MICROWAVE ASSISTED THERMAL CRACKING OF CASTOR OIL WITH ZEOLITE AS CATALYST FOR POSSIBLE BIOFUEL PRODUCTION

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Thesis submitted in fulfillment
of the requirements for the award of degree of
Bachelor of Chemical Engineering (Gas Technology)

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UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

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LIST OF ABBREVIATIONS

FTIR	Fourier Transform Infrared spectroscopy
GCMS	Gas Chromatography Mass Spectroscopy

LIST OF SYMBOLS

°C	Degree Celsius
%	Percentage
wt.	weight
USD	United States Dollar
RM	Ringgit Malaysia
Tons	Tonnes
$	Dollar
g	Gram
g/cm^3	Gram per centimeter cube
mm	Millimeter
mL	Milli-Liter
s	Second

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ABSTRACT

The gradual depletion of the global petroleum supplies gives rise to the possibility that petroleum based fuel will not be readily available soon and renewable energy sources, especially biofuel, have appeared as an important alternative. The aim of this investigation was to produce biofuel from castor oil through microwave assisted thermal cracking with zeolite ZSM-5 as catalyst. The obtained results showed that microwave assisted thermal cracking of castor oil with Zeolite ZSM-5 as catalyst generates products consisting of alcohol, methyl esters and fatty acids. The products obtained from this experimental procedure by the cracking of castor oil are components of biodiesel. Samples of cracked castor oil containing 1, 3 and 5wt % catalyst was analyzed, however, only the sample containing the 5wt % catalyst showed significant presence of condensate. FTIR and GCMS studies show that the condensate obtained is an unsaturated fatty acid, is 9, 12-octadecadienoic acid, suitable for biofuel use. 9,12-octadecadienoic acid is an unsaturated fatty acid with a molecular weight of 280.445 g/mol. Characterization of the sample demonstrates that functional group for the products from the three samples display a similar peak in the FTIR graph analysis at 1700 cm^{-1} and 3600 cm^{-1}. The result obtained from GCMS shows that there are 16 peaks obtained from the sample. The compound with the highest peak area is 9,12-octadecadienoic acid with a retention time of 9.941 and 24.65 peak area. All these compounds are organic material and can be characterized as biofuel and biodiesel.

PERETAKAN HABA MINYAK JARAK DIBANTU GELOMBANG MIKRO MENGGUNAKAN ZEOLITE SEBAGAI PEMANGKIN BAGI MENDAPATKAN BIOFUEL

ABSTRAK

Pengurangan bekalan petroleum secara global menimbulkan kemungkinan bahawa bahan api berasaskan petroleum tidak akan mudah diperolehi tidak lama lagi dan sumber tenaga boleh diperbaharui, terutamanya biofuel, telah muncul sebagai alternatif penting. Tujuan kajian ini adalah untuk menghasilkan biofuel daripada minyak jarak melalui peretakan haba melalui gelombang mikro dengan zeolite ZSM-5 sebagai pemangkin. Keputusan yang diperolehi menunjukkan peretakan haba dengan gelombang mikro minyak jarak dengan Zeolite ZSM-5 sebagai pemangkin menjana produk yang terdiri daripada alcohol, metil ester, dan asid lemak. Produk yang diperolehi daripada prosedur ini adalah komponen biodiesel. Sampel minyak jarak retak dicampur dengan 1,3 dan 5% berat dianalisa, bagaimanapun, hanya sampel yang mengandungi pemangkin 5%wt menunjukkan kehadiran kondensat yang ketara. Kajian FTIR dan GCMS menunjukkan bahawa kondensat yang diperolehi adalah asid lemak tidak tepu, 9, 12-octadecadienoic asid, sesuai sebagai biofuel. 9,12-octadecadienoic asid adalah asid lemak tidak tepu dengan berat molekul 280.445 g / mol. Pencirian sampel menunjukkan bahawa kumpulan berfungsi bagi produk dari tiga sampel memaparkan puncak yang sama dalam analisis graf FTIR pada 1700 cm-1 dan 3600 cm-1. Hasil yang diperolehi dari GCMS menunjukkan bahawa terdapat 16 puncak yang diperolehi dari sampel. Kompaun dengan kawasan puncak tertinggi adalah 9,12 octadecadienoic asid dengan masa tahanan 9.941 dan keluasan puncak 24.65. Semua sebatian ini adalah bahan organik dan boleh disifatkan sebagai biofuel dan biodiesel.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In order to obtain sustainable energy for the future of mankind, finding an efficient and appropriate substitute of crude oil and petroleum are of considerable importance. The probable scarcity of fossil fuels in the near future, combined with concerns over the consequences of dependency on this type of energy source, in terms of changes in the Earth's climate, has forced the world to find alternatives that are less harmful to the environment (Knothe *et al.*, 1997)..

