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RESPONSE SURFACE OPTIMIZATION CONDITION OF EXTRACTION OF RUBBER SEED OIL BY LIQUEFIED DIMETHYL ETHER

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ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาหลักสูตรปริญญาวิศวกรรมศาสตรบัณฑิต

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คณะวิศวกรรมศาสตร์ มหาวิทยาลัยนเรศวร อนุมัติให้ปริญญานิพนธ์ฉบับนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตรบัณฑิต สาขาวิศวกรรมเคมี

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บทคัดย่อ

การสกัดน้ำมันจากเมล็ดยางพาราสำหรับผลิตภัณฑ์ไบโอดีเซลด้วยสารทำละลายไดเมทิลอีเทอร์เหลว มีตัวแปรที่ส่งผลต่อร้อยละผลได้ของการสกัดน้ำมันคือ อัตราส่วนระหว่างตัวทำละลายกับตัวถูกละลาย อุณหภูมิและความชื้น การหาสภาวะที่เหมาะสมสำหรับการสกัดมี 2 วิธีการโดยวิธีการแรกคือการศึกษาผลที่เกิดจากปัจจัยเดียวพบว่าที่ความชื้นร้อนละ 40 โดยมวล อัตราส่วนระหว่างตัวทำละลายกับตัวถูกละลาย 6.73 ต่อ 1 และอุณหภูมิ 31 องศาเซลเซียส ได้ร้อยละผลได้สูงที่สุดที่ร้อยละ 48.14 จากนั้นนำสภาวะที่เหมาะสมที่สุดมาเปรียบเทียบกับวิธีที่สอง โดยวิธีที่สองคือการหาสภาวะที่เหมาะสมในการสกัดโดยวิธีการพื้นผิวตอบสนองพบว่าที่ความชื้นร้อยละ 56.43 อัตราส่วนระหว่างตัวทำละลายกับตัวถูกละลาย 6.66 ต่อ 1 และอุณหภูมิ 33.33 องศาเซลเซียส ซึ่งได้ร้อยละผลได้สูงที่สุดที่ร้อยละ 41.48

Title	RESPONSE SURFACE OPTIMIZATION CONDITION OF EXTRACTION OF RUBBER SEED OIL BY LIQUEFIED DIMETHYL ETHER		
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Abstract

In this study, the extraction of rubber seed oil for biodiesel production by liquefied dimethyl ether was investigated. The effect of extraction parameter including solvent to sample ratio, temperature and moisture content of rubber seed on the oil yield was firstly determined using single parameter study. The suitable conditions were found to be 40% moisture content, 6.73:1 solvent to solid ratio and 31 °C. The maximum yield of 48.14% can be obtained. The optimum extraction conditions were then compared to the optimum condition determined by response surface methodology (RSM). The optimum condition determined by RSM were at 56.43% moisture content, 6.66:1 solvent to solid ratio and 33.3 °C. By this condition, the maximum yield of 41.48% can be obtained.

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Apichard Tunwirat
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CHAPTER I

INTRODUCTION

Introduction

The green energy such as wind, solar and biofuel has been developed for the last decade alternative to the fossil fuel. Biodiesel is one of alternative fuel which is considered to have environmental benefits such as decrease in acid rain and emissions of CO_2, SO_x and unburned hydrocarbons during the combustion process; easy biodegradability; less toxicity; and safety in storage and handling [1]. Normally, biodiesel can be produced from various natural sources such as Neem, Milk weed, Ethiopian mustard, Desert date, Annona Squamosa, Sapindus, Koroch, Jatropha, Garciniaindica, and rubber seed [2]. Among of them, rubber seed containing approximately 40 to 60%wt of oil is one of the interesting source which is non-commercial use [3]. Rubber seed is produced by the rubber tree which is grown widely in Asian and South-East Asian countries including Thailand, Indonesia, Malaysia, India, and China. The tree requires heavy rainfall and produces seeds weighing from 2 to 4 g with high moisture content.

The various methods of rubber seed oil extraction have been studied by several researchers. Mechanical extraction, solvent extraction and supercritical carbon dioxide ($SC\text{-}CO_2$) extraction are previously reported [4-5]. Mechanical extraction is the simplest process. However, it gives lowest oil yield. Compared to mechanical process, solvent extraction provides higher extraction oil yield. However, it is energy consumption process caused by the solvent removal step which is normally evaporation. Although provided with the low temperature operation and the ease of solvent separation, simply achieved by depressurization of the extraction system, $SC\text{-}CO_2$ has some disadvantages, such as high operating pressures, which leads to high equipment and operating costs. In addition to those concerns, the drying process of rubber seed samples which is energy consumption step is required prior to extraction processes.

Alternatively, Liquefied Dimethyl ether (DME), the non-toxic solvent, is reported to have potential for the extraction of fat, oil, protein and active compounds [6]. Because of its low boiling point (-24.8 °C), it is therefore easily separated from final product by de-pressurizing. Liquefied DME is partially water soluble which shows the possibility for wet extraction. The process using liquefied DME as extractant is therefore attractive since it requires lower energy and time consumption due to solvent separation and drying of samples can be omitted. However, it has never been applied to extraction of rubber seed oil and the suitable conditions for rubber seed oil extraction using liquefied DME have never been reported.

To determine the suitable conditions, design of experiment (DOE) is normally employed for this purpose. DOE can reduce number of experiment which leads to the less chemical and time consumptions. Response surface methodology (RSM) is one of the DOE method for optimization, finding the best set of factor levels to achieve some target. Central Composite Designs (CCD) and Box-Behnken Designs are two major Response Surface Designs which are different in the specified boundary. However, the effect of parameter cannot be determined by RSM since it focuses on the optimization. The single parameter or single factor study which the experiment is carried by fixing other factors but varying one factor is usually done in order to study the effect of interested parameter. In the research work, both RSM and single factor study therefore must be determined.

In the first part of this work, the extraction of rubber seed oil using liquefied DME is therefore studied. The single factor study to determine the effect of moisture content, solid to solvent weight ratio and extraction temperature on rubber seed oil yield are investigated. The DOE using RSM with Central Composite Designs (CCD) was then studied in the second part of this work for optimization of extraction condition.

Objectives

1.2.1. To study the effect of extraction parameters including, solvent to sample ratio, temperature and moisture content of rubber seed on the oil yield.

1.2.2. To investigate the optimum condition of rubber seed oil extraction using liquefied DME as extractant by response surface analysis.

Scopes of research

1.3.1 Determine the effect of moisture content of rubber seed on extracted rubber oil yield at 5.4, 20, 40, 60, 74.6%wt

1.3.2 Determine the effect of solvent to sample mass ratio on extracted rubber oil yield at 1.4:1, 2.5:1, 4:1, 5.5:1, 6.6:1 g/g.

1.3.3 Determine the effect of temperature on extracted rubber oil yield at 31-49 °C

Time table

Table 1.1 Time table

procedure	1st Semester															
	September				October				November				December			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Learn educational information and research - based knowledge	→	→														
Planning experiment	→	→														
Rubber seed preparation for experiment			→	→												
Do the experiment single parameter condition					→	→	→	→	→	→	→					
Compile all of the results											→	→				
Analysis results of experiment								→			→					
Making report and presentation											→	→	→	→	→	

procedure	2st Semester															
	January				February				March				April			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Planning experiment	→															
Rubber seed preparation for experiment	→	→														
Do the experiment DOE condition			→	→	→	→	→	→	→	→						
Compile all of the results							→		→		→					
Analys is results of experiment											→	→				
Making report and presentation												→	→	→	→	→

CHAPTER II

BACKGROUND & LITERATURE REVIEWS

Rubber seed

The Hevea brasiliensis is known as Rubber tree, belongs to the family Euphorbiaceae. The rubber tree is originated from the Amazon rainforest (Brazil). The Hevea brasiliensis tree is the primary source of natural rubber and it produces 99% of world's natural rubber.It is grown mainly in Indonesia, Malaysia, Liberia, India, Srilanka, Sarawak, and Thailand. Natural rubber tree producers in the world are Thailand (35%), Indonesia (23%), Malaysia (12%), India (9%), and China (7%) [3]. Growing up to 3-4 meter height. The tree requires heavy rainfall and produces seeds (show in Figure 2.1) weighing from 2 to 4 gram. Useless any major industrial applications [7-9]. On an average, a strong tree can give about 500 grams of useful seeds during a normal year and this run into an estimated availability of 150 kg of seeds per hectare. The seed contains an oily endosperm. Generally 37% by weight of the seed is shell and the rest is kernel. Rubber seed oil is an inedible vegetable oil, which contain 50 - 60 %wt oil and nucleus contain 40 - 50 %wt of sable color oil. The oil is high in unsaturated fatty acid such as linoleic (39.6 %wt), oleic (24.6 %wt), and linolenic (16.3 %wt) acids. Other fatty acids found in rubber seed oil include saturated fatty acid such as palmitic (10.2 wt%) and stearic (8.7%wt) acids [4-11].

Figure 2.1 Rubber seed

Rubber seed oil

Since rubber seed have high amount of oil, rubber seed extraction is widely interested. Classified of the extracted rubber seed oil is non-edible oil so its application is to use as fuel but crude rubber seed oil has high viscosity and it is not suitable to use as diesel. It was reacted with alcohol to improve its properties for biodiesel production by esterification of transesterification reaction. The properties of rubber seed oil compared with petroleum diesel are shown in the Table 2.1

Table 2.1 The properties of rubber seed oil compared with petroleum

Properties	Rubber seed oil	Diesel
Specific gravity	0.91	0.835
Viscosity (mm^2/s)	76.4	7.50
Flash point (°C)	198	50
Calorific value (kJ/kg)	37,500	42,250
Saponification value	206	-
Iodine value	135.3	38.3
Acid value	53.0	0.062

Aigbodion AI and Pillai CKS, 2000 [12]

The fatty acid composition and the important properties of rubber seed oil in comparison with other oils is given in Table 2.2 [8-27]. It have 18.9% saturation comprising of palmitic and stearic acids. And 80.5% of un-saturation comprising mainly of oleic, linoleic and linolenic acids. Saturation fatty acid methyl esters increase the cloud point, cetane number and improve stability but more poly un-saturates reduce the cloud point and cetane number and stability. The type and percentage of fatty acids contained in vegetable oil. Theirs depends on the plant species and on the growth conditions of the plant. Though vegetable oils are very low volatility in nature, it quickly produces volatile.

Property Rubber seed oil Diesel

When flammable compounds is heating. The free fatty acid content of mixed rubber seed oil was about 17%, i.e. acid value of 34. The yield of esterification process decreases exceedingly, If FFA value is greater than 2%. Canakci and Van Gerpan [28-29] found that transesterification would not occur if FFA content in the oil were about 3%. It has been found, the alkaline catalyzed transesterification process is not appropriate to produce esters from mixed oils. In order to reduce the acid value (i.e. for reducing FFA), the oil is to be refined.

Table 2.2 Properties of rubber seed oil in comparison with other vegetable oils.

Property	Rubber seed oil	Sunflower oil	Rapeseed oil	Cotton seed oil	Soybean oil
Fatty acid composition (%)					
(I) Palmitic acid $C_{16:0}$	10.2	6.8	3.49	11.67	11.75
(ii) Stearic acid $C_{18:0}$	8.7	3.26	0.85	0.89	3.15
(iii) Oleic acid $C_{18:1}$	24.6	16.93	64.4	13.27	23.26
(iv) Linoleic acid $C_{18:2}$	39.6	73.73	22.3	57.51	55.53
(v) Linolenic acid $C_{18:3}$	16.3	0	8.23	0	6.31
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity (mm^2/s) at 40 °C	66.2	58	39.5	50	65
Flash point (°C)	198	220	280	210	230
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value	34	0.15	1.14	0.11	0.2

Oil extraction techniques

The three main methods: (i) Solvent extraction, (ii) Soxhlet extraction and (iii) Dimethyl ether extraction are reviewed in this section. The methods have been identified for the extraction of the oil. For commercial oil extraction, solvent extraction methods is the most commonly used. For chemical extraction only kernels and seeds are used as feed. In addition, supercritical fluids extraction also shows the possibility for oil extraction but the operating cost and equipment cost are still high. It is therefore better for the high value compounds extraction.

