การสกัดน้ำมันจากเมล็ดยางพาราโดยไดเมทิลอีเทอร์เหลว
EXTRACTION OF RUBBER SEED OIL BY LIQUEFIED DIMETHYL ETHER

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ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาหลักสูตรปริญญาวิศวกรรมศาสตรบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมอุตสาหการ
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EXTRACTION OF RUBBER SEED OIL BY LIQUEFIED DIMETHYL ETHER

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A Thesis Submitted in Partial Fulfillment of the Requirements for the
Bachelor Degree in Chemical Engineering
Naresuan University
Academic Year 2015

ใบรับรองปริญญานิพนธ์

ชื่อหัวข้อโครงงาน	การสกัดน้ำมันจากเมล็ดยางพาราด้วยไดเมทิลอีเทอร์เหลว
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ปีการศึกษา	2558

คณะวิศวกรรมศาสตร์ มหาวิทยาลัยนเรศวร อนุมัติให้ปริญญานิพนธ์ฉบับนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตร์บัณฑิต สาขาวิศวกรรมเคมี

ปณัฐพงศ์ บุญนวล ......ที่ปรึกษาโครงงาน
(ดร.ปณัฐพงศ์ บุญนวล)

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....กรรมการ

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บทคัดย่อ

ปริญญานิพนธ์นี้ศึกษาการสกัดน้ำมันจากเมล็ดยางพาราด้วยตัวทำละลายไดเมทิลอีเทอร์เหลวบริสุทธิ์ ทำการศึกษาพารามิเตอร์ต่างๆ ดังนี้ อุณหภูมิที่ใช้ในการสกัด (30 35 40 45 และ 50 องศาเซลเซียส) อัตราส่วนของเมล็ดยางพาราต่อตัวทำละลาย (1:2 1:3 1:4 และ 1:5 โดยมวล) เวลาที่ใช้ในการสกัด (15 30 45 60 และ 75 นาที) ตัวทำละลายร่วม และเปรียบเทียบค่าร้อยละการนำกลับของน้ำมัน (%Recovery) ผลการทดลองพบว่าอุณหภูมิการสกัด 30 องศาเซลเซียส อัตราส่วนของเมล็ดยางพาราต่อตัวทำละลาย 1:3 โดยมวล เวลาสกัด 30 นาทีจะได้ค่าร้อยละการนำน้ำมันกลับมาสูงสุด คือ 67.85% โดยน้ำหนัก สำหรับการสกัดด้วยตัวทำละลายร่วมจะทำให้ได้ค่าร้อยละการนำน้ำมันกลับมาน้อยลง โดยการใช้ตัวทำละลายร่วมเอทานอล 5% และ 7% จะได้ค่าร้อยละการนำน้ำมันกลับเท่ากับ 56.13% และ 52.36% ตามลำดับ ในขณะที่ตัวทำละลายร่วมเมทานอล 5% และ 7% จะได้ค่าร้อยละการนำน้ำมันกลับมาเท่ากับ 51.94% และ 44.40% ตามลำดับ การศึกษาสมบัติทางกายภาพและทางเคมีของน้ำมันที่ได้จากเมล็ดยางพารานี้เพื่อใช้ในการประมาณความเหมาะสมต่อการนำไปผลิตเป็นน้ำมันไบโอดีเซล โดยทำการวิเคราะห์สมบัติต่างๆ ของน้ำมันด้วยเครื่องวิเคราะห์สมบัติทางความร้อน (TGA) เครื่องฟูเรียร์อินฟาเรด (FTIR) และเครื่องสแกนค่าความร้อน (DSC) จากผลการทดลองพบว่าเส้นสเปกตรัมโปรตอนแม่เหล็กนิวเคลียร์ (^1H NMR) ของน้ำมันเมล็ดยางพารา ประกอบด้วยกรดไขมันอิ่มตัวของ กรดลิโนเลนิก 17.19% กรดลิโนเลอิก 39.50% กรดโอเลอิก 26.10% และกรดไขมันอิ่มตัว 17.21% และมีความสอดคล้องกันกับผลการวิเคราะห์ด้วยเครื่องแก๊สโครมาโทกราฟี

Title	EXTRACTION OF RUBBER SEED OIL BY LIQUEFIED DIMETHYL ETHER
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Program	Chemical Engineering
Department	Industrial Engineering
Academic Year	2015

ABSTRACT

The extraction of rubber seed oil using liquefied dimethyl ether is investigated in this study. The effects of extraction parameters including extraction temperature (30, 35, 40, 45 and 50°C), extraction time (15, 30, 45, 60 and 75 min), ratio of rubber seed to solvent (1:2, 1:3, 1:4 and 1:5 w/w), and co-solvent on %recovery are reported. The maximum 67.85% oil recovery was obtained during the experiment conducted with liquefied dimethyl ether as solvent at the condition of 1:3 w/w solute to solvent ratio, 30 min extraction time and 30°C extraction temperature. For the effect of co-solvent, %recovery was reduced by increasing the amount of both co-solvent ethanol 5% and 7% (oil recovery 56.13% and 52.36%) methanol 5% and 7% (oil recovery 51.94% and 44.40%). Physico-chemical properties of oil obtained from the rubber seed were estimated to measure its suitability for biodiesel production. Other characterization of oil including thermal gravimetric analysis (TGA), FTIR and differential scanning calorimeter (DSC) were also determined. Proton nuclear magnetic resonance (^{1}H NMR) spectra of the obtained rubber seed oil (RSO) revealed 17.19% linolenic, 39.50% linoleic, 26.10% oleic and 17.21% saturated fatty acid in its composition. These compositional data were qualitatively confirmed with GC analysis which is slightly different.

ACKNOWLEDGEMENTS

We are deeply grateful to Dr.Panatpong Boonnoun for his valuable advice and his patient proofreading towards the completion of this study. His ideas are so useful that this study becomes more helpful for worldwide transportation in future. Furthermore, we also sincerely thank Assistant Professor Dr.Isarawut Prasertsung for his kindness in lending some experimental equipment.

Additionally, we would like to thank those whose names are not mentioned here but have greatly inspired and encouraged us until this study comes to a perfect end.

Lalita Deechanuan
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LIST OF CONTENTS

Page

Chapter

LIST OF CONTENTS (CONT.)

LIST OF CONTENTS (CONT.)

Chapter **Page**

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Rationale

As concerns on the depletion fossil fuels and global warming has a rised in the last decade, alternative forms of energy including biofuels have become a center of attention. Biofuels are produced from sources such as corn, soybean, flaxseed, rapeseed, sugarcane, palm oil, sugar beet, raw sewage, food scraps, animal fats, and rubber seed [1]. As current transportation energy relies heavily on diesel fuels, production of biodiesel to replace petroleum diesels remains to be the field that gains particular interests from researchers worldwide. Biodiesel is a mixture of fatty acid alkyl esters obtained from trans-esterification (ester exchange) of feedstock esters [2]. Various raw materials can be used for biodiesel production such as oil seeds (vegetable oil), animal fats, algae and waste such as waste cooking oil, and greases [3]. The use of edible raw materials for biodiesel production has recently been of great concern due to the sustainability issues related to the food versus fuel dilemma. As such, non-edible oils from various natural sources such as rubber seeds, soap nut, cassava, sal, mahua, neem, karanja, kusum and jatropha therefore have gained increasing interests as a biodiesel source [4]. Of particular interests in Asia and South-East Asia, rubber seeds which contain 50-60 wt% oil and rubber kernels containing 40-50 wt% oil [5-14] are of great potentials for biodiesel production as the plants are grown widely in the regions and the oil has no other current commercial applications.

The extractions of rubber seeds by variety of methods have been studied by some research groups. Henry et al., 2013 [15] reported the most suitable operating condition for extraction of rubber seed oil with mechanical hydraulic press to be at 120 bar and 90 min pressing time, at which condition, the oil yield of 32% (g extracted oil/g seeds) was obtained. The yield obtained by mechanical press was however lower than that obtained extraction with organic solvents such as hexane and petroleum ether, whose oil yield was about 55% (Nian-Yian et al., 2013 [16], Ali et al., 2015 [17]). Nevertheless, the main disadvantage of solvent extraction is the requirement for solvent evaporation, which is typically an energy intensive process. Alternatively, Nian-Yian et al., 2013 [16] has attempted to employ supercritical carbon dioxide (SC-

CO_2) for oil extraction from rubber seeds, the yield obtained was however rather low (30%). Despite the fact that SC-CO_2 requires no solvent separation step, it is however carried out at high pressure (30 MPa), the low extraction oil yield would make the process uneconomical.

