referred to as significant at an individual 0.05 significant level as mentioned earlier. The quadratic terms, A^2, B^2 and interaction terms AB, not significantly contribute to the response model at a = 0.05. As a result, the final model for the response variable oil yield (Y) is concluded as follows:

Y = -0.118393 - 0.000769329*T + 0.0131979*P - 0.00000999583*T^2 + 0.000019565*T*P - 0.0000730281*P^2

Where Y is the oil yield, T is the temperature and P is the pressure.

The regression coefficients of the model are represented in the Table 9.

Table 4.10: Regression coefficients of predicted second order polynomial model for the response variable for rice bran oil

Coefficient	Estimate
constant	-0.118393
A:T	-0.000769329
B:P	0.0131979
AA	-0.00000999583
AB	0.000019565
BB	-0.0000730281

Since the response surface is explained by the second-order model, it is necessary to analyze the optimum setting. The graphical visualization is very helpful in understanding the second-order response surface. Specifically, contour plots can help characterize the shape of the surface and locate the optimum response approximately. The contour plot of oil yields are shown in Fig, 11-12.

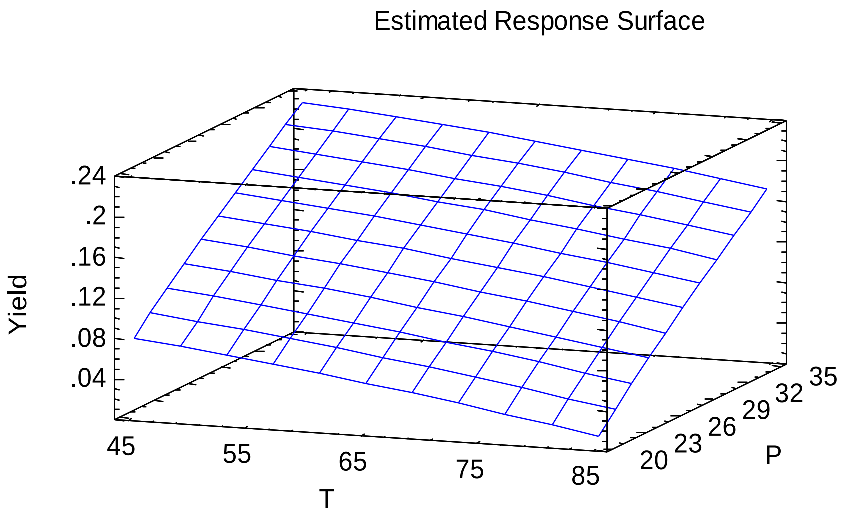


Figure 4.11: 3D contour plots of rice bran oil yield

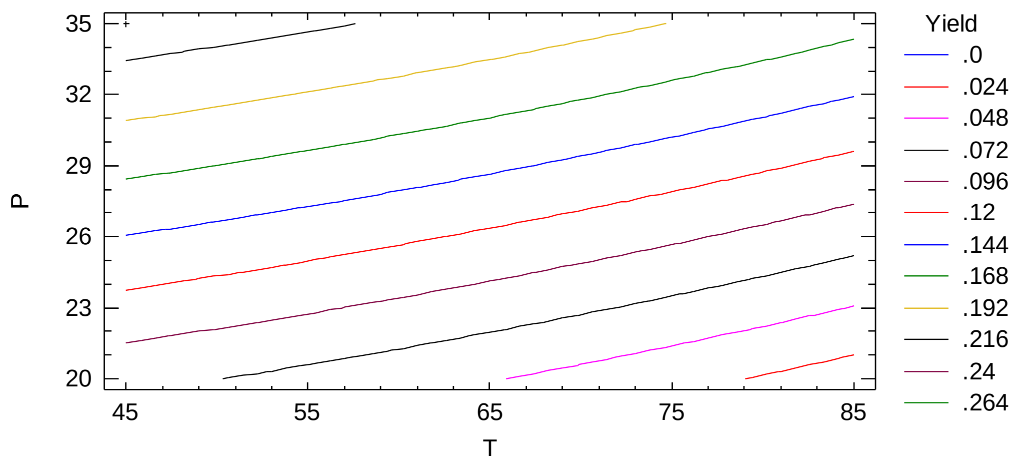


Figure 4.12: Contour plots of rice bran oil yield

4.2.8 Optimize Response for Rice Bran Oil Yield

This table shows the combination of factor levels which maximizes oil yield over the indicated region. The optimum conditions of the oil extraction process indicated by the software are summarized in the table below:

Optimum value = 0.230027

Table 4.11: Optimum conditions for rice bran oil yield

Factor	Low	High	Optimum	Unit
T	45.0	85.0	45.0	^{o}C
P	20.0	35.0	35.0	MPa

4.2.9 Main Effect of Pressure and Temperature to the Rice Bran Oil Yield

At constant temperature, the amount of oil extracted from rice bran was increased with increasing pressure. Same result as the extraction of wheat bran oil. This happened due to the increase in solvent density and hence the solvating power of SC-CO_2. The increased solvating power and the strength of intermolecular physical interactions considered as belonging to the effect of pressure.

At a constant pressure, the amount of oil extracted was decreased with increasing temperature. The temperature increases from 45 to 85 ^{o}C, result in the decrease of the solvent density, due to the decrease of the solvent density, whose effect seems to have dominated over the increase of the solute vapor pressure. Perakis et al. [39]

reported the similar effect of temperature on supercritical fluid extraction of black pepper oil.

Table 11 below shows the main effect of pressure and temperature to the oil yield at some conditions within the experimental range.

Table 4.12: Main effect of pressure and temperature to the oil yield

No.	Temperature (^oC)	Pressure (MPa)	Oil yield (kg/kg of rice bran)
Effect of pressure			
1	45.00	20.00	0.08
2	45.00	27.50	0.16
3	45.00	35.00	0.23
Effect of temperature			
7	45.00	35.00	0.23
8	65.00	35.00	0.21
9	85.00	35.00	0.17

4.2.10 Comparison of Rice Bran Oil Yields between the Result from Experiment and from Second Order Polynomial Model

The results of oil yield from the experiment and from second order polynomial model were compared here at different two main variables on SC-CO_2 extraction. From the result in Table 12 shows that the second order polynomial model was sufficient to be used and best fit of the data.

Table 4.13: Comparison of rice bran oil yield between the result from experiment and from second order polynomial model

Run	Temperature (^oC)	Pressure (MPa)	Oil yield (kg/kg of rice bran)	
			Experiment	Model equation
1	45.00	35.00	0.23	0.23
2	65.00	27.50	0.13	0.13
3	45.00	27.50	0.17	0.16
4	85.00	20.00	0.02	0.01
5	65.00	20.00	0.05	0.05
6	45.00	20.00	0.08	0.08
7	85.00	35.00	0.18	0.17
8	65.00	35.00	0.21	0.21
9	85.00	27.50	0.09	0.10

4.2.11 Validation of the Response Surface Modeling for Rice Bran Oil Yield

Method validation is used to confirm that the second order polynomial model from response surface modeling employed for rice bran oil extraction is suitable. Model from this software can be used to find the oil yield at different operating conditions within the specified range. The results of oil yield estimated by using this model must give the same or similar results to the experiment. Table 13 shows the validation of the response surface modeling at various parameter testing points and it gives the satisfactory results.