Solvent extraction (Chemical Extraction)

Solvent extraction is the technique to removing one constituent from a solid with a liquid solvent. It also called leaching. There are many factors influencing the rate of extraction such as the type of liquid chosen, particle size, temperature and agitation of the solvent. The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low to circulate freely. The small particle size is preferable as it allows for a greater interfacial area between the solid and liquid. Temperature also affects the extraction rate. The solubility of the material will increase with the increasing temperature. Agitation of the solvent also affects, it increases the purl diffusion and therefore increases the transfer of material from the surface of the particles.

Soxhlet extraction

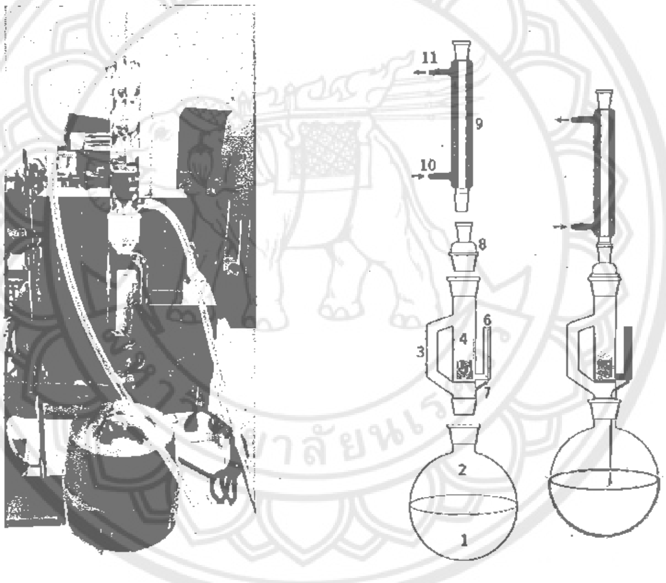
A Soxhlet extractor is a piece of laboratory apparatus. It was invented in 1879 by Franz von Soxhlet. It was originally designed for the extraction of a lipid from a solid material. In common a Soxhlet extraction is used when the desired compound has a limited solubility in a solvent, and the impurity is insoluble in that solvent. It allows for unmonitored and unmanaged operation while efficiently recycling a small amount of solvent to dissolve a larger amount of material.

The solvent is heated to reflux. The solvent vapor travels up a distillation arm, and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapor cools, and drips back down into the chamber housing the solid material. The chamber containing the solid material slowly fills with warm solvent. Some of the desired compound dissolves in the warm solvent.

When the Soxhlet chamber is almost full, the chamber is emptied by the siphon. The solvent is returned to the distillation flask. The thimble ensures that the rapid motion of the solvent does not transport any solid material to the still pot. This cycle may be allowed to repeat many times, over hours or days.

During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled.

After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound. The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded.



(a) (b)

Figure 2.2 (a) extraction in progress (b) A schematic of a Soxhlet extractor

Dimethyl ether extraction

Dimethyl ether is proposed for use as an extraction solvent for the separation of lipids from a range of dairy foods. At ambient pressure (1 atmosphere), dimethyl ether exists as a gas at temperatures above -24 °C. It is compressed, under high pressure, for use as a liquid extraction solvent in the course of food processing. The evidence assessed provided adequate assurance that the proposed use of dimethyl ether is technologically justified and has been demonstrated to be effective in achieving its stated purpose.

Animal and human data on inhalational exposure to dimethyl ether indicate a very low degree of toxicity. Adverse effects have been reported only at atmospheric concentrations greater than 20,000 parts per million (ppm) for acute exposure and 2,000 ppm for chronic exposure. Because of its low boiling point, dietary exposure to dimethyl ether will be negligible due to rapid evaporation of any residual dimethyl ether present in food following processing. A maximum permitted level (MPL) for dimethyl ether of 2 mg/kg is proposed which is equivalent to the MPL for the two ether extraction solvents that are currently permitted for use in food manufacture: diethyl ether and dibutyl ether. This MPL is considered to be appropriate. Dimethyl ether is considered to pose no public health and safety issues associated with its proposed use.

The overall conclusion of this risk and technical assessment is that the use of dimethyl ether as a processing aid is technologically justified and raises no public health and safety issues.

The following information regarding the identity and chemical and physical properties of the extraction solvent dimethyl ether has been taken from the Application and various references [31-35].

Chemical and physical properties

Dimethyl ether is a colourless gas at room temperature and pressure with a characteristic sweet ethereal smell. It is readily liquefied when compressed to produce a colourless liquid. It is highly flammable but is safe when handled appropriately. Relevant chemical and physical properties for dimethyl ether are provided in Table 2.3.

Table 2.3 Chemical and physical properties of dimethyl ether

Characteristic	Property
Boiling point	-24.8 °C at 1 atmosphere
Freezing point (melting point)	-141.5 °C at 1 atmosphere
Flash point	-41 °C
Density of liquid	0.665 g/cm^3 at 25 °C, when liquefied
Density of gas	1.92 g/L at 1 atmosphere and 25 °C
Octanol/water partition coefficient	Log KOW 0.10
Vapour pressure	4450 mmHg (593 kPa) at 25 °C
Solubility in water	7% by weight at 18 °C and 1 atmosphere

As can be seen from Table 2.3, dimethyl ether is partially soluble in water. It is also soluble in organic solvents that are relatively polar, such as methanol, ethanol, isopropanol, diethyl ether, chloroform, acetone, chlorinated hydrocarbons and toluene.

Dimethyl ether is quite stable under an inert atmosphere. It also does not form any reaction products when it is used to treat food.

The main purpose of using dimethyl ether as an extraction solvent is to extract lipids from both liquid and dry foods. The solvent has unique properties that make it an effective solvent for extracting both polar and non-polar lipids from food. One of these properties is that it can extract lipids without denaturing the residual proteins in the food, which for some uses is a very important and useful attribute. Dimethyl ether has unique extraction properties compared to other extraction solvents due to the following attributes:

- It is a gas at room temperature and pressure so residues can be easily removed from the final product.
- It is a powerful polar solvent when it is compressed to a liquid and used for extraction near its critical point (40-50 °C).
- It is inert, so there are no by-products produced during extraction.
- Because it is used at relatively mild extraction conditions of temperature and pressure its use does not damage the food it is extracting, which retain most, if

not all, of their natural properties such as appearance, flavour, solubility and bioactivity.

- Since it is partially soluble in water it is able to extract lipids from aqueous foods.

Design of experiment (DOE)

Response Surface Methods (RSM)

We are now going to shift from screening designs where the primary focus of previous lessons was factor screening (two-level factorials, fractional factorials being widely used), to trying to optimize an essential process and look for the factor level combinations that give us the maximum yield and minimum costs. In many applications, this is our goal. However, in some cases we are trying to hit a target or aim to match some given specifications - but this brings up other issues which we will get to later. Here the objective of Response Surface Methods (RSM) is optimization, finding the best set of factor levels to achieve some target. This lesson aims to cover the following goals: Response Surface Methodology and its sequential nature for optimizing a process First order and second order response surface models and how to find the direction of acutest ascent (or descent) to maximize (or minimize) the response

How to deal with several responses simultaneously (Multiple Response Optimization) Central Composite Designs (CCD) and Box-Behnken Designs as two of the major Response Surface Designs and how two generate them using Minitab 17 Design and Analysis of Mixture Designs for cases where the sum of the factor levels equals a constant, i. e. 100% or the totality of the components Introductory understanding of designs for computer models.

The actual variables in their natural units of measurement are used in the experiment. However, when we design our experiment we will use our coded variables, X_1 and X_2 which will be centered on 0, and extend +1 and -1 from the center of the region of experimentation. Therefore, we will take our natural units and then center and rescale them to the range from - 1 to + 1.

Our target is to start somewhere using our best prior or current knowledge and search for the optimum spot where the response is either maximized or minimized.

Here are the models that we will use.

Screening Response Model

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \varepsilon \qquad (1)$$

The screening model that we used for the first order situation involves linear effects and a single cross product factor, which represents the linear X linear interaction component.

Steepest Ascent Model

If we ignore cross products which gives an indication of the curvature of the response surface that we are fitting and just look at the first order model this is called the steepest ascent model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon \qquad (2)$$

Optimization Model

Then, when we think that we are somewhere near the 'top of the hill' we will fit a second order model. This includes in addition the two second-order quadratic terms.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \varepsilon \qquad (3)$$

Central Composite Designs

In this section we examine a more general central composite design. For k = 2 we had a 2^2 design with center points, which was required for our first order model; then we added 2*k star points. The star or axial points are, in general, at some value. There are various choices of α . If α = 1, the star points would be right on the boundary, and we would just have a 3^2 design. Thus α = 1 is a special case, a case that we considered in the 3^k designs. A more common choice of α is $\alpha = \sqrt{K}$

which gives us a spherical design as shown next page.

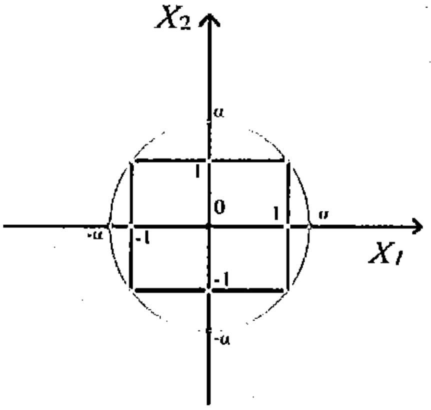


Figure 2.3 Spherical design 1

Our 2^2 design gives us the box, and adding the axial points (in green) outside of the box gives us a spherical design where $\sqrt{K}$. The corner points and the axial points at α are all points on the surface of a ball in three dimensions.

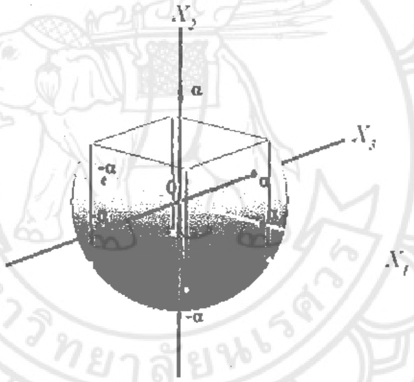


Figure 2.4 Spherical design 2

If we have *k* factors, then we have, 2^k factorial points, 2*k axial points and n_c center points. Below is a table that summarizes these designs and compares them to 3^k designs:

Table 2.4 summarizes these designs and compares them to 3^k designs

		k = 2	k = 3	k = 4	k = 5
Central Composite	Factorial points 2^k	4	8	16	32
Designs	Star points 2^k	4	6	8	10
	Center points n_c (varies)	5	5	6	6
	Total	13	19	30	48
3^k Designs		9	27	81	243
Choice of α	Spherical design ($\alpha = \sqrt{K}$)	1.4	1.73	2	2.24
	Rotatable design ($\alpha = (n_F)^{\frac{1}{4}}$)	1.4	1.68	2	2.38

Compare the total number of observations required in the central composite designs versus the 3^k designs. As the number of factors increases you can see the efficiencies that are brought to bear.

The spherical designs are rotatable in the sense that the points are all equidistant from the center. Rotatable refers to the variance of the response function. A rotatable design exists when there is an equal prediction variance for all points a fixed distance from the center, 0. This is a nice property. If you pick the center of your design space and run your experiments, all points that are equal distance from the center in any direction, have equal variance of predict [36-37].

Research of Literature

Author	Title	Raw material	Method	Condition	Results
Zaharaddeen N. Garba, (2016)	Optimization of adsorption conditions using central composite design for the removal of copper (II) and lead (II) by defatted papaya seed	Papaya seed	Using the soxhlet extraction method with hexane as solvent	Cu(II) Adsorbent dosage 0.6 g Shaking speed 150 rpm Initial concentration 180 mg/L Pb(II) Adsorbent dosage 0.6 g Shaking speed 200 rpm Initial concentration 103 mg/L	The Cu (II) and Pb (II) percentage removals ranged between 34.65 - 98.24% and 36.46 - 96.82% respectively.