Alternatively, liquefied dimethyl ether (DME) is a strong solvent for lipids and has a wide range of potential use in food, pharmaceutical, and cosmetic applications. DME is non-toxic, non-reactive, does not cause a pH change in aqueous solution. Because of its low boiling point (-24.8°C), virtually complete solvent removal can be carried out easily at moderate, or ambient, temperatures [18-19]. DME is also partially miscible with water, with a solubility of water in DME of between 10 and 20 mole% [19]. This allows simple extraction of wet samples without the requirements for high energy consuming pre-drying step. Peng Li et al. [20] reported that bio-crudes (predominant components were lipids with carbon number from C16 to C18 which consists of both saturated and unsaturated fatty acids) can be extracted from spent coffee ground, tea leaf waste, orange peel and gramineous weed by DME extraction at 20°C and 0.51 MPa. The extraction yields calculated were 97.6%, 852.6%, 688.8% and 214.8%, respectively, based on soxhlet extraction with hexane (100% basis). The extremely high extraction bio-crudes yield obtained in their study was due to the fact that about 88% of water was removed from the biomass. Catchpole et al. [19, 21] studied the extraction of lipids from a specialist dairy stream and fermentation biomass using near critical DME extraction (temperature 40-60°C, pressure 0.4-4 MPa). Kanda et al. [22] studied wet extraction of green crude from microalgae and the results show that more than 99% yield (based on Bligh-Dyer's method) can be achieved. This study therefore aims to investigate the extraction of oil from raw rubber seeds (without drying) using liquefied DME. The effect of extraction parameters including agitation rate, solvent to rubber seeds sample mass ratio, temperature and time on oil yield are determined along with the effect of using ethanol and methanol as co-solvents.

Objectives

1. To investigate the possibility to use liquefied dimethyl ether as extractant for extraction of oil from rubber seed.

2. To study the effect of extraction parameters including temperature sample to solvent ratio, and time on the recovery of extracted oil from rubber seed.

Scope of research

1. Determine the effect of temperature on extracted rubber oil recovery at 30, 35, 40, 45, 50°C.

2. Determine the effect of solvent to sample mass ratio on extracted rubber oil recovery at 1:2, 1:3, 1:4, 1:5.

3. Determine the effect of time on extracted rubber oil recovery at 15, 30, 45, 60, 75 min.

4. The rubber seed oil obtained at the best condition is characterized by differential scanning calorimeter (DSC), Fourier transform infrared (FT-IR) spectroscopy and Thermal-gravimetric analysis (TGA).

5. The rubber seed oil obtained at the best condition is analyzed by GC to determine the fatty acid composition and compare the properties with petroleum diesel (data from literature).

6. The rubber seed oil obtained at the best condition is analyzed by titration to determine the free fatty acid.

Expected benefits

The rubber seed which is a waste from agriculture is expected to become an important source for biodiesel production.

CHAPTER II

BACKGROUND AND LITERATURE

Rubber seed

Hevea brasiliensis tree, commonly referred to Rubber tree, belongs to the family Euphorbiaceae. This rubber tree originates from the Amazon rainforest (Brazil). The tree is the primary source of natural rubber and produces 99% of world's natural rubber. Moreover, the tree's sap-like extract (known as latex) can be collected and used in various applications. It is distributed mainly in Indonesia, Malaysia, Liberia, India, Srilanka, Sarawak, and Thailand. Natural rubber tree producer in the world are Thailand (35%), Indonesia (23%), Malaysia (12%), India (9%), and China (7%). Growing up to 34 min height, the tree requires heavy rainfall and produces seeds (show in Figure 1) weighing from 2 to 4 g that do not currently have any major industrial applications [5-8]. On an average, a healthy tree can give about 500 g of useful seeds during a normal year and this works out to 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 a non-edible vegetable oil, which contain 50-60 wt% oil and kernel contain 40-50 wt% of brown color oil. The oil is high in unsaturated constituents 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 species such as palmitic (10.2 wt%) and stearic (8.7 wt%) acids [5-14].

Figure 1 Rubber seed

Source : http://www.hxcorp.com.vn/news/653-advantages-of-using-rubber-seed-to-produce-biodiesel.html

Rubber seed oil

Since rubber seed contains high amount of oil, the extraction of oil from rubber seed is widely interested. The extracted rubber seed oil is classified as non-edible oil so its application is to use as fuel. However, crude rubber seed oil has high viscosity and it is not suitable to replace diesel. It is therefore reacted with alcohol to adjust its properties for biodiesel production (esterification of transesterification). The properties of rubber seed oil compared with petroleum diesel are shown in the Table 3

Table 3 The properties of rubber seed oil in comparison with diesel.

Property	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 [23]

The fatty acid composition and the important properties of rubber seed oil in comparison with other oils is given in Table 4 [2-27]. It consists of 18.9% saturation comprising of palmitic and stearic acids and 80.5% un-saturation comprising mainly of oleic, linoleic and linolenic acids. Saturation fatty acid methyl esters increase the cloud point, cetane number and improve stability whereas more poly un-saturates reduce the cloud point and cetane number and stability. The type and percentage of fatty acids contained in vegetable oil depends on the plant species and on the growth conditions of the plant. Though vegetable oils are of very low volatility in nature, it quickly produces volatile.

Property of Rubber seed oil Diesel

Combustible compounds upon heating. The free fatty acid content of unrefined rubber seed oil was about 17%, i.e. acid value of 34. The yield of esterification process decreases considerably 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 that the alkaline catalyzed transesterification process is not suitable to produce esters from unrefined oils. In order to reduce the acid value (i.e. for reducing FFA), the oil is to be refined.

Table 4 Properties of rubber seed oil in comparison with other 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

There are two main methods that have been identified for the extraction of the oil: (i) Soxhlet extraction and (ii) Dimethyl ether extraction. Before the oil extraction takes place, seeds have to be dried. Seed can be either dried in the oven (60°C) for 2 days. 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.

1. Soxhlet extraction

A Soxhlet extractor is a piece of laboratory apparatus invented in 1879 by Franz von Soxhlet. It was originally designed for the extraction of a lipid from a solid material. Typically, 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.

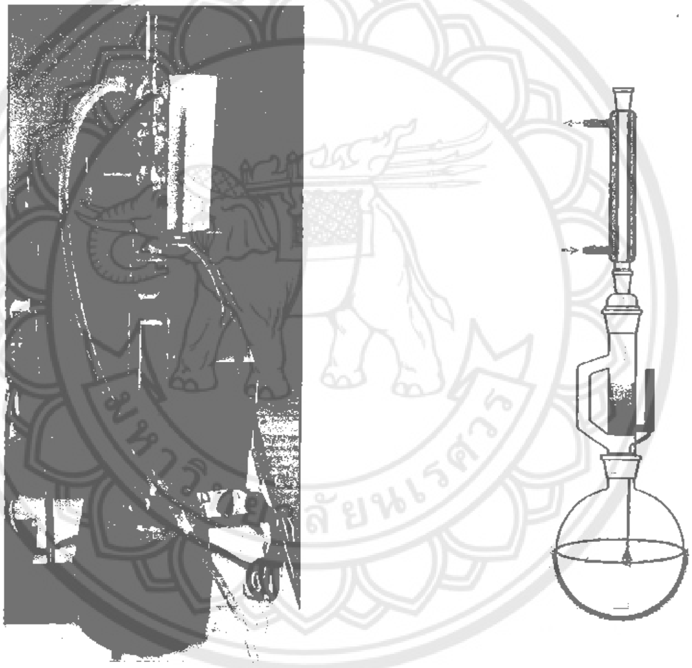
During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent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

Mass transfer to or from suspended solids is important in many processing situations. Solid–liquid mass transfer may be rate limiting in heterogeneous catalysis, during dissolution of solids, adsorption, as well as in other cases. The rate of mass transfer to or from the suspended particle depends on the solid–liquid mass transfer coefficient (k_L), the total solid–liquid interfacial area (A_S), and the concentration driving force; thus,

$$V_L \frac{dC_L}{dt} = k_L A_S (C^* - C_L) \qquad (1)$$

Where : C_L is the concentration of the transferring component in the liquid at time t, C^* is the saturation concentration (or solubility) of the transferring component, and V_L is the volume of the suspending liquid. Equation 36 is written for transfer from the solid to the liquid. By analogy with the film model of mass transfer, the coefficient k_L conceptually equals the diffusivity of the solute divided by the thickness of the stagnant liquid film at the solid–liquid interface; k_L is needed for quantifying the rate of mass transfer. Methods for estimating the solid–liquid or solid–gas (also gas–liquid if liquid is adsorbed as a very thin film on the surface of the solid) mass transfer coefficient k_L in various situations are discussed in a later section of this monograph.



