UNIVERSITI PUTRA MALAYSIA

OPTIMIZATION AND KINETICS OF SOLID LIQUID EXTRACTION OF MALAYSIAN *JATROPHA CURCAS* SEEDS

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By

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OPTIMIZATION AND KINETICS OF SOLID LIQUID EXTRACTION OF MALAYSIAN *JATROPHA CURCAS* SEEDS

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September 2009

Chairman: Zurina Zainal Abidin, PhD

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The Jatropha is a plant which grows in most of tropical and subtropical regions of the world. The oil from the Jatropha seeds can be used as fuel alternative and for making biodiesel. This work aimed to determine the optimum parameters to achieve maximum oil yield in solid liquid extraction of Jatropha seeds under experimental conditions. The optimum condition was then applied in ultrasound assisted and microwave pretreatment extraction methods to determine the amount of yield. The kinetics of the extraction was also studied based on the assumption of a second order mechanism. The extraction was carried out using a soxhlet extractor equipped with condenser and hot plate. The effects of five main factors which are namely type of solvents, temperature, solvent to solid ratio, reaction time and size of the raw material were investigated experimentally on the solid liquid extraction of Jatropha seed to optimize the extraction process. The optimum condition was found at eight hours reaction time, temperature of around 68°C, coarse particle size (0.5-0.75 mm), solvent to solid ratio of 6:1 (v/w) and using hexane as the solvent. The maximum amount of yield at optimized condition was at 47.3 % by wt. The activation energy was found to be 7145.05 (J/mol) and the highest initial extraction rate was calculated to be and 4.21 (g/L min). The maximum amount of oil extracted by ultrasound assisted and microwave pretreatment methods were 51.4 and 49.4% respectively. The oil extracted by conventional, ultrasound assisted and microwave pretreatment extraction methods contained, respectively, 0.62, 0.67 and 0.63% free fatty acid and 98.3, 97 and 97.7% triglyceride.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGOPTIMUMAN DAN KINETIK BAGI PENGEKSTRAKAN PEPEJAL CECAIR BIJI JARAK DARI MALAYSIA

Oleh

SEPIDAR SAYYAR

September 2009

Pengerusi: Zurina Zainal Abidin, PhD

Fakulti: Kejuruteraan

Pokok Jarak merupakan tumbuhan yang hidup di kebanyakan kawasan tropika dan subtropika seluruh dunia. Minyak yang diperoleh daripada biji Jarak boleh digunakan sebagai bahan api alternatif dan untuk membuat biodiesel. Penyelidikan ini bertujuan untuk mengkaji parameter optimum untuk mendapatkan kadar pengeluaran minyak yang maksima dalam pengekstrakan pepejal-cecair biji Jarak di bawah keadaan ujikaji. Keadaan optimum tersebut kemudiannya diterapkan ke dalam kaedah pengekstrakan menggunakan bantuan ultrabunyi dan praolahan mikrogelombang untuk menentukan amaun kadar pengeluaran minyak. Kinetik pengekstrakan juga dikaji berdasarkan andaian daripada mekanisme tertib kedua. Proses tersebut dijalankan menggunakan pengekstrak Soxhlet yang dilengkapi dengan pemeluwap dan plat pemanas. Bagi mengoptimumkan proses tersebut, kesan lima faktor utama iaitu jenis-jenis pelarut, suhu, nisbah pelarut kepada pepejal, masa tindak balas dan saiz bahan mentah dikaji melalui eksperimen pengekstrakan ke atas biji Jarak. Keadaan optimum ditemui pada masa tindak balas selama lapan jam,

suhu sekitar 68°C, saiz partikel yang kasar (0.5-0.75 mm), nisbah pelarut kepada pepejal sebanyak 6:1 (isipadu/berat) dan menggunakan heksana sebagai pelarut. Amaun kadar pengeluaran maksima pada keadaan optimum adalah 47.3 % mengikut berat. Tenaga pengaktifan adalah 7145.05 (J/mol) dan kadar pengekstrakan awal tertinggi ditentukan sebanyak 4.21 (g/L min). Peratusan jumlah minyak maksima yang diekstrak menggunakan kaedah bantuan ultrabunyi dan praolahan mikorgelombang adalah masing-masing 51.4 dan 49.4%. Minyak yang diekstrak menggunakan kaedah konvensional, bantuan ultrabunyi dan praolahan mikrogelombang masing-masing mengandungi 0.62, 0.67 dan 0.63% asid lemak bebas (FFA) serta 98.3, 97 dan 97.7% trigliserida.