Author	Title	Raw material	Method	Condition	Results
Rai A. etal, (2016)	Supercritical extraction of sunflower oil: A central composite design for extraction variables	Sunflower seed	The supercritical CO_2 extraction	Temperature 80 °C , pressure 400 bar, particle size 0.75 mm, solvent flow 10 g/min, with 5% co-solvent	The maximum yield for sunflower oil is found to be about 54.37 %wt.

Author	Title	Raw material	Method	Condition	Results
Bajer T. etal. , (2015)	Central composite design of pressurised hot water extraction process for extracting capsaicinoids from chili peppers	Seven chili pepper fruit samples	HPLC-APCI-MS	extraction pressure (20 MPa), extraction temperature ranging from 120 to 240 °C and static extraction time ranging from 5 to 60 min	Extraction of capsaicinoids from 10 chili samples was performed using pressurised hot water extraction (PHWE) and compared to the Soxhlet extraction (SOX). The quantification of target capsaicinoids in extracts was performed by HPLC-MS method.

Author	Title	Raw material	Method	Condition	Results
Herry Santoso Iryanto Maria Inggrid (2013)	Effects of Temperature, Pressure, Preheating Time and Pressing Time on Rubber Seed Oil Extraction Using Hydraulic Press	Rubber seeds	Mechanical pressing method.	-The rubber seed flakes are then preheated inside the metallic cylinder using a heater at various temperatures (60, 70 and 80 °C) and preheating times (45, 60 and 75 min.). The metallic cylinder are pressed using hydraulic press machine at various pressures (80, 100 and 120 bar) and pressing times (30, 60 and 90 min.).	-The lowest rubber seed oil yield is from conditions: temperature = 60 °C, pressure = 80 bar, time = 45 min and pressing time =30 min, with the oil yield of 19.82%. The best rubber seed oil yield is from conditions: temperature = 70 °C, pressure = 100 bar, time = 60 min and pressing time =60 min, with the oil yield of 29.82%.

Author	Title	Raw material	Method	Condition	Results
Widayat **Agam Duma** **Kalista** **Wibowo,** **Hadiyanto** **(2013)**	Study on production process of biodiesel from rubber seed (*hevea brasiliensis*) by in situ (trans)esterification method with acid catalyst	Rubber seeds	Situ method with acid catalyst with a goal for obtaining environmentally friendly alternative fuels from non edible raw material.	-Preparation The seed kernels was macerated, blended and dried in an oven at 55 °C for 2 hours -Aqueous methanol and H_2SO_4 were added and then heated and mixed. The solution was heated to 60 °C at atmospheric pressure. The in situ process (extraction-reaction process) was done for 120 minutes.	-The lowest rubber seed oil yield is from conditions: H_2SO_4 0.5% (v/v), with the oil yield of 13.21%. The best rubber seed oil yield is from conditions: H_2SO_4 0.25% (v/v) with the oil yield of 21.54%.

Author	Title	Raw material	Method	Condition	Results
Morshed M. etal,(2011)	Rubber seed oil as a potential source for biodiesel production in Bangladesh.	Rubber seed	- Mechanical press with and without solvent and cold percolation. - Three-step method comprises with saponification of oil, acidification of the soap and esterification of FFA.	- Found from combined method using seed to hexane wt. ratio of 1:0.8. - Esterification of FFA to prepare FAME is studied using different methanol to FFA molar ratio in which 5:1.The effect of catalyst concentration is 5 %wt.	- The maximum yield of oil is 49%. - FFA content in the oil is found as high as 45–46%. - Overall yield of FFA from RSO is found to be around 86%. - Effect of seed storage time on free fatty acid (FFA) content of the oil is studied an it is found that the FFA content increases from 2 wt.% (fresh seed) to 45 %wt after 2 months of storage at room temperature.

Author	Title	Raw material	Method	Condition	Results
Widyarani etal,(2014)	Biorefinery methods for separation of protein and oil fractions from rubber seed kernel.	Rubber seed	Pressing the rubber seed kernel to separate the oil fraction.	- Protein recovery from press cake that was pre-dried and pressed at 60 °C	- Oil and protein can be extracted simultaneously in one process. Oil separation is not necessary for high protein recovery. - Seed type and handling before processing were most determining for high oil and protein recoveries. - Higher pre-drying temperature tends to decrease protein recovery from press cakes and meals, therefore pre-drying at low temperature is preferred. - Suggesting that seed pressing can give optimised results to obtain both oil and protein from rubber seed kernel.

Author	Title	Raw material	Method	Condition	Results
Herry Santosoa, Iryantoa, Maria Inggrida	Effects of Temperature, Pressure, Preheating Time and Pressing Time on Rubber Seed Oil Extraction Using Hydraulic Press	Rubber seed	Mechanical pressing machine	-31.88% oil yield. -it is found that pressure and pressing time affect the rubber seed oil yield significantly. On the other hand, temperature and preheating time do not affect the oil yield significantly.	-The highest pressure (120 bar) and the longest pressing time (90 minutes)

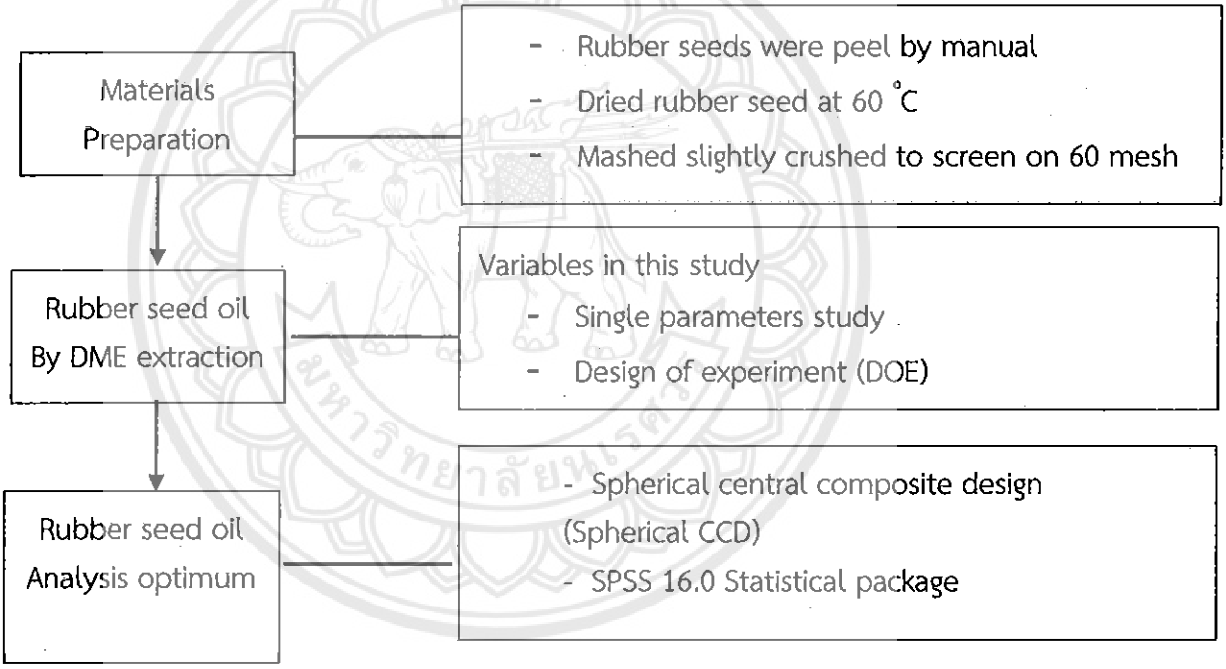
CHAPTER III

MATERIALS AND METHODS

Materials and chemicals

The fresh rubber (Heveabrasilliensis) seeds were obtained from a local farm located in Wangthong, Phitsanulok, Thailand. The large quantity of rubber seeds had been purchased in order to make sure the profiling of the sample maintain the same throughout the experiment. Dimethyl ether was purchased from Tamiya, Japan. Hexane (99%) was obtained from V.S. Chem house.

Methodology



Sample preparation

The rubber seeds were manually peeled off, kernels and seeds were collected. The sample were dried for 72 hours at 60 °C and slightly crushed to screen in 40 - 60 mesh. The crushed rubber seeds were kept in desiccator to maintain the moisture content before extraction.

DME extraction

The apparatus used for DME extraction is shown in Figure 3.1. The experiment began with weighing approximately 10 g of the crushed rubber seed then put into 100 ml beaker to mix with de-ionized water at desired moisture content. The sample along with an 8-mm diameter of magnetic bar were then loaded into a thimble (cellulose 30 x 100 mm) then placed into an extractor (100 ml stainless-steel). Liquefied DME were filled into the extractor at required solvent to solid weight ratio. The temperature of the system was controlled at desired temperature by heating jacket connecting with control box. The extractor was placed on to a hot plate stirrer. The agitation rate was adjusted to 500 rpm and the extraction was taken place for 30 min. After extraction, the ball valve was turned to open then DME and oil were transferred to the 100 ml beaker through the stainless-steel filter (5-μm pore diameter) which can separate the solid residues from the extracts.

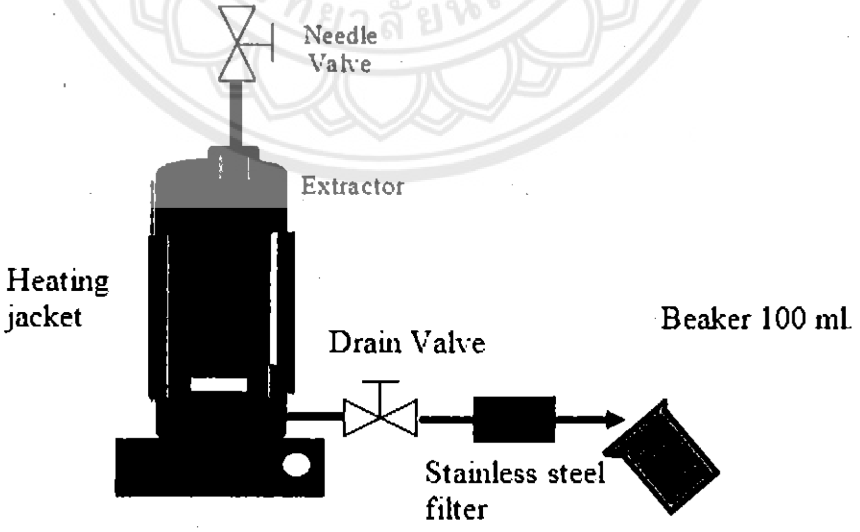


Figure 3.1 DME extraction apparatus

Single parameter study

The experimental was designed to study effect of temperature, Ratio DME:g sample and moisture content on %yield of the extracted rubber seed oil. The experimental began with one by one parameter to find the best of condition as shown in Table 3.1.

Table 3.1 Condition of single parameter study

Run	Moisture content %wt	Ratio DME:g sample	Temperature (°C)
1	5.4	3	31
2	20	3	31
3	40	3	31
4	60	3	31
5	74.6	3	31
6	Best from the previous study	3	31
7	Best from the previous study	4	31
8	Best from the previous study	5	31
9	Best from the previous study	6	31
10	Best from the previous study	6.73	31
11	Best from the previous study	Best from the previous study	35
12	Best from the previous study	Best from the previous study	40
13	Best from the previous study	Best from the previous study	45
14	Best from the previous study	Best from the previous study	49

Design of experiment (DOE)

Optimization of conditions for extraction of total rubber seed oil from DME with water system was carried out using a spherical central composite design (Spherical CCD). Three independent variables were chosen : Moisture %wt (X_1),Ratio weight DME:g sample (X_2) and temperature (X_3).The levels of factor were designed by $\alpha = \sqrt{K}$ where k is the number of variables (K = 3).This design puts all the factorial and axial design points on the surface of a sphere of radius $\sqrt{K}$. The low, middle and high levels of each variable were designated to be -1.73, 0, and +1.73, respectively. The corresponding actual values for each variable are listed in Table 3.2. It should be noted that the range of temperatures selected was between the room temperature and the maximum possible temperature of the solvent mixtures used for extraction.