(a) (b)

Figure 2 (a) Extraction in progress (b) A schematic of a Soxhlet extractor

Source : https://en.wikipedia.org/wiki/Soxhlet_extractor

2. 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 [30-35].

2.1 Chemical and physical properties

Dimethyl ether is a colourless gas at room temperature and pressure with a characteristic sweet ethereal odour. 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 4.

Table 5 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 5, 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.

Analytical technique of extracted rubber seed oil

1. Gas chromatography (GC)

Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound. In preparative chromatography, GC can be used to prepare pure compounds from a mixture.

In gas chromatography, the mobile phase (or "moving phase") is a carrier gas, usually an inert gas such as helium or an un-reactive gas such as nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a piece of glass or metal tubing called a column (an homage to the fractionating column used in distillation). The instrument used to perform gas chromatography is called a gas chromatograph (or "aerograph", "gas separator").

The gaseous compounds being analyzed interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound. The comparison of retention times is what gives GC its analytical usefulness.

Gas chromatography is in principle similar to column chromatography (as well as other forms of chromatography, such as HPLC, TLC), but has several notable differences. First, the process of separating the compounds in a mixture is carried out between a liquid stationary phase and a gas mobile phase, whereas in column chromatography the stationary phase is a solid and the mobile phase is a liquid. (Hence the full name of the procedure is "Gas-liquid chromatography", referring to the mobile and stationary phases, respectively.) Second, the column through which the gas phase passes is located in an oven where the temperature of the gas can be controlled, whereas column chromatography (typically) has no such temperature control. Finally, the concentration of a compound in the gas phase is solely a function of the vapor pressure of the gas.

Gas chromatography is also similar to fractional distillation, since both processes separate the components of a mixture primarily based on boiling point (or vapor pressure) differences. However, fractional distillation is typically used to separate components of a mixture on a large scale, whereas GC can be used on a much smaller scale (i.e. micro scale).

Gas chromatography is also sometimes known as vapor-phase chromatography (VPC), or gas-liquid partition chromatography (GLPC). These alternative names, as well as their respective abbreviations, are frequently used in scientific literature. Strictly speaking, GLPC is the most correct terminology, and is thus preferred by many authors.

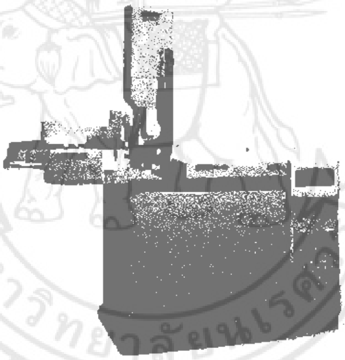


Figure 3 Gas Chromatography (GC)

Source : http://www.env.eng.chula.ac.th/?q=content/gas-chromatography-gc

2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry or DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

Types of DSC:

- Power compensated DSC ; keeps power supply constant
- Heat flux DSC ; keeps heat flux constant

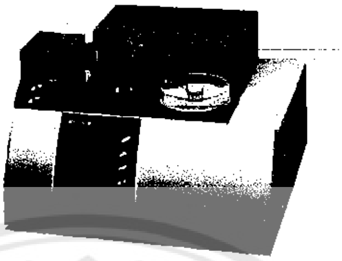


Figure 4 Differential scanning calorimetry (DSC)

Source : http://www.lihyuan.com.tw/en/product/dsc-204-f1.html

The result of a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions: exothermic reactions in the sample shown with a positive or negative peak, depending on the kind of technology used in the experiment. This curve can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using equation (2):

$$\Delta H = KA \qquad (2)$$

Where ΔH is the enthalpy of transition, K is the calorimetric constant, and A is the area under the curve. The calorimetric constant will vary from instrument to instrument, and can be determined by analyzing a well-characterized sample with known enthalpies of transition.

Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures T_g. DSC can also be used to study oxidation, as well as other chemical reactions. Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs.

As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (T_m). The melting process results in an endothermic peak in the DSC curve. The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase diagrams for various chemical systems.

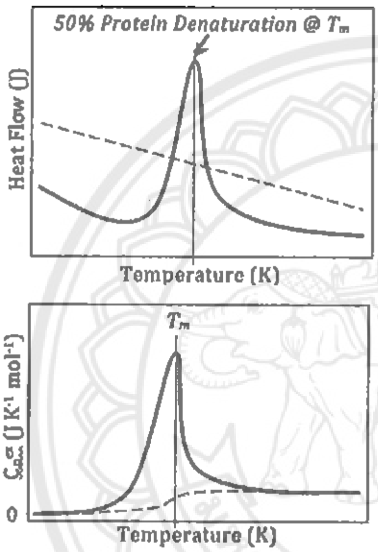


Figure 5 Top: A schematic DSC curve of amount of energy input (y) required to maintain each temperature (x), scanned across a range of temperatures.

Bottom: Normalized curves setting the initial heat capacity as the reference. Buffer-buffer baseline (dashed) and protein-buffer variance (solid).

Source :https://en.wikipedia.org/wiki/Differential_scanning_calorimetry

3. Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum. For other uses of this kind of technique, see Fourier transform spectroscopy.

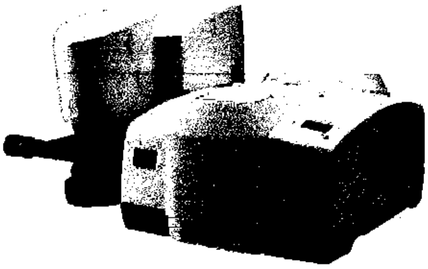


Figure 6 Fourier transform infrared spectroscopy (FT-IR)

Source : https://www.laboratory-equipment.com/spectrophotometers-electrophoresis/spotlight-400-ft-ir-microscopy-system-perkin-elmer.php

The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most straightforward way to do this, the "dispersive spectroscopy" technique, is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength. (This is how UV-Vis spectrometers work, for example.)

Fourier transform spectroscopy is a less intuitive way to obtain the same information. Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength.

The beam described above is generated by starting with a broadband light source one containing the full spectrum of wavelengths to be measured. The light shines into a Michelson interferometer a certain configuration of mirrors, one of which is moved by a motor. As this mirror moves, each wavelength of light in the beam is periodically blocked, transmitted, blocked, transmitted, by the interferometer, due to wave interference. Different wavelengths are modulated at different rates, so that at each moment, the beam coming out of the interferometer has a different spectrum.

As mentioned, computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferogram"

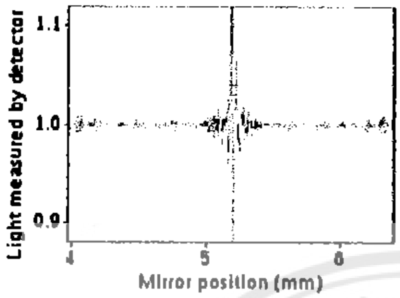


Figure 7 An FTIR interferogram. The central peak is at the ZPD position ("Zero Path Difference" or zero retardation) where the maximum amount of light passes through the interferometer to the detector.

Source :https://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy

4. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction).

TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). Common applications of TGA are (1) materials characterization through analysis of characteristic decomposition patterns, (2) studies of degradation mechanisms and reaction kinetics, (3) determination of organic content in a sample, and (4) determination of inorganic (e.g. ash) content in a sample, which may be useful for corroborating predicted material structures or simply used as a chemical analysis. It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings and paints. Discussion of the TGA apparatus, methods, and trace analysis will be elaborated upon below. Thermal stability, oxidation, and combustion, all of which are possible interpretations of TGA traces, will also be discussed.

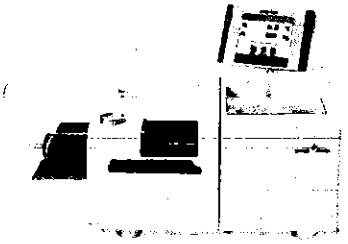


Figure 8 Thermal gravimetric analysis (TGA)

Source : http://www.azom.com/equipment-details.aspx?EquipID=3868

5. Titration

Free Fatty Acids (FFA) are the result of the breakdown of oil. %FFA is usually used to describe the FFA content of oils. With a little math from equation (3), we can use the same titration procedure we use to titrate rubber seed oil to determine %FFA.

$$\%FFA = \frac{V_{KOH} \text{ x } [KOH] \text{ x } 25.6}{\text{Weight of sample}} \tag{3}$$

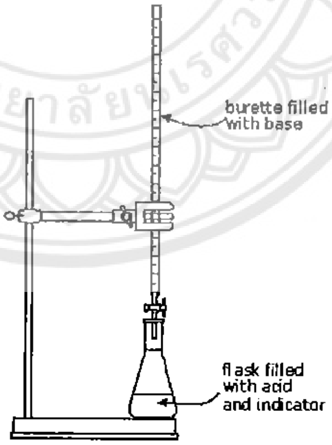


Figure 9 Titration

Source : http://www.web-formulas.com/Formulas_of_Chemistry/Process_of_Titration.aspx

6. Viscosity Measurement

The viscosity is related to the flow, the spray nozzle in a combustion chamber. The small spray can cause complete combustion in diesel engines. The viscosity of biodiesel production depends on the type of vegetable oil as raw material. The viscosity of the oil can be analyzed by a viscometer standard ASTM-D 445.

Figure 10 Ubbelohde Viscometer

Source : http://www.lauda-brinkmann.com/glasscapillary.html

7. Density Measurement

The density of fuel related to energy from the fuel. Fuel has more density, provides more energy. Density is weight per unit volume. Density can be analyzed according to the standard EN ISO 3657/12185.

CHAPTER III

MATERIALS AND METHODS

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. Hexanes (99%), Ethyl Acetate (99.8%), Acetone (99.5%) and Ethanol (99.9%) are obtained from Merck, Thailand. Liquefied DME spray can obtain from Tamiya Thailand.

Methods

The rubber seeds were firstly de-shelled manually, kernels and seeds were collected. They were slightly crushed to approximately 1 mm diameter and dried for 24 hours at 60°C. The crushed rubber seeds were kept in desiccators to maintain the moisture content before extraction.

1. DME extraction

The apparatus was designed to evaluate the extraction efficiency of the DME extraction as shown in Fig. 3.1. Approximately 10 g. of the crushed rubber seed was firstly loaded into an extractor (100 ml stainless steel) along with a 8 mm diameter of magnetic bar. Liquefied DME and co-solvent (ethanol or methanol) were filled into the extractor at required composition. The temperature of the system was controlled at desired temperature by heating jacket connecting with control box. The extractor was the placed onto a hot plate stirrer and the agitation rate was adjusted. After extraction, the extractor was connected to a separation unit which made of pressure-resistant glass coated with polycarbonate. Needle valve was turned to open then DME and only compounds were transferred to the separation unit through membrane filter (0.65 μm pore diameter) and stainless steel filter (5 μm pore diameter) which can separate the solid residues from the extracts. The DME was evaporated by opening the reducing valve of the separation unit. The remained liquid sample was then dried at 120°C and weighted then analyzed its composition by GC.

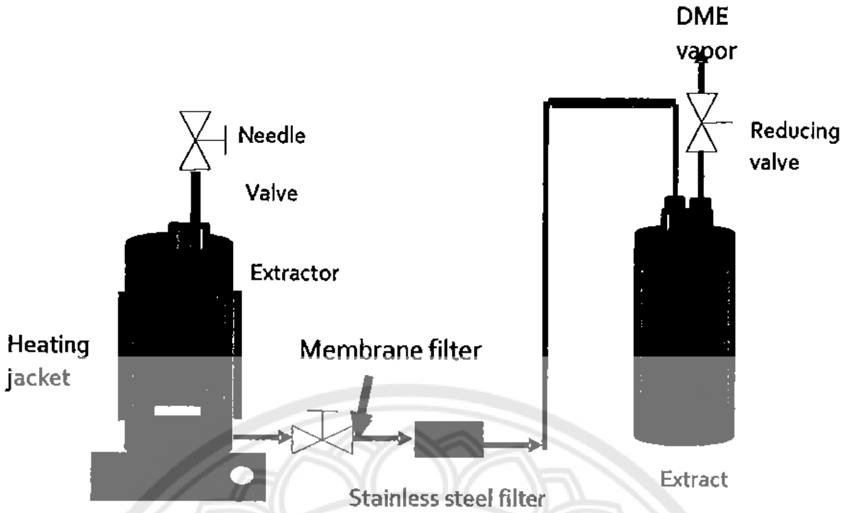


Figure 11 DME extraction apparatus

Table 6 The extraction condition with fixed time 30 minute and 1:3 sample to solvent (w/w)

Temperature	Weight oil	%Recovery
30		
35		
40		
45		
50		

Table 7 The extraction condition with fixed time 30 minute and temperature 30°C

Ratio	Weight oil	%Recovery
1:2		
1:3		
1:4		
1:5		

Table 8 The extraction condition with fixed temperature 30°C and 1:3 sample to solvent (w/w)

Time	Weight oil	%Recovery
0		
15		
30		
45		
60		
75		

2. Soxhlet extraction

10 grams of dried kernels and seeds were extracted with 200 ml of the suitable solvent determined by the previous experiment using soxhlet apparatus for 15 hours. The total amount of oil was analyzed by weighting and the composition of extracted oil was analyzed by GC, DSC, FT-IR, and TGA. The total oil content extracted by this method was used as a basis to calculated %recovery of rubber seed oil extracted by DME extraction from equation (4).

$$\%\text{Recovery} = \frac{\text{Oil content extracted by DME}}{\text{Oil content extracted by soxhlet}} \times 100\% \qquad (4)$$

Characterization of extracted rubber seed oil

1. Gas chromatography (GC)

Gas chromatography analysis the fatty acid composition of the fatty acid methyl ester was analyzed using an Agilent 6890N series Gas Chromatography equipped with a flame ionization detector (FID) on a split injector. A fused silica capillary column (DB-225, 30 mm-0.32 mm i.d., J&W Scientific, USA) was used with the injector and detector temperature maintained at 230 and 250°C, respectively. The oven temperature was programmed at 160°C for 2 min and then increased to 230°C at 4°C/min. The carrier gas used was nitrogen at a flow rate of 1.5 mL/min.

2. Differential scanning calorimeter (DSC)

DSC plots helped measuring the phase change points. DSC analysis was conducted on extracted oil (10 mg) using DSC1 stare system (Metteler Toledo) with aluminium crucible. Thermal program was set with heating rate of 5°C/min for (1) heating from 25°C to 50°C and, holding for 10 min. To homogenize and dissolving any waxy material present (2) cooling from 50°C to -25°C (3) heating from -25°C to 50°C. DSC analysis was conducted for three cycles (repeated) with same sample and excellent reproducibility was observed.

3. Fourier transforms infrared (FT-IR) spectroscopy

IR spectra of the oil, kernel and cake were obtained using FT-IR instrument (Shimandzu:IR Affinity) using KBr as background for functional group identification. To obtain the IR spectra of oil sample (0.2-0.4 mg), KBr is used in pellet form and for solid sample (moisture free) analyses KBr was mixed in powder form with the sample (100:1 ratio) to get homogenous mixture. Pure KBr (pellet/powder) and then KBr with sample (liquid/solid) placed in sample holder and the infrared solution was analysed in the range of wave number 400-4000 cm^{-1}. FT-IR spectrums of the samples were used.