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Finally, I would like to express my thanks to my parents in Iran for their patience, ever constant encouragement and love during my studies.

I certify that a Thesis Examination Committee has met on 14 September 2009 to conduct the final examination of Sepidar Sayyar on his thesis entitled "Optimization and Kinetics of Solid Liquid Extraction of Malaysian *Jatropha curcas* Seeds" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Maste of Science.

Members of the Thesis Examination Committee were as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date: 10 December 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

SEPIDAR SAYYAR

Date: 10 June 2009

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

Abbreviation	Definition
A	Temperature independent factor (L/g min)
AOAC	Association of Analytical Communities
AOCS	American Oil Chemists' Society
BSTFA	N, O-Bis (trimethylsilyl) trifluoroacetamide
GC	Gas Chromatography
FFA	Free Fatty Acid
LLL	Trilinolein
LLO	1, 2 -Dilinoleoyl – 3-oleoyl – rac-glycerol
OOL	1, 2 Dioleoyl-3-linoleoyl – rac-glycerol
OPO	1, 3-Dioleyl – 3-palmitoyl – rac-glycerol
Pet	Petroleum Ether
POL	1-Palmitoyl – 2– oleoyl-3 linoleoyl-rac-glycerol
POO	1-Palmitoy – 2-3 dioleoyl – rac-glycerol
POP	Dipalmitoyl – 2-oleoyl – rac-glycerol
PORIM	Palm Oil Research Institute of Malaysia
PPP	Triplamitin
SOP	1-Stearoyl – 2-Oleoyl –3-palmitoyl – rac-glycerol

Notation	Definition
Conv	Conventional solid liquid extraction
MW	Microwave pretreatment extraction method
US	Ultrasound assisted extraction

Glossary	**Definition**
C	Concentration of the solute (kg/m3)
c	Speed of light (m/s)
C_s	Extraction capacity (g/L)
C_t	Concentration of oil in the solution at any time (g/L)
C_p	Specific heat of the water (4.184 J/g °C)
D	Diffusion coefficient
D_0	Maximum diffusion coefficient at infinite temperature
D_L	Diffusivity of the solute through the solvent (m2/s)
E_A	Activation energy (J/mol)
f	Frequency (Hz)
h	Initial extraction rate (g/L min)
k	Second order extraction rate constant (L/ g min)
M	Mass of solute transferred (kg)
m	Water mass (g)
M_0	Mass of oil extracted from the sample (g)
M_s	Mass of the sample (g)
N	Normality of NaOH solution used (ml)
N_s	mass flux (kg/m^2s)
O_o	Amount of oil extracted from 100 g sample (g)
O_s	Initial amount of oil (%)
R	Ideal gas constant (8.314 J/mol K)
R_0	Resonant cavity size
T	Temperature (K, °C)
T_f	Water final temperature (°C)

T_i	Water initial temperature (^oC)
t	time (min)
W	Weight of the oil sample (g)
Z	Distance inside the pore (m).
γ	Special heat ratio of the gas
λ_0	Wavelength (m)
ρ_0	Total pressure (Pa)
ρ	Density of the media (kg/m^3)

CHAPTER 1

INTRODUCTION

1.1 Background

Diesel is the major fuel used in transportation especially for vehicles such as trucks and trains. Compared to gasoline engines, diesel engines provide lower fuel costs and higher efficiency, resulting in an increasing trend for utilization of diesel cars. There is a growing demand for transportation fuel in most countries in spite of the current energy crisis. Thus, it is important to explore the feasibility of substituting diesel with an alternative fuel that can be produced on a massive scale for commercial utilization.