Table 3.2 Levels of actual and coded factors

X_i	-1.73	-1	0	1	1.73
Moisture %wt (X_1)	5.4	20	40	60	74.6
Ratio weight DME:g sample (X_2)	3.27	4	5	6	6.73
Temperature (X_3)	31	35	40	45	49

The range of Ratio weight DME:g sample was selected based on the preliminary data which indicated that the selected range cover the optimal condition for extraction of total rubber seed oil. The range of Moisture %wt was within the limit of Moisture %wt normally used in pharmaceutical application. Finally, the extraction Temperature (°C) for this study were in the suitable range based on the preliminary extraction results. The spherical CCD including the factors, their levels, and the results from each test are shown in Table 3.3. The correlation between the independent variables and the response was described by the following second-order polynomial model (4)

$$Yield = \beta_0 + \sum_{i=1}^{3}\beta_i x_i + \sum_{i=1}^{3}\beta_{ii} x_i^{2} + \sum_{i=1}^{3}\sum_{i=1}^{3}\beta_{ij} x_i x_j \qquad (4)$$

Where X_i = coded variables of input variables, β_0 = interception, β_{ii} = regression coefficient and β_{ij} = cross product coefficient.

Table 3.3 Spherical CCD experimental results for extraction condition

Run	X_1	X_2	X_3
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
9	-1.73	0	0
10	1.73	0	0
11	0	-1.73	0
12	0	1.73	0
13	0	0	-1.73
14	0	0	1.73
15	0	0	0
16	0	0	0
17	0	0	0

The analysis of the central composite experimental design was carried out using SPSS 23.0 statistical package. The optimal extraction conditions for both Ratio weight DME:g sample and Moisture %wt systems can be calculated from the following equation:

$$\left[\frac{\partial Y}{\partial X_i}\right]_{X_j X_k} = 0 \text{ ,Where I = 1,2,3} \qquad (5)$$

; j=1, 2, 3 ;K=1, 2, 3, ;i≠j≠K

The spherical CCD experimental design was used to evaluate the main and the interaction effects on the extraction of total rubber seed oil from DME. The yields of the total rubber seed oil extracted with Ratio weight DME:g sample and moisture %wt summarized in a the analysis of variance (ANOVA) was conducted using SPSS 23.0 program to determine the factors that have significant effects on rubber seed oil.

%yield calculation

The total amount of oil was weighted and used a basis equation to calculated. %yield of rubber seed oil extracted can calculate by the following (6).

$$\%\text{yield}=\frac{\text{amount of oil extracted by DME}}{\text{dried sample}}\times 100\% \qquad (6)$$

CHAPTER IV

RESULT AND DISCUSSION

In this chapter, the effects of extraction parameters including moisture content (%wt), solvent to solid ratio (w/w) and temperature on %yield of rubber seed oil were firstly studied by single parameter method. The design of experimental (DOE) parameter study using response surface was then reported in the second part.

Single parameter study

Effect of Moisture content

For study of effect of moisture content on oil yield, the solvent to solid ratio, temperature were fixed at 1:3 w/w and 31 °C, respectively. As shown in Figure 4.1, oil yield was increased by increase in moisture content from 5.4% to 40% but it was decreased by increase in moisture content from 40% to 74.5%. The highest yield was found to be 30.82% at 40% moisture content. The increase in the amount of water might firstly help DME to diffuse into the matrices of rubber seed but too large amount of water might increase the overall solvent polarity caused the lower oil yield since oil is the non-polar compound [38].

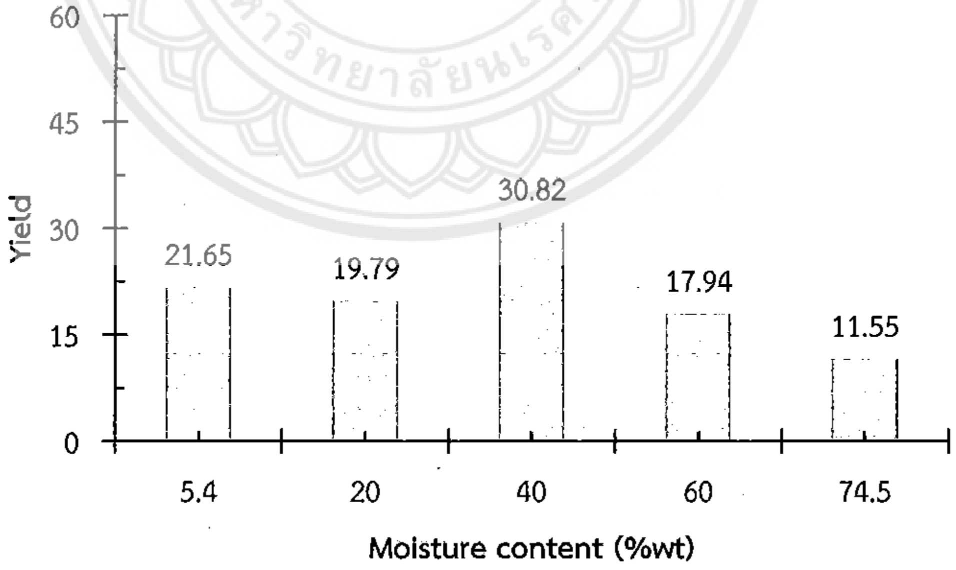


Figure 4.1 Effect of Moisture content (%wt)

Effect of solvent to solid ratio (g/g)

For study of effect of solvent to solid ratio on yield, the moisture content, temperature were fixed at 40 %wt and 31 °C, respectively. The results shown in Figure 4.2 revealed that increase in solvent to solid ratio from 3:1 to 6.76:1 resulted in increase in oil yield. The maximum oil yield was 48.14%. The results might be explained by the fact that increase in amount of solvent help increase the equilibrium of oil in the solvent.

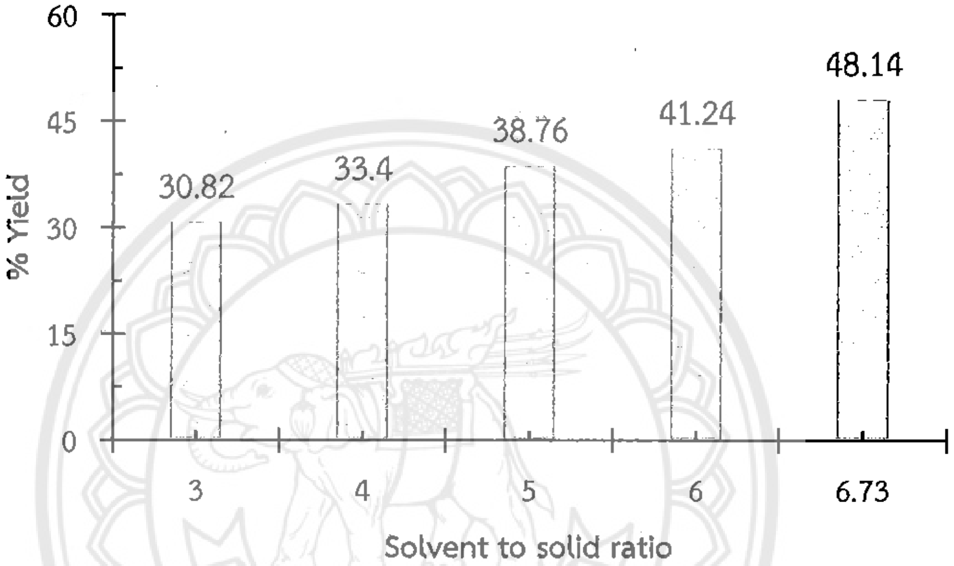


Figure 4.2 Effect of solvent to solid ratio (g/g)

Effect of temperature

The effect of temperature on oil yield was studied at the solute to solvent ratio, moisture content of 1:6.73 w/w and 40 %wt, respectively. The results shown in Figure 4.3 indicated that oil yield was remained constant by increase in temperature from 31 °C to 40 °C but decreased by increase in temperature from 40 °C to 49 °C. The maximum oil yield was found to be 48.14% at 31 °C. The results might be explained by the increase in solubility of oil and decrease in the density of liquefied DME by increasing temperature [39]. By increase in temperature, it normally increases solubility of solute in solvent but also decreases the solvent density and viscosity [40]. At the increase in temperature from 31 °C to 40 °C, the solubility of oil in DME might increase significantly compared to the effect of solvent density resulting in increase in oil yield. At the increase in temperature from 40 °C to 49 °C, the solvent density might be decrease led to decrease in solvent power resulting in the lower oil yields.

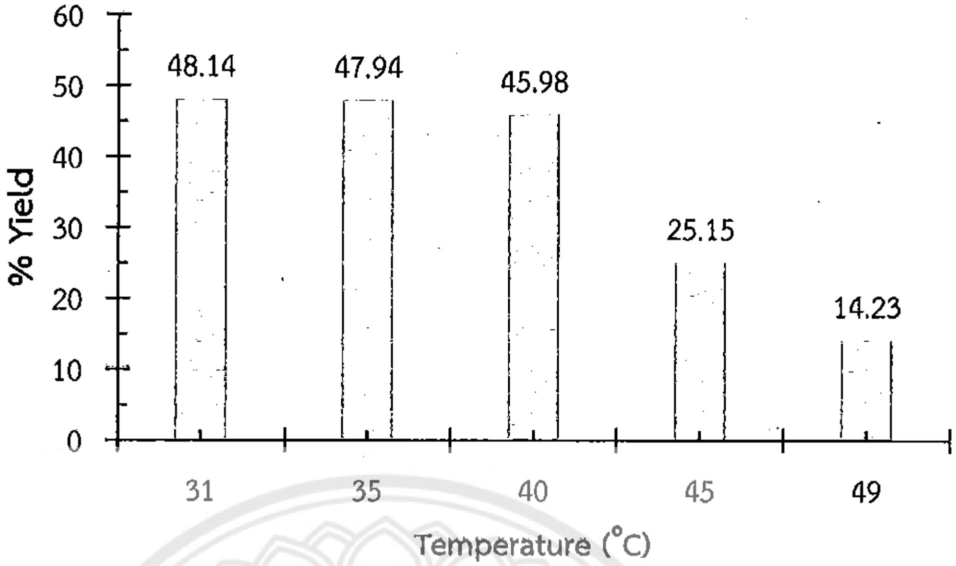


Figure 4.3 Effect of temperature

Design of experimental study (DOE)

The spherical CCD experimental design was used to estimate the main and the interaction effects on the extraction of rubber seed oil (response %Yield). The oil yields of rubber seed extracted by DME are show in the Table 4.1. From the table, the analysis of variance (ANOVA) was analyzed on SPSS program to find the factor that have significant effects on oil yield at 95% confidence (sig < 0.05). The result were show in Table 4.2.

From the ANOVA analysis (Table 4.2), the main effect of factor, moisture content (X_1) and solvent to solid ratio (X_2) were significant to the amount of %yield of oil extracted.

The response surface equation were show with quadratic models described in Eq. 1 was analyzed from Table 4.2. The ANOVA of the quadratic regression models show the models to be significant with low probability ($p \doteq 0.006$). The predicted vs the results from the experiment of the %yield of oil for both system show good agreement between the polynomial regression model and the experimental data, with R-square = 0.913. (Table 4.3)

$$\text{Yield} = 35.369 + 3.249x_1 + 5.498x_2 - 0.260x_3 + 0.980x_1x_2 - 1.392x_1x_3 - 1.804x_2x_3 - 2.163x_1^2 - 2.128x_2^2 - 1.646x_3^2 \quad (7)$$

$$\text{Yield} = -258.1 + 1.399\,X_1 + 43.2\,X_2 + 7.07\,X_3 - 0.00542\,X_1^2 - 2.132\,X_2^2 - 0.0594\,X_3^2 - 0.0490\,X_1X_2 - 0.0139\,X_1X_3 - 0.361\,X_2X_3 \quad (8)$$

Table 4.1 Spherical CCD experimental results for extraction yields of rubber seed oils.