4. Thermal-gravimetric analysis (TGA)

Thermal stability behavior, onset and thermal decomposition temperatures of extracted oil was analyzed using TGA system (Netzsch:STA449F3A00). Non-isothermal TGA experiments of oil, cake and kernel (10 mg) were performed from ambient temperature to 800°C at a heating rate of 10°C/min. Inert gas was used as purge gas (flow rate of 60 ml/min) as well as protective gas (flow rate of 20 ml/min).

5. Viscosity Measurement

Determination of the viscosity of the oil can be measured with an instrument called a viscometer, according to standard ASTM D445. Ubbelohde viscometer is used in the experiment. First, charge the viscometer with the rubber seed oil. Put into the first, large tube: the reservoir. Between the two lines on the tube so that the amount of liquid charged will not obstruct the Air Tube during use. Next, connect clean, dry rubber tubing to the timing tube and the Air Tube, and place the viscometer in a temperature controlled liquid bath. The capillary must be vertical. The oil must come to the same temperature in the bath (40°C), take about 20 minutes. Seal off the rubber tubing that is connected to the air tube and gently suction it to the Timing Tube until the liquid reaches about 5 mm above the upper timing mark. Hold the liquid at this level by sealing the tube. This point is at least 2 cm below the bath liquid level. Release the air tube to allow the liquid to fall away from the upper timing mark of the capillary tube and timers until oil falls away from the lower timing mark then stop timers. Use this time to calculate the viscosity from equation (5).

$$\mu = Ct \qquad (5)$$

Where; μ = Constant of viscosity (cSt)

C = capillary constant of viscosity measurement depending on the size of the capillary. (cSt/s)

t = duration between upper timing mark and lower timing mark (s)

CHAPTER IV

RESULT AND DISCUSSION

The results of extraction parameters including temperature, solute to solvent ratio (w/w), extraction time and co-solvent (methanol and ethanol) on %recovery of rubber seed oil were reported in the first part of this section. The physicochemical properties such as acid value, viscosity and %FFA and characterization of rubber seed oil such as FTIR, ^{1}H NMR, fatty acid composition, cold flow properties comparison with DSC and thermal stability analyzed by TGA were then reported.

Extraction of rubber seed oil by dimethyl ether

1. Effect of temperature

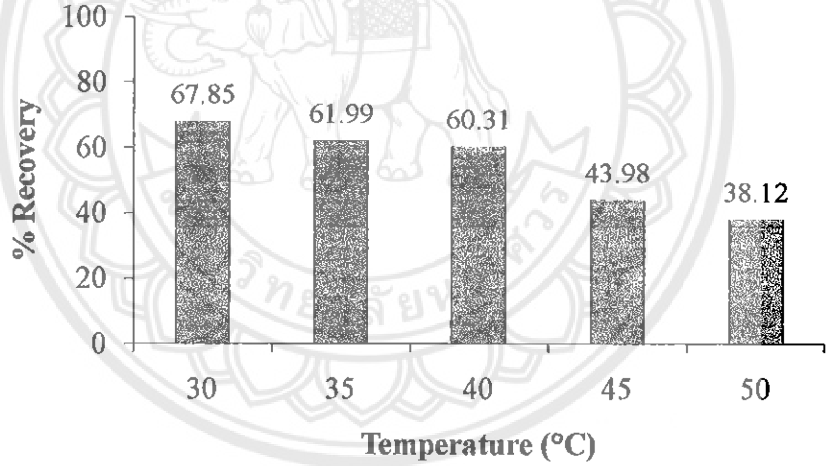


Figure 12 %recovery at various temperature (°C)

For study of effect of temperature on %recovery, the solute to solvent ratio, extraction time were fixed at 1:3 w/w and 30 minutes, respectively. The obtained results are shown in Figure 12. The maximum %recovery 67.85 was obtained with 30°C then slight decrease to 61.99 and 60.31 at 35°C and 40°C respectively. The results might be explained by the decreasing of solvent density (liquid phase) and some of solvent change from liquid to vapor phase caused by the increasing temperature. The data of liquefied DME density at various temperatures was reported by Flick, Ernest W. [36] as shown in Table 9.

Table 9 Liquefied DME density at various temperatures

T (°C)	ρ (g/ml)	
	Liquid	**Vapor**
20	0.6610	0.0104
30	0.6455	0.0142
40	0.6292	0.0188
50	0.6116	0.0241
60	0.5932	0.0306

2. Effect of solute to solvent ratio

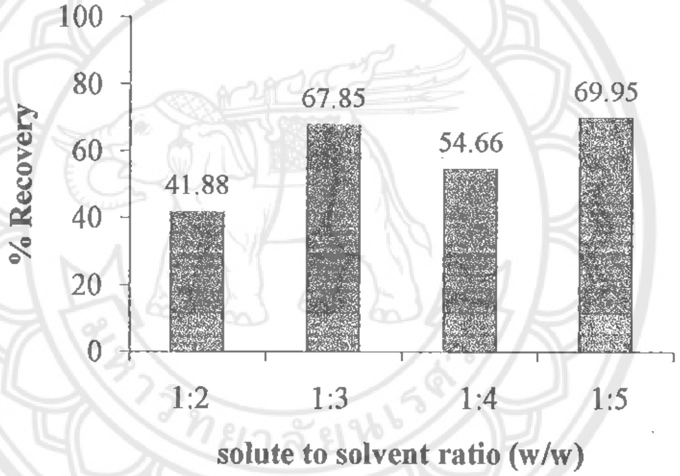


Figure 13 %recovery at various solute to solvent ratio (w/w)

For study of effect of solute to solvent ratio on %recovery, the extraction time and temperature were fixed at 30 minutes and 30°C (the best condition from the previous experiment), respectively. From figure 13, %recovery of RSO was increased from 41.88% to 67.85% by increasing solute to solvent ratio from 1:2 to 1:3 w/w. However %recovery at 1:3 and 1:5 solute to solvent ratio are not different. The results might be explained by the equilibrium of RSO in liquefied DME occurred at the solute to solvent ratio of 1:3 w/w. As a result 1:3 solute to solvent ratio more suitable to be selected in term of less solvent used.

3. Effect of time

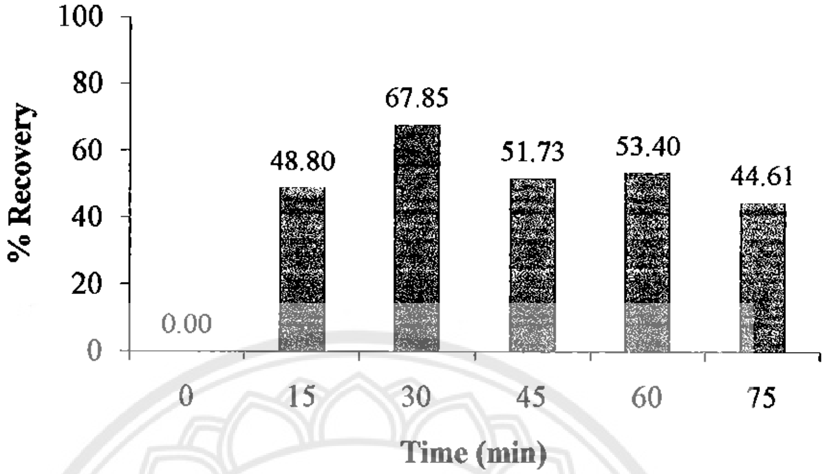


Figure 14 %recovery at various time (min)

For study of effect of time on %recovery, the solute to solvent ratio and temperature were fixed at 1:3 w/w and 30°C (the best condition from the previous experiments), respectively. From figure 14, %recovery was increased from 48.796% to 67.853% by increasing extraction time from 15 to 30 minutes. However, %recovery of RSO was slightly decreased by increasing extraction time from 30 to 75 minutes. In general, %recovery after 30 minute should be constant because the system access to equilibrium.