Table 4.14: Validation of response surface modeling for rice bran oil

Parameter		Range	Value in the model		
T (oC)		Max	85.00		
		Medium	65.00		
		Min	45.00		
P (MPa)		Max	35.00		
		Medium	27.50		
		Min	20.00		
R2 (%)			99.52		
Max yield (kg/kg of rice bran)		0.23	0.23		
Max yield error (%)		28.18			
Temperature (°C)	Pressure (MPa)	Testing point	Exp. yield (kg/kg of rice bran)	Estimated yield (g/12g of wheat bran)	Yield error (%)
45	20.0	1	0.076	0.079	4.47
	27.5	2	0.166	0.159	4.40
	30.0	3	0.195	0.183	6.17
	35.0	4	0.226	0.230	1.74
65	20.0	5	0.048	0.050	2.76
	27.5	6	0.134	0.132	1.17
	30.0	7	0.164	0.158	4.02
	35.0	8	0.206	0.206	0.11
85	20.0	9	0.017	0.012	28.18
	27.5	10	0.089	0.097	10.02
	30.0	11	0.111	0.124	11.76
	35.0	12	0.179	0.175	2.33

CHAPTER 5

PROCESS ECONOMICS AND COST ESTIMATION

5.1 Introduction

Process economics and cost estimation is carried out with a purpose to decide whether it is economically justified to invest in this supercritical carbon dioxide extraction of rice bran oil process. In this particular chapter, the economics of carrying out of the process will be discussed; the capital costs, operating costs and economic potential will be estimated.

The economic evaluation of a process is important to determine the profitability of a process in generating profit. To evaluate the profitability of the plant, economic analysis was done to determine the total equipment cost, fixed capital cost, working capital and operating cost. In order to evaluate design options and carry out process optimization, we need to consider what happens to the revenue from product sales after the process has been commissioned. The sales revenue must pay for both fixed costs that are independent of the rate of production and variable costs, which are depend on the rate of production. Taxes are deducted to give the net profit.

However for preliminary process design, the first estimate of the Economic Potential, EP is calculated. EP is just a rough estimation in which the calculation does not take into account other factors such as depreciation, plant lifetime and so on. Further analysis of the profitability of the project using the price as in the table below is conducted.

In order to ease calculations, some relevant guidelines and assumptions are made:

- Currency conversion rate : 1 Euro = 3.9904 Ringgit Malaysia
- 2,500 ton of rice bran oil is produced per year in 345 annual working days.
- Ratio of **Raw material : Product (rice bran oil)** = **4.5 : 1** [the practical value of ratio = 4.5 has been assumed , 22% oil produced from the total rice bran]

For this supercritical carbon dioxide extraction of rice bran oil process, the detail of assumptions and the targets are listed below:

- Rice bran oil production = 2,500 ton per year
- Raw Material prediction (Rice bran) = 11,250 ton per year

[Refer to scale of ratio Raw material : RBO production = 4.5 : 1]

- Price for rice bran oil in South East Asia market = RM 10,000 per metric ton

The list given above is current study about rice bran oil production in Malaysia. Those targets that we assume can be achieved once complete calculations have been done below for the Economic Potential (EP) of the plant. This EP is predicted until 10 years forward but a few study need to be done in order to get a better calculation.

5.2 Capital cost or Capital Expenditure (CAPEX)

5.2.1 Equipment cost

The total purchase cost of the major equipment is summarized in Table 5.1

Table 5.1: Estimated cost for equipment

Equipment Unit	Cost,€ (Euro)	RM
Equipment cost	4,440,912.003	17,721,015.26
Total	4,440,912.003	17,721,015.26

The equipment cost take into account of escalation based on the Chemical Plant Cost Index (CEPCI) (average over year).

Cost index, year 2005: 468.2 Price: € 3,550,000

Cost index, year 2011: 585.7 Price: € 3,550,000*585.7/468.2 = € 4,440,912.003

5.2.2 Working Capital

Working capital is the additional investment needed, over and above the fixed capital, to start the plant up and operate it to the point when income is earned. It includes the cost of start-up, raw material and intermediate in process, and others. To determine the working capital for supercritical carbon dioxide extraction process, 5% of fixed capital to cover cost of initial raw material charge is allowed (Coulson and Richardson, 1996).