Run	Moisture content	Solvent to solid ratio	Temperature	Yield (%) from experiment	Predicted yield (%)
1	-1	-1	-1	15.567	16.733
2	1	-1	-1	29.897	28.061
3	-1	1	-1	32.990	33.289
4	1	1	-1	37.629	40.697
5	-1	-1	1	23.402	22.593
6	1	-1	1	26.392	28.361
7	-1	1	1	27.835	31.949
8	1	1	1	32.680	33.797
9	-1.73	0	0	24.845	23.201
10	1.73	0	0	35.979	34.598
11	0	-1.73	0	18.660	19.489
12	0	1.73	0	42.371	38.513
13	0	0	-1.73	31.340	30.896
14	0	0	1.73	32.577	29.997
15	0	0	0	35.876	35.370
16	0	0	0	33.814	35.370
17	0	0	0	36.392	35.370

Table 4.2 ANOVA of spherical CCD of the yields of DOE extraction

Coefficients

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	35.369	1.795		19.704	.000
	Moisture	3.294	.831	.440	3.962	.005*
	Solvent ratio	5.498	.831	.735	6.613	.000*
	Tempurature	-.260	.831	-.035	-.313	.764
	X1X1	-2.163	.892	-.293	-2.425	.046
	X1X2	-.980	1.099	-.099	-.891	.402
	X1X3	-1.392	1.099	-.141	-1.266	.246
	X2X2	-2.128	.892	-.289	-2.386	.048
	X2X3	-1.804	1.099	-.182	-1.641	.145
	X3X3	-1.646	.892	-.223	-1.845	.108

* Significant, moisture content (0.005) and solvent to solid ratio (0.000) are significant.

Table 4.3 ANOVA for the model summary

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.956[a]	.913	.802	3.10909	.913	8.213	9	7	.006

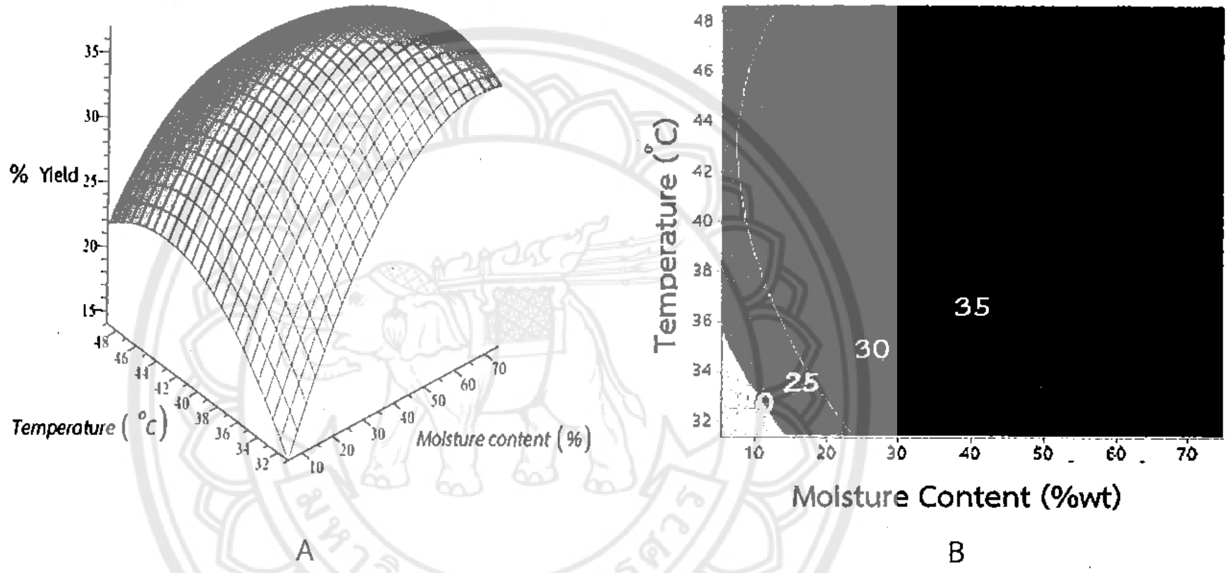
a. Predictors: (Constant), X3X3, X2X3, X1X3, X1X2, Temperature, Ratio, Moisture, X2X2, X1X1

Model	Sum of Squares	df	Mean Square	F	Sig.
Regression	714.548	9	79.394	8.213	.006[b]
Residual	67.665	7	9.666		
Total	782.213	16			

b. Predictors: (Constant), X3X3, X2X3, X1X3, X1X2, Temperature, Solvent to solid ratio, Moisture content, X2X2, X1X1

Response surface plots and response optimization

Response surface methodology was used to determine the optimal conditions for DME extraction. The three-dimensional plots of predicted response base on the model in (8) as a function of the combination of two test variables with the other maintained at its respective zero level are show in Figure 4.4-4.6. The optimal conditions obtaining the maximum response were 56.43 %wt of moisture content, 6.66 of solvent to solid ratio and 33.3 °C of temperature which gave 41.4818 %yield for 30 minute extraction time and 500 rpm agitation rate.

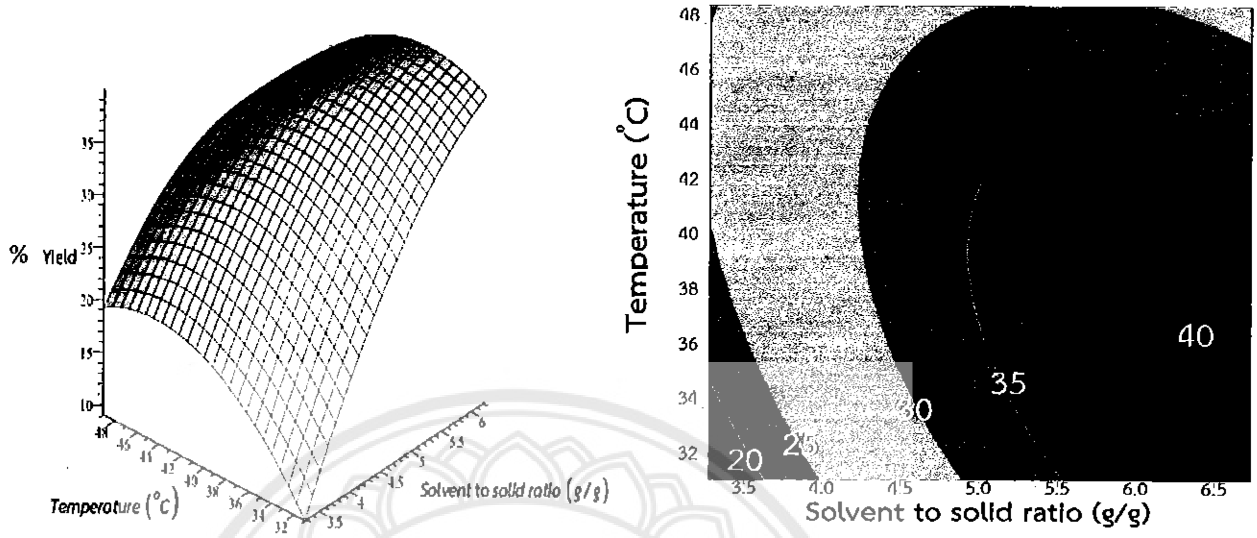


A

B

Figure 4.4 Response surfaces of %yield and contour plot for moisture content (%wt) and Temperature (°C) as function of A and B respectively.

The 3D plot and contour plot of temperature vs moisture content vs %yield are shown in Figure 4.4 a-b. From the Figure, the higher oil yield can be obtained at higher moisture content but it seems to be decreased at too excess moisture content for all extraction temperature. The higher temperature also seems to give lower oil yield. The optimum condition was observed to be 50-70% moisture and 36-38 °C. The results was observed to have same trend with single parameter study. The increase in the amount of water might firstly help DME to diffuse into the matrices of rubber seed but too large amount of water might increase the overall solvent polarity caused the lower oil yield since oil is the non-polar compound [38]. For the effect of temperature, it normally increases solubility of solute in solvent but also decreases the solvent density and viscosity by increase in temperature [40]. At lower, the solubility of oil in DME might increase significantly compared to the effect of solvent density resulting in increase in oil yield. At higher temperature, the solvent density might be decrease led to decrease in solvent power resulting in the lower oil yields.

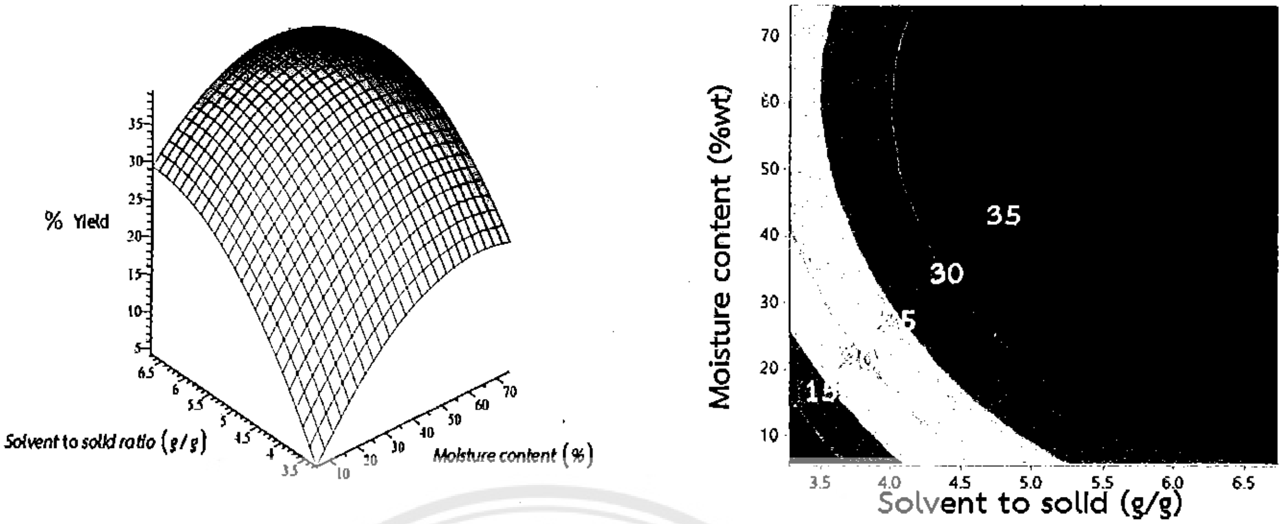


C

D

Figure 4.5 Response surfaces and contour plot of %yield for Solvent to solid ratio (g/g) and Temperature (°C) as function of C and D respectively.

The 3D plot and contour plot of temperature vs solvent to solid ratio (g/g) vs %yield are shown in Figure 4.5 a-b. From the Figure, the higher oil yield can be obtained at higher solvent to solid ratio for all extraction temperature. The higher temperature also seems to give lower oil yield. The optimum condition was observed to be at higher than 6.5:1 solvent to solid ratio (g/g) and 34-36 °C. The results was observed to have same trend with single parameter study. The results of solvent to solid ratio might be explained by the fact that increase in amount of solvent help increase the equilibrium of oil in the solvent. For the effect of temperature, it normally increases solubility of solute in solvent but also decreases the solvent density and viscosity by increase in temperature [40]. At lower, the solubility of oil in DME might increase significantly compared to the effect of solvent density resulting in increase in oil yield. At higher temperature, the solvent density might be decrease led to decrease in solvent power resulting in the lower oil yields.



E

F

Figure 4.6 Response surfaces and contour plot of %yield for Solvent to solid ratio (g/g) and Moisture content (%wt) as function of E and F respectivel

The 3D plot and contour plot of solvent to solid ratio (g/g) vs moisture content vs %yield are shown in Figure 4.6 a-b. From the Figure, the higher oil yield can be obtained at higher moisture content but it seems to be decreased at too excess moisture content for all solvent to solid ratio. The optimum condition was observed to be 50-60% moisture and solvent to solid ratio (g/g) of 6:1 to 6.5:1. The results was observed to have same trend with single parameter study. The increase in the amount of water might firstly help DME to diffuse into the matrices of rubber seed but too large amount of water might increase the overall solvent polarity caused the lower oil yield since oil is the non-polar compound [38]. The results of solvent to solid ratio might be explained by the fact that increase in amount of solvent help increase the equilibrium of oil in the solvent.