There is an increasing interest in using vegetable oils as fuels or fuel sources. One of these vegetable oils is non-edible oil of Jatropha which has a tremendous potential to be used not only directly as fuel but also as a source for biodiesel production (Gubitz *et al*., 1999; Forson *et al*., 2004; Tiwari *et al*., 2007; Vasudevan and Briggs, 2007).

Jatropha is a genus of over 170 plants from the Euphorbiaceae family, native to the Central America but commonly found and utilized across most of the tropical and subtropical regions of the world. It is believed that the Portuguese traders brought Jatropha to Africa and Asia and it was initially used as hedge plant. Jatropha tree bears both male and female inflorescence. Hardness, rapid growth, drought resistance and wide ranging usefulness are the main characteristics of the plant. The oil content of the Jatropha seeds is at least 30%

by weight so it is considered as a plant with high oil content seeds. It has a yield per hectare of more than four times that of soybean and ten times that of corn (Nobrega and Sinha, 2007). Among the different species of Jatropha, *Jatropha curcas l.* has a variety of uses and offers interesting scope of usage which could be of great economic significance. The oil of *Jatropha curcas l*., simply known as Jatropha oil, is a non-edible oil which is used for producing soap, candles, engines lubricant and, more importantly, as an alternative to diesel.

Excellent chemical properties, performance characteristics and ignition quality equivalent to diesel makes Jatropha oil a promising and sustainable alternative for diesel to overcome the source limitation problem. Nowadays, Jatropha tree is a significant fuel source in India and Southeast Asia (Demirbas, 2008) and as it can be seen in Figure 1.1, it is expected that in the near future, Jatropha seeds cover 19% of raw material source for biodiesel production (Mittelbach, 2006). Considering the mentioned potential and industrial significance of Jatropha oil, particularly in the fuel industry, it is important to undertake a systematic optimization study on the extraction process of the seeds.

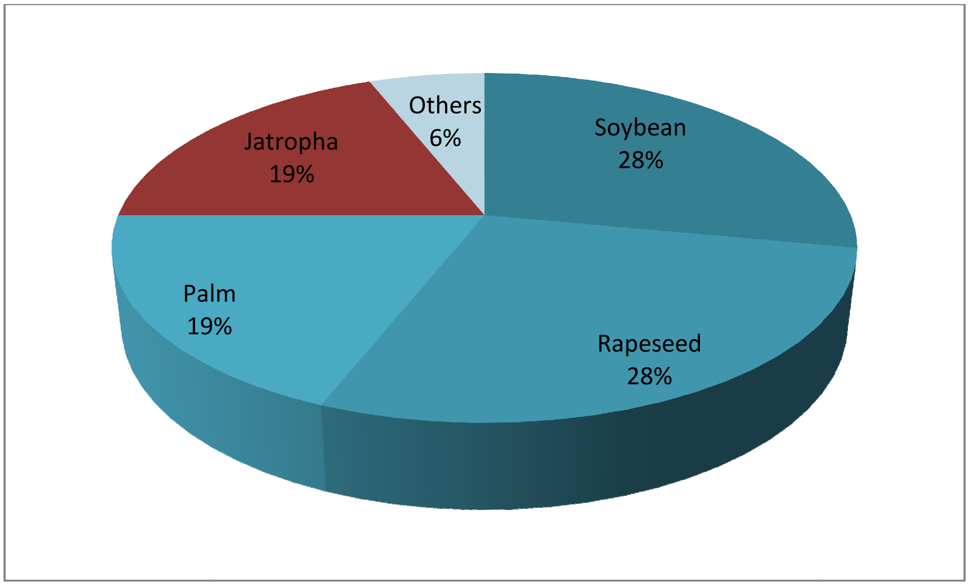

Figure 1.1: Raw material sources for tomorrow´s biodiesel production, worldwide (Data adapted from Mittelbach, 2006).