Renewable energy sources, especially vegetable fuel, have appeared as an important alternative. To overcome the energy crisis and depletion of crude oil, research and investigation has been done on vegetable oil to be made substitute of crude oil. The approach of processing vegetable oil into desired products such as biodiesel and biofuel has become increasingly popular in recent years (Santana *et al.*, 2010).

Realization on the climate change situation has been an important driver to the rise of biofuels because it assists climate change alleviation efforts by diminishing fossil fuel consumption. Knowing the massive role transportation plays in energy consumption, biofuels could contribute to the reduction of CO_2 emissions from the transport sector (Timilsina & Shrestha 2010).

Rudolph Diesel created the original diesel engine to run on vegetable oil where at the Paris Exposition of 1900, Dr. Rudolph Diesel used peanut oil to fuel one of this his engines. He used biofuel produced from different vegetable oils such as soybean, rapeseed and sunflower, which seems very promising for a number of reasons, for example it can replace the oil in boilers and internal combustion engines without major modifications and only a small reduction in performances is reported. The results reported almost zero emissions of sulfates, a small net contribution of carbon dioxide (CO_2) when the whole process is considered which includes cultivation, production of oil and conversion to biofuel, emission of pollutants comparable with that of fuel oil. Due to these reasons, several campaigns have been planned in many countries to introduce and endorse the practice of biofuel. In the early years, the vegetable oil fuels were not adequate because they were more expensive than petroleum fuels. With recent surges in petroleum rates and doubts regarding petroleum availability, there is transformed awareness in vegetable oil fuels (Bozbas, 2005). It is yet to be proven that castor oil is the ultimate substitute for petroleum in the production of biofuel.

The aim of this study is to produce biofuel by microwave assisted thermal cracking of castor oil using zeolite as catalyst.

1.2 Problem Statement

The gradual depletion of the global petroleum supplies gives rise to the possibility that petroleum based fuel will be available neither in sufficient quantities, nor at reasonable p rice in the near future. This induced the interest of scientists and engineers to explore alternate fuel sources for automotive vehicles, such as methanol, ethanol, biogas, hydrogen, and not to mention, vegetable oil. Despite this, more interest is given to alternates which are derived from indigenous sources, and preferably renewable sources. This is of course done, to avoid the issue of dependency. In this case, vegetable oils have the upper hand, of being extracted from oilseeds which indeed are renewable sources. They also have the advantage of being readily available in liquids.

Vegetable oils and their derivatives commonly known as biofuel have evolved from being in its experimental stages to becoming commercially viable products being as competitive to conventional fuels. They have the advantage of being sustainable, renewable and able to be produced domestically, they have the extra advantage of reduced emissions and high fuel economy. (Knothe *et al.*, 1997).

Biofuel is an alternative fuel made from biological sources such as vegetable oils and biodiesel fuel can be prepared from waste cooking oil, such as palm, soybean, canola, rice bran, sunflower, coconut, corn oil, fish oil, chicken fat and alga which would partly decrease the dependency on petroleum-based fuel (Hossain *et al* .,2008). Biofuel is biodegradable and nontoxic. It also has low emission profiles and is beneficial to the environment.