4. Effect of co-solvents

4.1 Dimethyl ether and ethanol

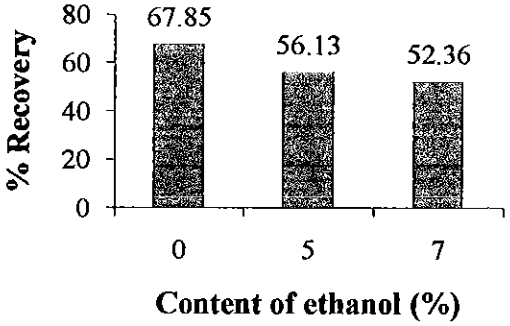


Figure 15 %recovery at various content of ethanol (%)

The best condition of extraction from the study result is temperature 30°C, time 30minute and 1:3 solute to solvent, use these condition to study the effect of co-solvents (DME and ethanol). From figure 15, maximum %recovery is 67.85 at 0% ethanol then slight decrease to 56.13% and 52.36% respectively because oil recovery extracted using non-polar solvents but ethanol and methanol has relative polarity 0.654 and 0.762 respectively, reduce %recovery.

4.2 Dimethyl ether and methanol

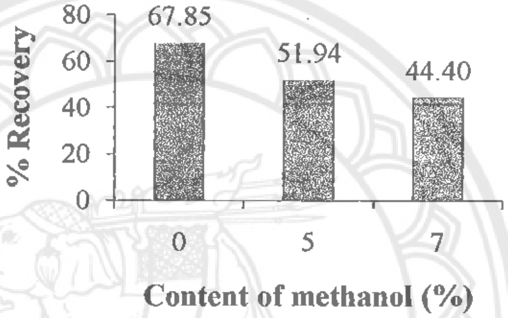


Figure 16 %recovery at various content of methanol (%)

The best condition of extraction from the study result is temperature 30°C, time 30 minute and 1:3 solute to solvent, use these condition to study the effect of co-solvents (Dimethyl ether and methanol). From figure 16, maximum %recovery is 67.85 at 0% ethanol then slight decrease to 51.94% and 44.40% respectively. But in methanol have more relative polarity than in ethanol so in same percentage, co-solvent (dimethyl ether and methanol) reduce more %recovery.

Characterization of rubber seed oil (RSO)

1. Physico-chemical properties of RSO

RSO obtained at optimum extraction condition was characterized for various physico-chemical properties using standard methods. The methods used and the values obtained are show in Table 10 Oil obtained using DME appeared to be yellow gold color. Dynamic viscosity of RSO at 25°C was measured by glass capillary viscometer and kinematic viscosity found to be 36.8 Cst which is higher compared to RSO from literature (Ali Shemsedin Reshad, Pankaj Tiwari, Vaibhav V. Goud, 2015), Jatropha curcas L. oil and it was higher compared to conventional diesel (<5 Cst). The acid value of the extracted RSO was showed in Table 10 The obtained result was 10.659 mg of KOH/g of oil and which was lower than the acid value of RSO from literature (Ali Shemsedin Reshad, Pankaj Tiwari, Vaibhav V. Goud, 2015) (24 mg of KOH/g of oil), Crude Pangium edule oil (19.62 mg of KOH/g of oil), Ceiba Pentandra oil (15.3 mg of KOH/g of oil) but It was higher compared to Jatropha curcas L. oil (2.24 mg of KOH/g of oil) and petroleum diesel (0.09 mg of KOH/g of oil). Free fatty acid content of RSO was obtained to be 5.062% which is lower than RSO from literature(Ali Shemsedin Reshad, Pankaj Tiwari, Vaibhav V. Goud, 2015) (12.12%). It can be implied that RSO obtained from DME extraction is still need to be proceed before use as biodiesel.

Table 10 Comparison of physico-chemical properties of different seed oils with rubber seed oil.

Properties	Rubber seed (this study)	Rubber seed (literature)	Petroleum diesel (Siddharth Jain 2012)	Standard biodiesel (Siddharth Jain 2012)	CP[1]	JCL[2]	CPE[3]	Testing methods
Color	Yellow gold	Golden yellowish	Greenish-blue	Golden brown	Yellow	-	-	
Kinematic viscosity, Cst at 25°C	36.8	30	2.6 (@ 30°C)	1.9-6.0 (@ 30°C)	34.456	77.4	27.17	ASTM (D445)
Acid value, mg of KOH/g of oil	10.659	24	0.09	0.8	15.3	2.24	19.62	AOCS (Te 1a-64)
Free fatty acid, %	5.062	12.12	-	-	7.69	-	-	AOCS (Te 1a-64)

[1] Ceiba Pentandra oil

[2] Jatropha curcas L. oil

[3] Crude Pangium edule oil

2. Thermal stability of RSO

A good thermal decomposition profile of oil can be obtained at heating rate of 10°C /min under inert atmosphere. Therefore in this study the same conditions were used for estimation of onset temperature of the samples. The overall thermal decomposition of RSO was observed to be a single stage process (Figure 17). A negligible weight loss (<0.2%) of RSO was observed at around 240°C due to presence of moisture (free water). TG curve also confirms the absence of solvent in the oil sample. Sudden decrease in weight of the oil sample was started from 310°C to 480°C which may be due to the breakdown of heavier hydrocarbon molecules to lower molecular hydrocarbon, CO_2 and CO. The TG analysis confirms that RSO is thermally stable up to temperature of 370°C (onset point). The oil weight loss of 50% and 90% were obtained at 420°C and 460°C respectively (Figure 17). The maximum rates of weight losses for extracted oil were occurred at temperature 425°C, the point is that the eutectic point.

3. Analysis compositions of RSO

Fatty acid compositions of the RSO were analyzed by ^{1}H NMR spectroscopy. Identified peaks (1-10) in NMR spectra (Figure 18) were used to determine linolenic (Ln), linoleic (L), oleic (O) and saturated (S) fatty acid present in the RSO. The percentage of fatty acids were obtained by Equations (6) – (9).

Where : A : 1, B : 2, C : 5, D : 6 and E : 7 are area of the peaks with Figure 18