Working capital, WC = RM 17,721,015.26 x 0.05 = RM 886,050.763

Start-up cost, SC = RM 17,721,015.26 x 0.08 = RM 1,417,681.221

The total investment required for the project

= fixed capital investment + working capital + start-up cost

= RM 17,721,015.26 + RM 886,050.763 + RM 1,417,681.221

= RM 20,024,747.24

Table 5.2: Overall Capital Cost Investment

Fix Capital	**Working Capital + Startup Cost**	**Capital Investment**
Equipment		**Fixed + Working Capital + Startup Cost**
RM 17,721,015.26	RM 886,050.763 + RM 1,417,681.221	RM 20,024,747.24 **(*approximately*)**

5.3 Annual Operating Cost

5.3.1 Manufacturing Cost

Cover of variable operating costs including raw materials, miscellaneous operating materials, utilities, shipping and packaging cost.

1. Raw materials
   a. Rice bran price = 0.47 RM/kg
      Rice bran used for production = 11,250 ton/year
      Cost of rice bran used annually = 5,287,500 RM/year

<u>Table below shows the variable operating cost of the plant:</u>

Table 5.3: Summary of Manufacturing Cost

Manufacturing expenses	RM/year
Raw material (rice bran)	5,287,500.00
Solvent CO_2	13,000,000.00
Steam	80,000.00
Cooling Water	80,000.00
Electricity	300,000.00
Miscellaneous	50,000.00

Total variable cost	18,797,500.00

Table 5.4: Direct production cost

Direct production cost	RM/year
Maintenance, take as 2% of fixed capital	354,420.31
Operating labour	200,000.00
Insurance, 0.4% of fixed capital	70,884.06
Local taxes, 1% of fixed capital	177,210.15
Operating Suppliers, 10% maintenance & repair	127,499.43
Direct Supervision & clerical labour , 10% operating labour	20,000.00
Total Expenses, raw material + utilities + maintenance + supply + labour+ supervision + lab charge	19,747,513.95

Table 5.5: Revenue generated

Revenue generated, product	RM/year
Rice bran oil	25,000,000
Total	25,000,000

Table 5.6: Total Cost of the entire project

Total Cost of Entire Project	RM/year
Total revenue generated	25,000,000.00
Total Annual Operating Cost (Total variable cost + Total Direct Production cost)	19,747,513.95
Profit per year	13,137,486.05

The forecast income from the sales of rice bran oil will be as below:

Income : production rate x rice bran oil price

: 2,500 ton/year x RM 10,000/ton = RM 25,000,000

CHAPTER 6

CONCLUSION AND RECOMMENDATION

The results from this work showed that the second-order polynomial from response surface modeling employed for wheat bran oil extraction is applied to describe and predict the response variable. From the statistical analysis tested, the operating parameters, pressure, temperature and CO_2 mass have significant impact on extracted oil yield. As increasing the pressure, temperature and CO_2 mass the oil yield was increased, the reasons were related to the solvent density and the solute vapor pressure. The optimum extraction condition predicted within the experimental ranges based on the proposed model would be at temperature of 60 ^{o}C, pressure of 29.39 MPa and CO_2 mass of 3250 g. Under such conditions, the oil yield was 2.97 g/12g of wheat bran. For rice bran oil the optimal predicted within the experimental ranges based on the proposed model would be at temperature of 45 ^{o}C and pressure of 35 MPa and the oil yield was 0.23 kg/kg of rice bran. The extraction process were not being optimized yet because the optimal operating conditions were predicted at the maximum value of each parameter. However, the suggestion is to further conduct additional experiments in a wider range of parameters in order to get the best result and more suitable optimum value of parameters. Lastly, the study of the economic feasibility for the supercritical carbon dioxide extraction of rice bran oil plant is economically justified.

Recommendations:

1. Further conduct the additional experiment at a wider range of parameters to find the real optimum operating conditions.

2. Suggestion to do the simulations of SC-CO_2 extraction process in order to get the accurate value of the utility used and cost estimation of the total SC-CO_2 plant.

3. For economic analysis, should also calculate the basic investment rules such as net present value and payback period.

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