CHAPTER V

CONCLUSION AND RECOMMENDATION

Conclusion

1. From single parameter study, the suitable conditions for rubber seed oil extraction using liquefied DME were found to be 40% moisture content, 6.73:1 solvent to solid ratio and 31 °C. By this condition, the maximum yield of 48.14% can be obtained.
2. From response surface study, the optimum condition for rubber seed oil extraction using liquefied DME are at 56.43% moisture content ,6.66:1 solvent to solid ratio and 33.3 °C. By this condition, the maximum yield of 41.48% can be obtained.

Recommendation

1. The drying process of rubber seed sample should be adjusted to avoid the change in seed properties resulting in lower yield obtained by extraction.
2. Effect of particle size of rubber seed should be further studied.

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APPENDIX

Appendix Table 1 of single parameter condition

Run	X_1	X_2	X_3	Oil (gram)	%yield
1	-1.73	0	-1.73	2.10	21.65
2	-1	0	-1.73	1.92	19.79
3	0	0	-1.73	2.99	30.82
4	1	0	-1.73	1.74	17.94
5	1.73	0	-1.73	1.12	11.55
6	0	-1.73	-1.73	3.24	33.40
7	0	-1	-1.73	3.76	38.76
8	0	1	-1.73	4.00	41.24
9	0	1.73	-1.73	4.67	48.14
10	0	1.73	-1	4.65	47.94
11	0	1.73	0	4.46	45.98
12	0	1.73	1	2.44	25.15
13	0	1.73	1.73	1.38	14.23

Appendix Table 2 of DOE condition

Run	X_1	X_2	X_3	Oil (gram)	%yield
1	-1	-1	-1	1.51	15.567
2	1	-1	-1	2.9	29.897
3	-1	1	-1	2.47	25.464
4	1	1	-1	3.65	37.629
5	-1	-1	1	2.27	23.402
6	1	-1	1	2.56	26.392
7	-1	1	1	2.7	27.835
8	1	1	1	3.17	32.680
9	-1.73	0	0	2.41	24.845
10	1.73	0	0	3.49	35.979
11	0	-1.73	0	1.81	18.660
12	0	1.73	0	4.11	42.371
13	0	0	-1.73	3.77	38.866
14	0	0	1.73	3.16	32.577
15	0	0	0	3.48	35.876
16	0	0	0	3.28	33.814
17	0	0	0	3.53	36.392

X1 = Moisture Content (%wt)

X2 = Solvent to Solid ratio (g/g)

X3 = Temperature (°C)

The moisture content of the sample is calculated using the following equation:

$$\%W = \frac{A-B}{B} \times 100$$

Where:

%W = Percentage of moisture in the sample

A = Weight of wet sample (grams)

B = Weight of dry sample (grams)

The %Yield of the sample is calculated using the following equation:

$$\%yield = \frac{A}{B} \times 100$$

Where:

A = Weight of rubber seed oil (grams)

B = Weight of dry rubber seed (grams)

Appendix Table 3 DME density

Temperature °C	Density (g/ml) Liquid phase	Density (g/ml) Vapor phase
30	0.6455	0.0142
40	0.6292	0.0188
50	0.6116	0.0241
60	0.5932	0.0306

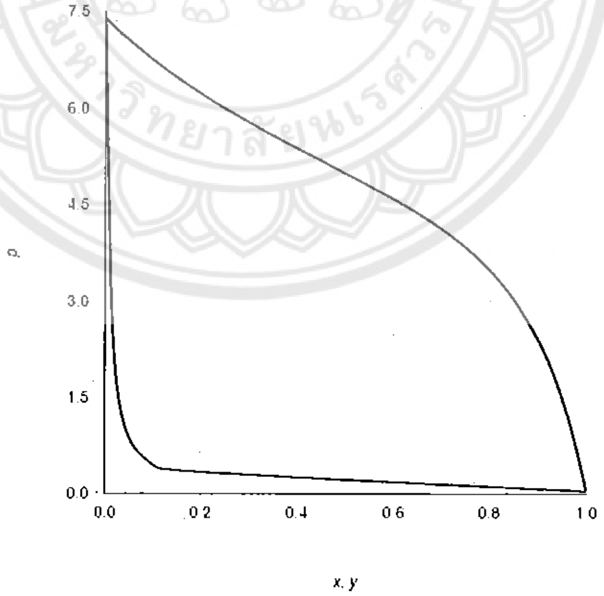
Appendix Table 4 Moisture content calculate mole fraction

g of water	Mol. water	g of DME	Mol. DME
0.22	0.012	32.7	0.711
1.64	0.091	40	0.870
3.58	0.199	50	1.087
5.52	0.307	60	1.304
6.9	0.383	67.3	1.463

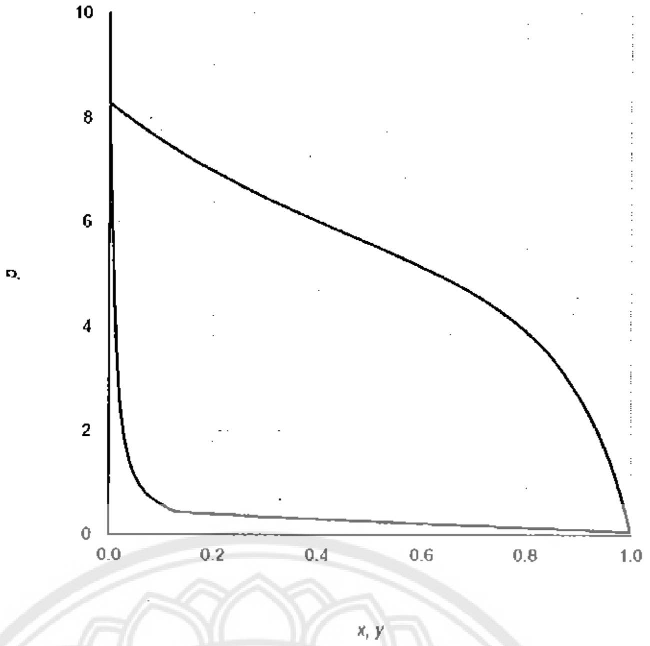
Example Condition water 3.58 g = 0.199 mole, DME solvent 50 g = 1.087 mole

$$\text{Mole fraction of water} = \frac{0.199}{0.199+1.087} = 0.154$$

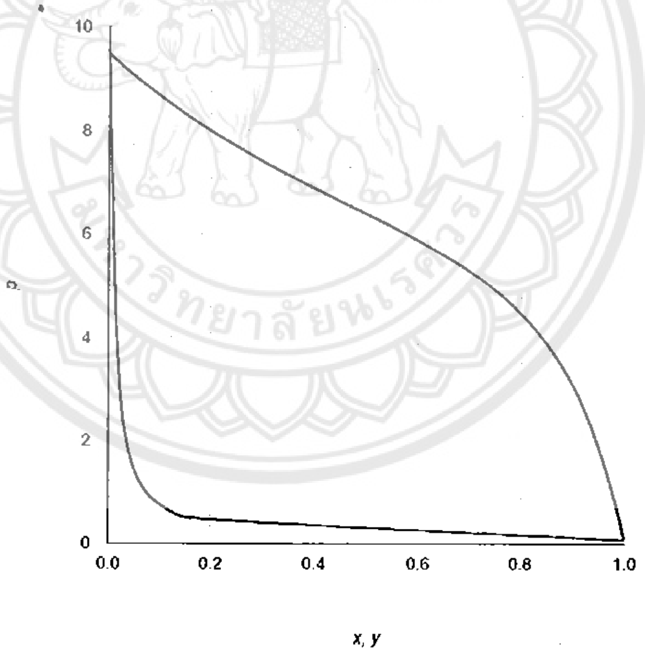
g of Water	g of DME	Mole fraction of water
3.58	60	0.132
3.58	67.3	0.119



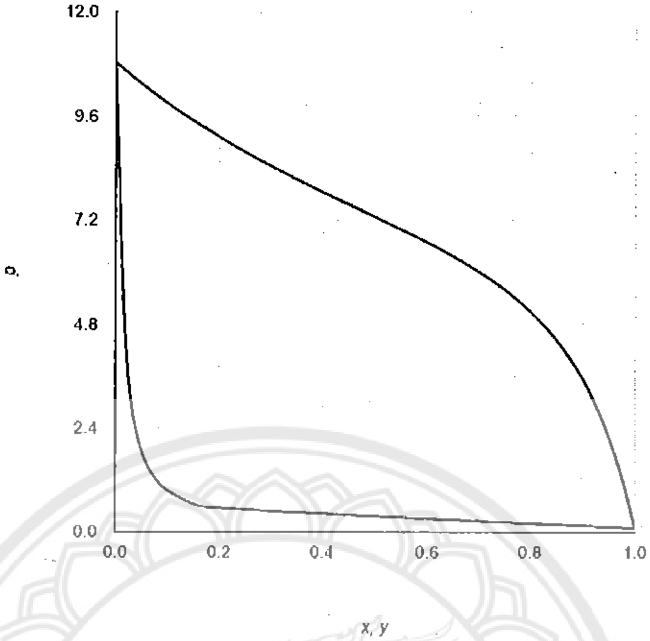
Appendix Figure 1 Vapor-liquid equilibrium diagram (phase diagram) (31 °C) Pressure (bar)



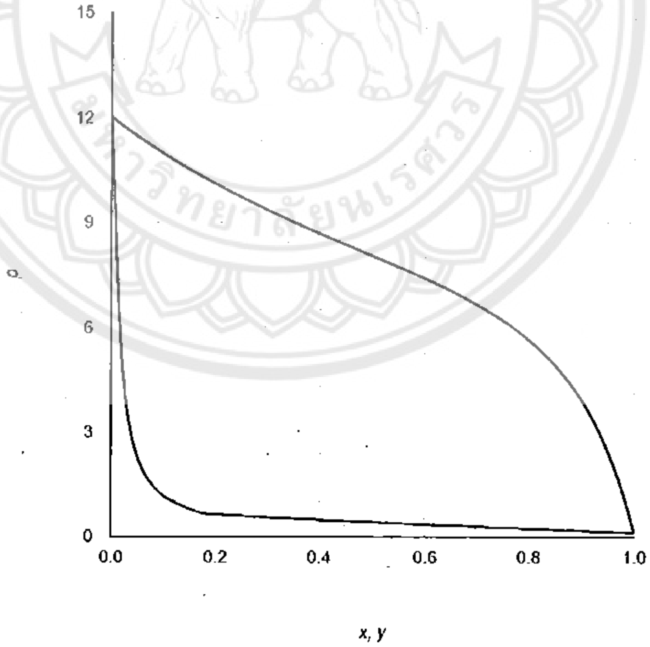
Appendix Figure 2 Vapor-liquid equilibrium diagram (phase diagram) (35 °C) Pressure (bar)



Appendix Figure 3 Vapor-liquid equilibrium diagram (phase diagram) (40 °C) Pressure (bar)



Appendix Figure 4 Vapor-liquid equilibrium diagram (phase diagram) (45 °C) Pressure (bar)



Appendix Figure 5 Vapor-liquid equilibrium diagram (phase diagram) (49 °C) Pressure (bar)

Appendix Table 5 Calculated vapor-liquid equilibrium data (31 °C)