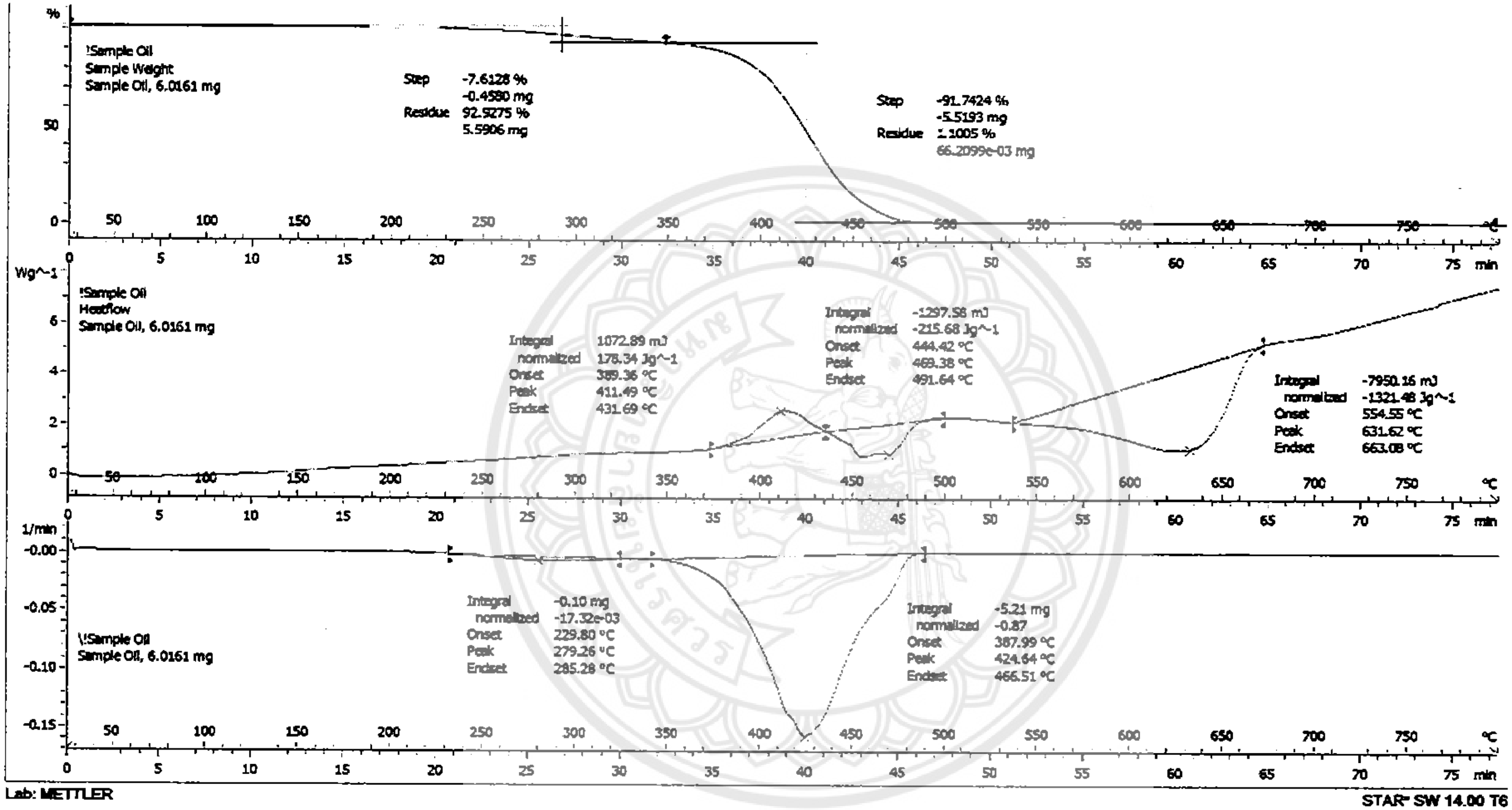


Figure 17 TGA curve of RSO at heating rate of 10°C/min under inert atmosphere.

$$\mathrm{Ln}(\%) = 100\left(\frac{\mathrm{B}}{\mathrm{A+B}}\right) \quad (6)$$

$$\mathrm{L}(\%) = 100\left[\frac{\mathrm{E}}{\mathrm{D}} - 2\left(\frac{\mathrm{B}}{\mathrm{A+B}}\right)\right] \quad (7)$$

$$\mathrm{O}(\%) = 100\left[\frac{\mathrm{C}}{2\mathrm{D}} - \frac{\mathrm{E}}{\mathrm{D}} + \left(\frac{\mathrm{B}}{\mathrm{A+B}}\right)\right] \quad (8)$$

$$\mathrm{S}(\%) = 100\left(1 - \frac{\mathrm{C}}{\mathrm{D}}\right) \quad (9)$$

^{1}H NMR analysis showed that RSO contains saturated, monounsaturated and polyunsaturated fatty acid (Table 11). The unsaturated fatty acids such as linoleic (polyunsaturated), linolenic (polyunsaturated) and oleic (monounsaturated) acid were foundby GC to be 41.21%, 15.25% and 23.10% respectively, with 15.59% as saturated acid. And fatty acids such as linoleic, linolenic, oleic acid were found by equation to be 39.50%, 17.19% and 26.10% respectively, with 17.21% as saturated acid. The fatty acids analysis by GC is similar to the calculation of the equation derived from the analysis by ^{1}H NMR. The fees vary only slightly. There are significant differences in fatty acid compositions of RSO compared to the reported value (Table 11). The data shows that linoleic acid is the prominent fatty acid in RSO. The high unsaturated fatty acid content of RSO contributes to its low temperature properties. Due to low profile of oleic acid (23.10%) RSO has less nutritional quality compared to olive (64.6-84.4%), canola (60-75%) and nusun oils (43.1-71.8%).

The signal assignments are listed in Table 12. The distinguishable groups are the protons of the terminal methyl of the FA chain, the methylene group next to the terminal methyl (1.597 ppm), methylene groups nearby one double bond (1.989 - 2.061 ppm), and methylene groups nearby to two double bonds (2.275 – 2.319 ppm). Other are methylene groups of glyceryl (α:4.137 – 4.152 ppm and β: 5.309 – 5.369 ppm) and protons attached to C=C

Table 11 Fatty acid composition of RSO analysis by GC and Equation

Fatty acid	Percentage	
	GC analysis	Calculation
Unsaturated fatty acid	80.01	82.79
Linoleic acid	41.21	39.5
Linolenic acid	15.25	17.19
Oleic acid	23.10	26.1
Palmitoleic acid	0.29	
Eicosenoic acid	0.16	
Saturated fatty acid	15.59	17.21
Myristic acid	0.12	
Stearic acid	6.39	
Arachidic acid	0.28	
Palmitic acid	8.80	

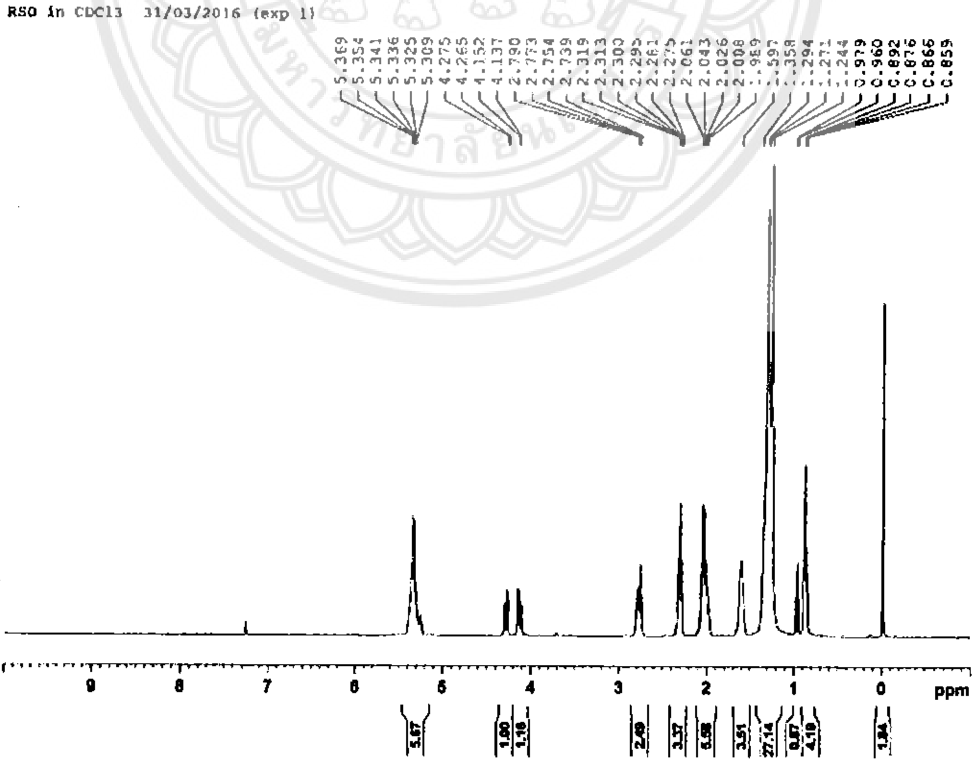


Figure 18 ^{1}H NMR spectra of RSO

Table 12 Signals present in ^{1}H NMR spectra of RSO and their assignment.

δ (ppm)	Assignment
0.859-0.979	-CH_3 terminal methyl
1.244-1.358	-CH_2 saturated aliphatic chain
1.597	-CH_2-C methylene α to terminal methyl
1.989-2.061	-CH_2-C=C allylic methylene
2.275-2.319	-CH_2-O-C=O acyl methylene
2.739-2.79	-C=C-CH_2-C=C- diallylic methylene
4.137-4.152	-CH_2-O-CO- in α position in glyceryl
4.265-4.275	-CH=CH- olefinic (FA chain)
5.309-5.369	-CH-O-CO- in β position in glyceryl

4. FT-IR analysis of RSO

FT-IR analysis of RSO. Figure 19 shows the FT-IR spectra of RSO. The main peaks and their assignment to functional groups are given in Table 13. The results in Table 12 show that the functional groups present in RSO are similar to those in other vegetable oils.