Solid liquid extraction is the most common and efficient technique in producing oil for fuel and biodiesel production (Forson *et al*., 2009; Yunus *et al*., 2006). Solid liquid extraction, mostly know as leaching in industry, involves the separation of solute component from the solid phase. The method is usually called extraction, and is carried out with organic solvent.

Among the newer techniques used in extraction technology, using ultrasound for extraction of oils and other plant components is more applicable and has led to better outcomes. Application of ultrasound has been found to enhance the efficiency of extraction process through mechanical effects and cavitation phenomenon. In more specific, ultrasound disrupts the wall structure of cell. As a result, penetration of solvent into the cellular materials and the release of the solid contents get facilitated (Vinatoru *et al*., 1997; Vinatoru, 2001; Li *et al*., 2004).

Microwave preheating of oil bearing seeds has been found to be an effective method for increasing the yield. Microwave treatment of the seeds before extraction can improve the amount of yield since microwave radiation ruptures the cell membrane of the seeds and thus facilitates releasing of the oil (Ramesh *et al*., 2005; Uquiche *et al*., 2008).

Different studies have already been done on Jatropha seeds such as extraction by combination of ultrasonication and aqueous enzymatic oil extraction (Shah *et al*., 2004), enzyme assisted three phase partitioning extraction (Shah *et al*., 2005) and oil extraction by pressing (Mbeza *et al*.,2002; Beerens, 2007). However, there is still little information about parameters affecting solid liquid extraction of oil from the seeds as well as the kinetics of extraction and also about ultrasound extraction and microwave pretreatment effect on amount of yield and quality of the obtained oil.

The overall goal of this study was to determine the optimum parameters in order to achieve maximum oil yield in solid liquid extraction of Jatropha seeds under experimental condition and to investigate the kinetics of the extraction. Further work was also done to use ultrasound and microwave as possible methods for improving the extraction process.

1.2 Objectives

The objectives of this study were:

1) To determine the optimum parameters to achieve maximum oil yield in solid liquid extraction of Jatropha seeds in lab scale.

2) To study the kinetics of extraction by using optimum parameters achieved in the first objective.

3) To Study the ultrasound-assisted and the microwave pretreatment extractions of Jatropha seeds considering the optimum parameters achieved in the first objective.

1.3 Organization of Report

The thesis comprises of five chapters. Chapter 1 covers the introduction and objectives of the thesis. Chapter 2 reviews the literatures and previous works done regarding the extraction of Jatropha seeds, solid liquid extraction, ultrasound extraction and microwave pretreatment extraction. Chapter 3 describes the materials and experimental methodology used in optimization of solid liquid extraction of Jatropha seeds as well as kinetics study, ultrasound assist extraction, microwave pretreatment extraction and investigation on the quality of the obtained oil. Results of extraction optimization, ultrasound assisted and microwave pretreatment extraction, oil quality experiments, extraction kinetics and modeling will be described and discussed in chapter 4. Finally, results and findings of the whole study as well as recommendations statements will be concluded in chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this literature review, the application of vegetable oils in industry, especially in fuel field, is discussed. *Jatropha curcas l.* which is the raw material used in this work investigated to study its properties, characteristics and usage as fuel. More importantly, different methods of oil extraction from Jatropha curcas, as well as their advantages and disadvantages, were also explored. Microwave pretreatment and ultrasound assisted extractions, which are novel methods of extraction, have also been investigated through the literature. In addition, the utilization of the second order mechanism for solid liquid extraction processes is also assessed.

2.2 Introduction to Vegetable Oil

Vegetable oils have a wide range of uses in many manufacturing industries. Beside extensive application in food industry, vegetable oils can be used for producing perfumes, soaps, lubricants, resins, emulsifiers and medicine. These oils can also be applied as insulators in electrical industry and as cooling agent in personal computers (Metcalfe, 2003). Vegetable oils have excellent environmental credentials such as biodegradability, low toxicity, and renewability. Apart from various usages in industry, one of the most important applications of vegetable oils is to use them as fuel or fuel source which is aimed to overcome current fuel crisis of the world.