Vapor Pressure bar	x_1 (water) mol./mol.	y_1 (water) mol./mol.
7.38929	0	0
7.31789	0.01	0.000211794
7.24825	0.02	0.000416969
7.18029	0.03	0.000615884
7.11393	0.04	0.000808875
6.98571	0.06	0.00117832
6.86307	0.08	0.00152761
6.74553	0.1	0.00185876
6.47121	0.15	0.00261856
6.22035	0.2	0.00329894
5.98825	0.25	0.00391797
5.77098	0.3	0.00449025
5.56504	0.35	0.00502828
5.36717	0.4	0.00554351
5.17404	0.45	0.00604736
4.98206	0.5	0.0065524
4.78694	0.55	0.00707396
4.58329	0.6	0.00763267
4.36382	0.65	0.00825892
4.11823	0.7	0.00900165
3.83117	0.75	0.0099475
3.47887	0.8	0.0112684
3.02265	0.85	0.0133634
2.39651	0.9	0.0174217
2.07455	0.92	0.0204192
1.69607	0.94	0.0253634
1.24612	0.96	0.0350952
0.988375	0.97	0.0446336
0.704825	0.98	0.0631575
0.39189	0.99	0.114663
0.0453775	1	1

Appendix Table 6 Calculated vapor-liquid equilibrium data (35 °C)

Vapor Pressure bar	x_1 (water) mol/mol	y_1 (water) mol/mol
8.27379	0	0
8.19401	0.01	0.000235062
8.11615	0.02	0.000463028
8.04012	0.03	0.000684269
7.96584	0.04	0.000899135
7.82222	0.06	0.00131103
7.68473	0.08	0.00170111
7.55285	0.1	0.00207149
7.24477	0.15	0.00292319
6.96275	0.2	0.00368777
6.7017	0.25	0.0043846
6.45731	0.3	0.00502949
6.22576	0.35	0.00563609
6.00342	0.4	0.00621699
5.7866	0.45	0.00678485
5.5713	0.5	0.00735365
5.35276	0.55	0.00794047
5.12494	0.6	0.00856833
4.87974	0.65	0.00927118
4.60564	0.7	0.0101036
4.28555	0.75	0.0111624
3.89285	0.8	0.0126394
3.3843	0.85	0.0149797
2.68589	0.9	0.0195082
2.3265	0.92	0.0228498
1.90377	0.94	0.0283564
1.40085	0.96	0.039176
1.11259	0.97	0.0497564
0.795336	0.98	0.0702352
0.445033	0.99	0.126705
0.0569426	1	1

Appendix Table 7 Calculated vapor-liquid equilibrium data (40 °C)

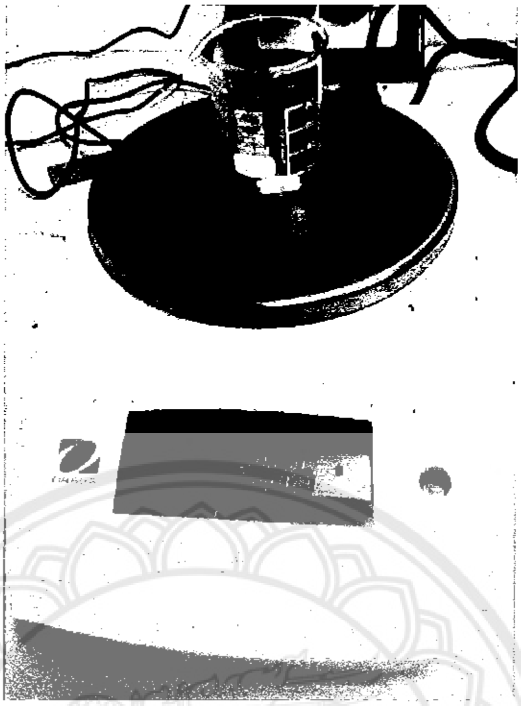
Vapor Pressure bar	x_1 (water) mol/mol	y_1 (water) mol/mol
9.48889	0	0
9.39765	0.01	0.000265825
9.30854	0.02	0.000523989
9.22145	0.03	0.000774877
9.13631	0.04	0.00101885
8.97153	0.06	0.00148739
8.8136	0.08	0.0019321
8.66196	0.1	0.0023552
8.30721	0.15	0.00333107
7.98201	0.2	0.00421014
7.68076	0.25	0.00501331
7.39868	0.3	0.00575786
7.13147	0.35	0.00645888
6.87507	0.4	0.00713042
6.62531	0.45	0.00778673
6.37762	0.5	0.00844365
6.1266	0.55	0.00912063
5.86537	0.6	0.00984391
5.5847	0.65	0.0106522
5.27147	0.7	0.0116079
4.90615	0.75	0.0128213
4.45834	0.8	0.0145113
3.87854	0.85	0.0171854
3.08188	0.9	0.0223518
2.67161	0.92	0.0261592
2.1887	0.94	0.0324248
1.61374	0.96	0.0447061
1.28396	0.97	0.0566786
0.92081	0.98	0.0797475
0.519607	0.99	0.142656
0.0748543	1	1

Appendix Table 8 Calculated vapor-liquid equilibrium data (45 °C)

Vapor Pressure bar	x_1 (water) mol/mol	y_1 (water) mol/mol
10.833	0	0
10.7292	0.01	0.000298342
10.6277	0.02	0.000588507
10.5284	0.03	0.000870886
10.4312	0.04	0.00114585
10.243	0.06	0.00167489
10.0625	0.08	0.00217819
9.88888	0.1	0.00265807
9.48219	0.15	0.00376844
9.10877	0.2	0.00477246
8.76251	0.25	0.00569241
8.43814	0.3	0.00654695
8.13092	0.35	0.00735257
7.83628	0.4	0.00812481
7.54954	0.45	0.00887957
7.26555	0.5	0.00963464
6.97819	0.55	0.010412
6.67971	0.6	0.0112414
6.35962	0.65	0.0121667
6.00306	0.7	0.0132587
5.58788	0.75	0.0146426
5.07956	0.8	0.0165667
4.42176	0.85	0.0196061
3.51773	0.9	0.0254681
3.05188	0.92	0.0297815
2.50325	0.94	0.0368695
1.84956	0.96	0.0507262
1.47438	0.97	0.0641884
1.06104	0.98	0.0900016
0.604135	0.99	0.159559
0.0973435	1	1

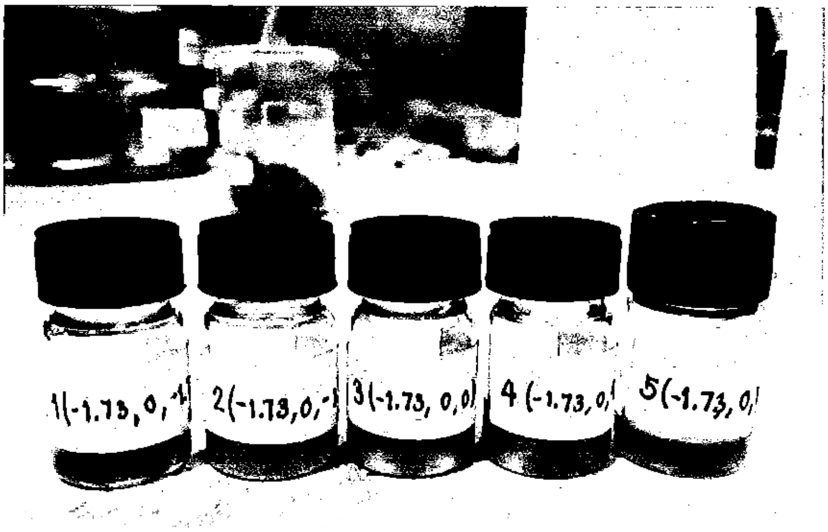
Appendix Table 9 Calculated vapor-liquid equilibrium data (49 °C)

Vapor Pressure bar	x_1 (water) mol/mol	y_1 (water) mol/mol
12.0066	0	0
11.8918	0.01	0.000325532
11.7794	0.02	0.000642515
11.6695	0.03	0.000951341
11.5619	0.04	0.00125238
11.3533	0.06	0.00183249
11.1529	0.08	0.00238545
10.9602	0.1	0.00291361
10.5079	0.15	0.00413897
10.092	0.2	0.00525059
9.70599	0.25	0.00627168
9.34425	0.3	0.00722193
9.00161	0.35	0.00811892
8.67312	0.4	0.00897937
8.35365	0.45	0.00982051
8.03756	0.5	0.0106618
7.71814	0.55	0.0115273
7.38685	0.6	0.0124498
7.03218	0.65	0.0134776
6.63774	0.7	0.0146887
6.17915	0.75	0.0162211
5.61832	0.8	0.0183483
4.89307	0.85	0.0217036
3.89637	0.9	0.0281649
3.38259	0.92	0.0329129
2.77727	0.94	0.0407049
2.05565	0.96	0.0559032
1.64129	0.97	0.0706256
1.18462	0.98	0.0987373
0.679623	0.99	0.173727
0.11923	1	1

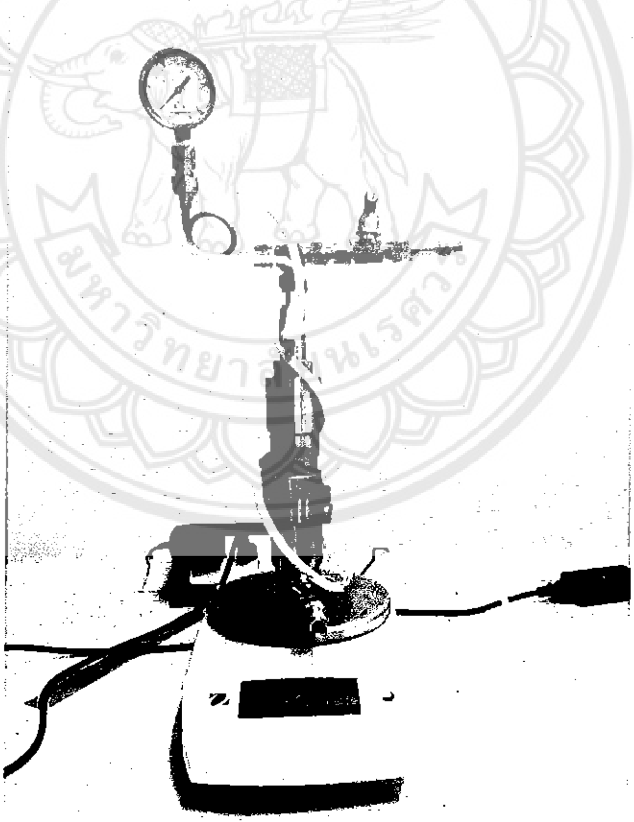


Appendix Figure 6 Rubber seed oil after extracted

Appendix Figure 7 Rubber seed



Appendix Figure 8 Rubber seed oil

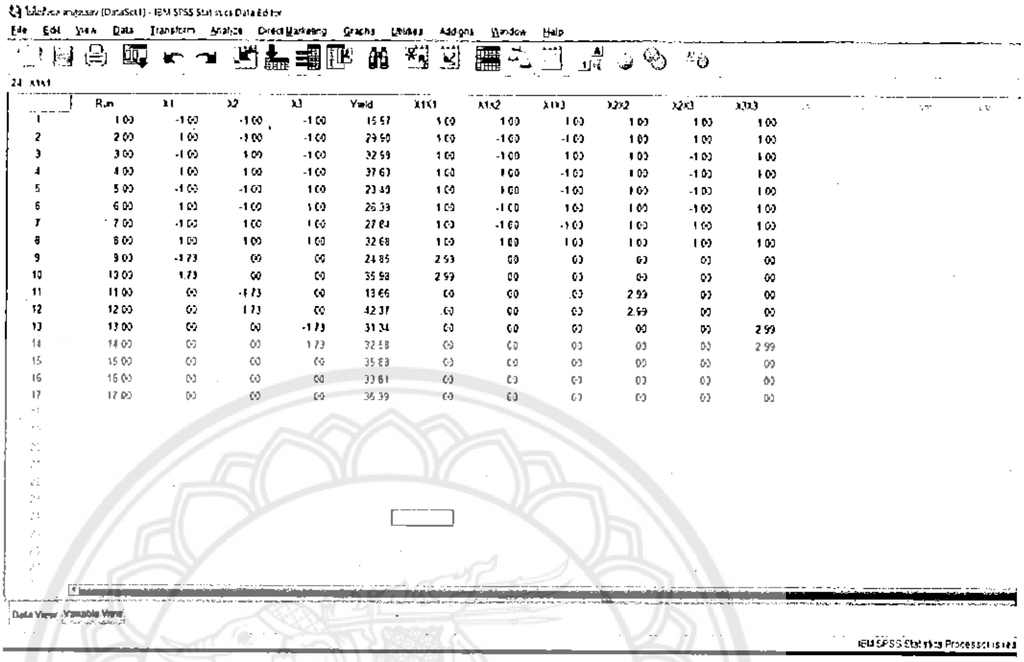


Appendix Figure 9 Reactor

Step to analyze the ANOVA from SPSS.