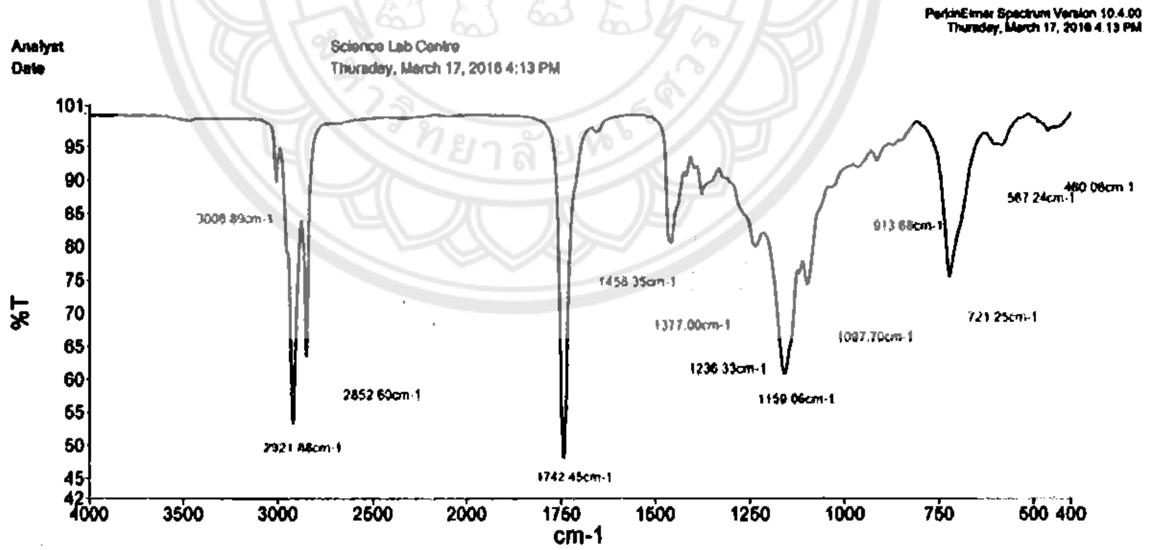


Figure 19 FT-IR spectra of RSO

Table 13 The main peaks in the FT-IR spectra of RSO

Peak (cm^{-1})	Functional group
3008, 2921, 2852	C-H stretching vibration (aliphatic)
1742	C=O stretching vibration (ester)
1435	C=C bending vibration (aliphatic)
1236, 1159, 1097	C-O-C stretching vibration (ester)
721	C-H group vibration (aliphatic)

5. Cold flow properties comparison with DSC

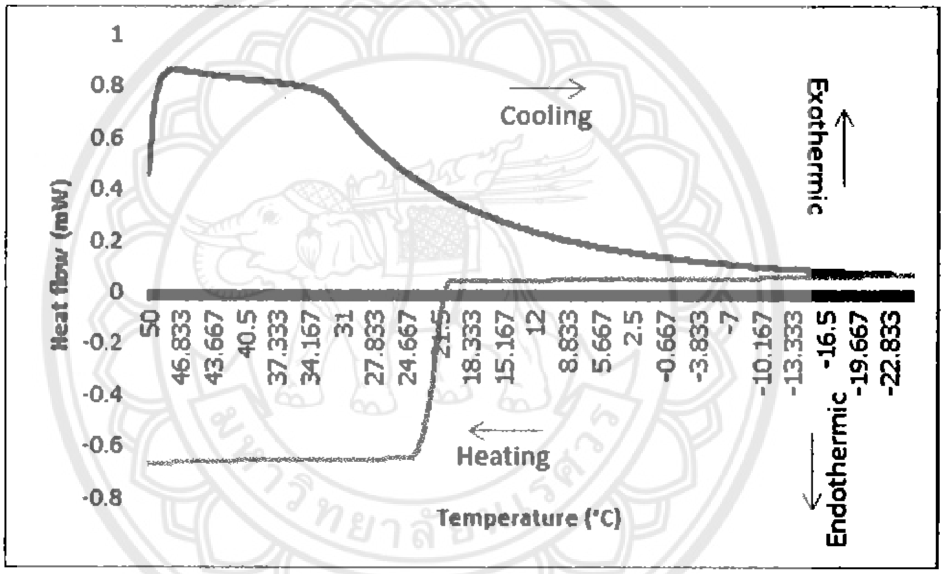


Figure 20 DSC curve at 5°C/min, heating and cooling rate under inert atmosphere, of RSO.

The saturated fatty acids content in RSO responsible for its poor cold flow property. The DSC profile for RSO is showed in Figure 20 Crystallization point of RSO was used to estimate the pour point on DSC curve. There were 2 exothermic peaks in the cooling zone of DSC curve associated with the change in phase from liquid to solid. The melting point can be determined from the heating zone when the sample temperature increase can be seen from the endothermic, a graph of the change in phase. Which is melting point is around 21°C at under inert atmosphere. The freezing point can be determined from the cooling zone when the temperature drops, the test sample is exothermic, the thermal accumulation rapid decline which is around -10°C. It is lower than the literature because of the lower amount of saturated fatty acid in oil [23, 26].

CHAPTER V

CONCLUSION AND RECOMMENDATION

Conclusion

Rubber seed oil was extracted using DME extraction techniques. The effect of different process parameters such as extraction time, solute to solvent ratio, temperature and co-solvent on oil recovery. The effect of time, solute to solvent ratio and temperature are found to be significant. An optimum %recovery of 67.85% on oil from DME extraction was obtained at conditions 1:3 w/w of solute to solvent ratio, 30 min extraction time, 30°C of temperature without co-solvent. The fatty acid compositions of RSO analysis by GC was found to be linoleic (41.21%), linolenic (15.25%), oleic (23.10%) and saturated fatty acid (15.59%). And estimated by ^{1}H NMR technique was found to be linoleic (39.5%), linolenic (17.19%), oleic (26.10%) and saturated fatty acid (17.21%). The physic-chemical characteristic of oil reveals that it can be considered as a potential source for biodiesel production.

Recommendation

- RSO should be further proceeded from the tranesterification, to get the RSO suitable to produce biodiesel fuel.

- The design of experiment such as response surface methodology (RSM) should be further used to optimize the process parameters to achieve maximum %recovery.

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APPENDIXES

Oil content extracted by Soxhlet = 4.775 g.

Table 14 Weight of RSO @ conditions fixed ratio 1:3, time 30 min.

Temperature	Weight oil	%Recovery
0	0	0.000
30	3.24	67.853
35	2.96	61.990
40	2.88	60.314
45	2.1	43.979
50	1.82	38.115

Table 15 Weight of RSO @ conditions fixed temp. 30°C, time 30 min

Ratio	Weight oil	%Recovery
1:2	2	41.885
1:3	3.24	67.853
1:4	2.61	54.660
1:5	3.34	69.948
1:6	1.6	33.508

Table 16 Weight of RSO @ conditions fixed ratio 1:3, Temp 30°C

Time	Weight oil	%Recovery
0	0	0.000
15	2.33	48.796
30	3.24	67.853
45	2.47	51.728
60	2.55	53.403
75	2.13	44.607

Table 17 Weight of RSO @ conditions fixed ratio 1:3, temp. 30°C, time 30 min extracted with Ethanol

%Ethanol	Weight(g)
0	3.24
3	2.37
5	2.68
7	2.5

Table 18 Weight of RSO @ conditions fixed ratio 1:3, temp. 30°C, time 30 min extracted with Methanol

%Methanol	Weight(g)
0	3.24
3	2.25
5	2.48
7	2.12

Table 19 Fatty acid composition of RSO analysis by GC

Fatty acids	Percentage		
	Test 1	Test 2	Average
Linoleic acid	41.16	41.26	41.21
Linolenic acid	15.25	15.25	15.25
Oleic acid	23.12	23.07	23.10
Palmitoleic acid	0.29	0.30	0.29
Elcosenoic acid	0.16	0.16	0.16
Myristic acid	0.13	0.12	0.12
Stearic acid	6.37	6.40	6.39
Arachidic acid	0.29	0.26	0.28
Palmitic acid	8.82	8.77	8.80

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