Response surface equation

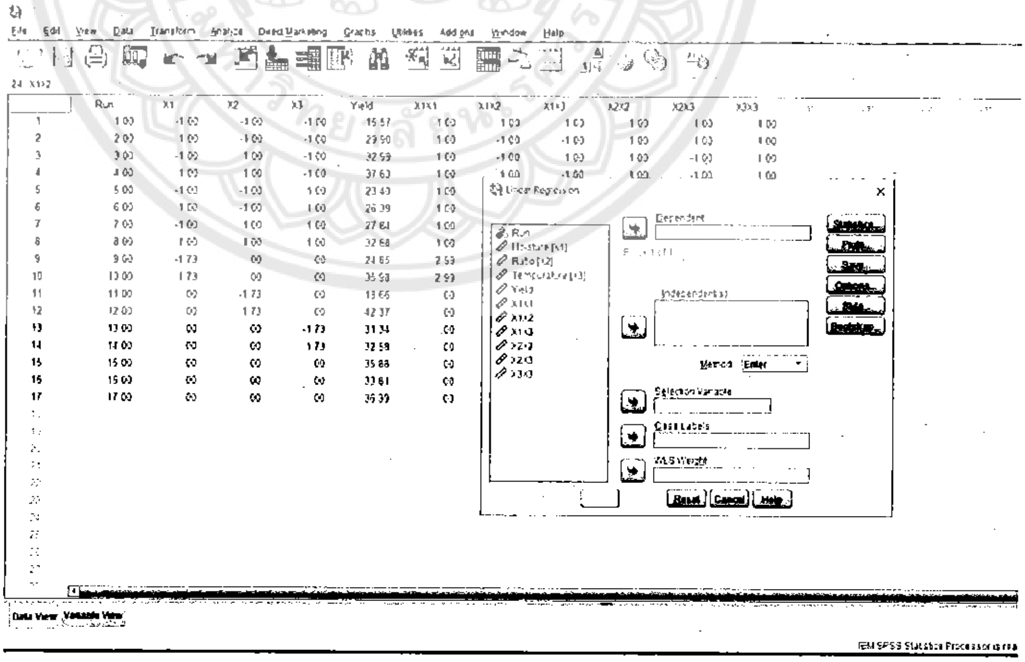
1. After we filled the data into Table.



	Run	X1	X2	X3	Yield	X1X1	X1X2	X1X3	X2X2	X2X3	X3X3
1	1.00	-1.00	-1.00	-1.00	15.57	1.00	1.00	1.00	1.00	1.00	1.00
2	2.00	1.00	-1.00	-1.00	29.90	1.00	-1.00	-1.00	1.00	1.00	1.00
3	3.00	-1.00	1.00	-1.00	32.59	1.00	-1.00	1.00	1.00	-1.00	1.00
4	4.00	1.00	1.00	-1.00	37.63	1.00	1.00	-1.00	1.00	-1.00	1.00
5	5.00	-1.00	-1.00	1.00	23.40	1.00	1.00	-1.00	1.00	-1.00	1.00
6	6.00	1.00	-1.00	1.00	26.39	1.00	-1.00	1.00	1.00	-1.00	1.00
7	7.00	-1.00	1.00	1.00	27.84	1.00	-1.00	-1.00	1.00	1.00	1.00
8	8.00	1.00	1.00	1.00	32.68	1.00	1.00	1.00	1.00	1.00	1.00
9	9.00	-1.73	.00	.00	24.85	2.99	.00	.00	.00	.00	.00
10	10.00	1.73	.00	.00	35.98	2.99	.00	.00	.00	.00	.00
11	11.00	.00	-1.73	.00	13.66	.00	.00	.00	2.99	.00	.00
12	12.00	.00	1.73	.00	42.37	.00	.00	.00	2.99	.00	.00
13	13.00	.00	.00	-1.73	31.34	.00	.00	.00	.00	.00	2.99
14	14.00	.00	.00	1.73	32.58	.00	.00	.00	.00	.00	2.99
15	15.00	.00	.00	.00	35.83	.00	.00	.00	.00	.00	.00
16	16.00	.00	.00	.00	33.81	.00	.00	.00	.00	.00	.00
17	17.00	.00	.00	.00	36.39	.00	.00	.00	.00	.00	.00

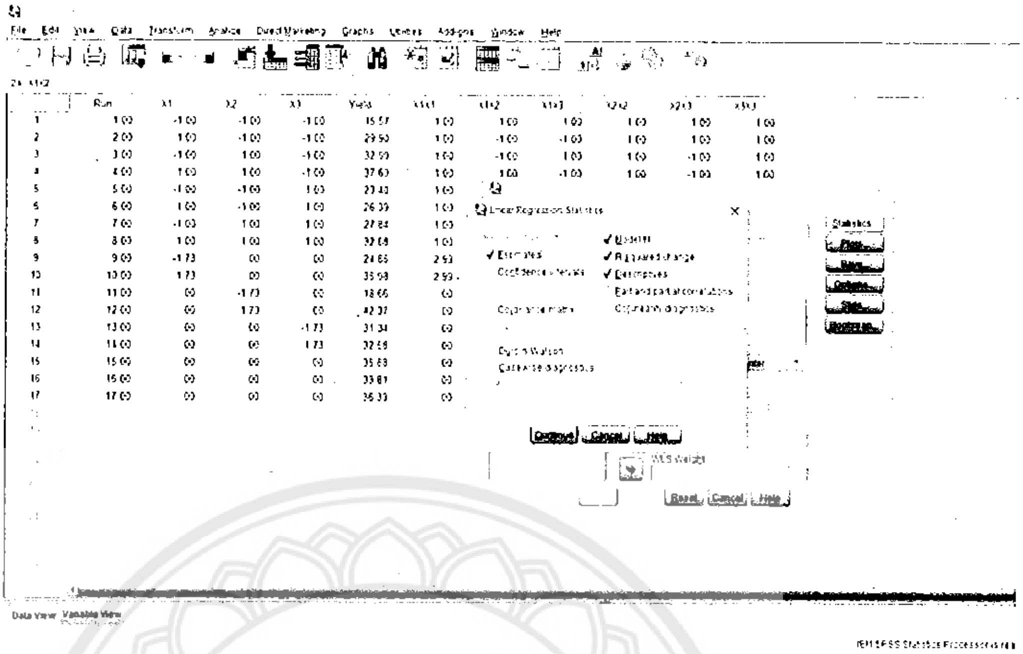
2. From the menu, select Analyze > Regression > Linear.

   (select variable and choose to Dependent or Independent variable)



	Run	X1	X2	X3	Yield	X1X1	X1X2	X1X3	X2X2	X2X3	X3X3
1	1.00	-1.00	-1.00	-1.00	15.57	1.00	1.00	1.00	1.00	1.00	1.00
2	2.00	1.00	-1.00	-1.00	29.90	1.00	-1.00	-1.00	1.00	1.00	1.00
3	3.00	-1.00	1.00	-1.00	32.59	1.00	-1.00	1.00	1.00	-1.00	1.00
4	4.00	1.00	1.00	-1.00	37.63	1.00	1.00	-1.00	1.00	-1.00	1.00
5	5.00	-1.00	-1.00	1.00	23.40	1.00					
6	6.00	1.00	-1.00	1.00	26.39	1.00					
7	7.00	-1.00	1.00	1.00	27.84	1.00					
8	8.00	1.00	1.00	1.00	32.68	1.00					
9	9.00	-1.73	.00	.00	24.85	2.99					
10	10.00	1.73	.00	.00	35.98	2.99					
11	11.00	.00	-1.73	.00	13.66	.00					
12	12.00	.00	1.73	.00	42.37	.00					
13	13.00	.00	.00	-1.73	31.34	.00					
14	14.00	.00	.00	1.73	32.58	.00					
15	15.00	.00	.00	.00	35.83	.00					
16	16.00	.00	.00	.00	33.81	.00					
17	17.00	.00	.00	.00	36.39	.00					

3. Click Statistics and choose follow the figure

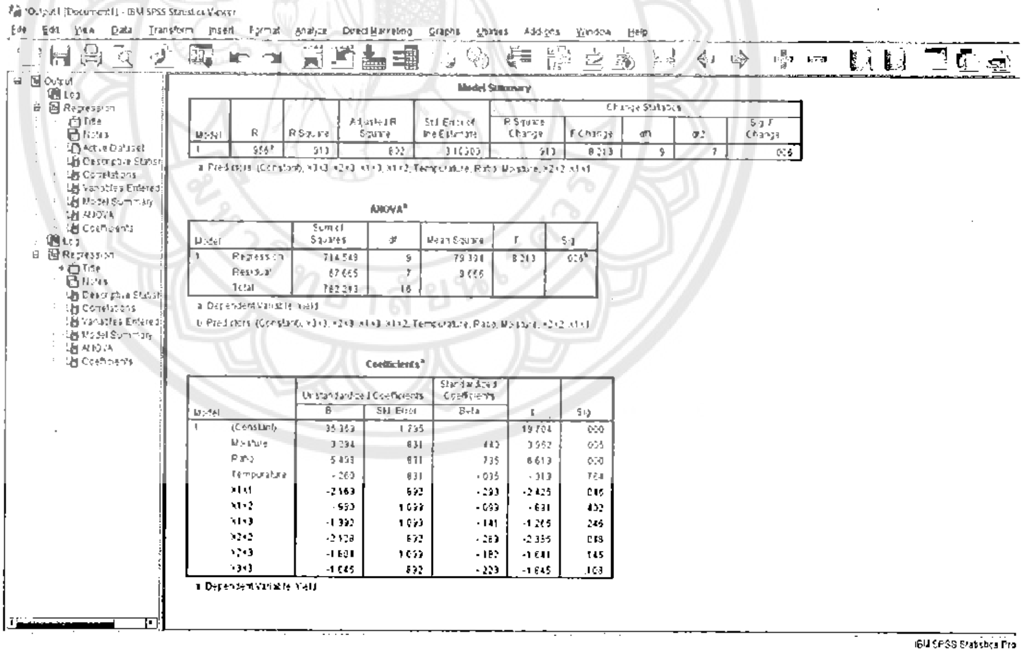


Linear Regression: Statistics

✓ Estimates
Confidence intervals
Covariance matrix
✓ Model fit
✓ R squared change
✓ Descriptives
Part and partial correlations
Collinearity diagnostics
Durbin-Watson
Casewise diagnostics

Continue Cancel Help

4. Click continue and OK



Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
1	.956[a]	.913	.802	3.10903	.913	8.213	9	7	.006

a. Predictors: (Constant), x3x3, x2x3, x1x3, x1x2, Temperature, Ratio, Moisture, x2x2, x1x1

ANOVA[a]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	714.549	9	79.394	8.213	.006[b]
	Residual	67.665	7	9.666		
	Total	782.213	16			

a. Dependent Variable: Yield

b. Predictors: (Constant), x3x3, x2x3, x1x3, x1x2, Temperature, Ratio, Moisture, x2x2, x1x1

Coefficients[a]

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	35.363	1.795		19.704	.000
	Moisture	3.294	.831	.443	3.962	.005
	Ratio	5.493	.831	.735	6.613	.000
	Temperature	-.260	.831	-.035	-.313	.764
	x1x1	-2.163	.892	-.293	-2.425	.046
	x1x2	-.693	1.099	-.069	-.631	.548
	x1x3	-1.390	1.099	-.141	-1.265	.246
	x2x2	-2.100	.892	-.283	-2.355	.048
	x2x3	-1.801	1.099	-.182	-1.641	.145
	x3x3	-1.467	.892	-.223	-1.645	.143

a. Dependent Variable: Yield

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