One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine (Shay, 1993). With the rise of cheap petroleum, appropriate crude oil fractions were refined to serve as fuel, and hence the engines evolved alongside the fuel. However, during 1930s and 1940s, vegetable oil was used as fuel from time to time, but only for emergency purposes. But in the 21st century, we are facing numerous problems such as the hiking of crude oil price, depleting source of crude oil, and also environmental issues such as pollution. Continued usage of petroleum will intensify local air pollution and magnify the global warming problems caused by CO_2 emission (Shay, 1993). Biofuel has the ability to reduce the level of pollutants and probable carcinogenic compounds (Krawczyk, 1996).

Despite the invention of the vegetable oil fuelled engine by Rudolf Diesel dated back in the 1900s, full exploration of vegetable oil based fuel such as biodiesel only came into light in the 1980s as a result of renewed interest in renewable energy sources for reducing greenhouse gas (GHG) emissions, and alleviating the depletion of fossil fuel reserves. (Janaun & Ellis, 2009)

Technically, vegetable oil can be used as an alternative fuel for automotive engines. Vegetable oils also have good potential to be used as emergency fuel. However, there are certain problems regarding using vegetable oil as alternative fuel. Firstly, the usage of vegetable oil causes inefficient combustion in the engine. This is due to the fact that vegetable oil has a high viscosity and low volatility values. When the viscosity of the fuel is high, the fuel is poorly atomized in the engine, causing inefficient combustion with subsequent formation of carbon deposit on the injector nozzle and other engine parts (Ma, F., & Hanna, M. A. 1999).

To solve this problem, vegetable oil must be derivatized into biofuel, in order to be compatible with existing engines. The primary production method of biofuel has been studied extensively. This paper reviews the feasibility of using the pyrolysis or thermal cracking method on castor oil, with zeolite as catalyst in order to yield biofuel.

However, before biofuels can be commercialized, there are a few concerns that industries have to be prepared to address.

1. As demand increases for biofuel, industries must be able to continuously supply biomass feedstock's. At the pilot stage of commercialization, waste materials can be a contributor, but with increasing demands in time, feedstock's will have to be intentionally grown for production of biofuels. To produce good crops, bioengineering will a significant tool, to create faster growth, disease resistivity and lower water requirements and etc.
2. Logistically, new crops mean new equipment and methods of harvesting, storage and processing while being economical. Production of biofuels annually will demand a continuous supply whilst maintaining enough for consumption.
3. Biofuel production requires combined biorefineries and operational use of co-products such as heat and electrical power for economic operation.
4. Biofuel has to be compatible with existing infrastructure, and has to meet all applicable product specifications.

5. The obtainability of biofuels-compatible vehicles must be extended. To assure consumer satisfaction, these vehicles must offer performance equivalent to conventional vehicles. (Hoekman, 2009)

1.2 Objectives

This study adopts the qualitative approach with a view to find a substitute or alternative to petroleum and crude oil. The objectives of this study are stated as follows:

- To investigate whether microwave assisted thermal cracking with zeolite as catalyst is a viable method of producing biofuel from castor oil
- To identify and analyze the product oil

1.3 Scope of research

The study will look for a proper substitute for petroleum and crude oil in order to achieve sustainable energy. This research will focus on using castor oil as the alternative to crude oil and petroleum. Areas of study are limited to the following:

1. Performing microwave assisted pyrolysis or thermal cracking on refined castor oil using zeolite as catalyst in a reaction flask, attached to a condensing and receiving units.

2. Identifying the product oil which is produced by Gas Chromatography Mass Spectrometry (GCMS) and Fourier Transform Infrared Spectroscopy (FTIR)

CHAPTER 2

LITERATURE REVIEW

2.1 Castor Oil

Castor oil is a type of vegetable oil which is extracted from castor beans, or castor seed. Castor beans are obtained from the castor plants, *Ricinus Communis* . Even though it is called castor beans, but technically they do not belong in the bean family. Castor oil is a thick golden liquid that has no scent or odor. The intensity of the colour of castor oil depends on the level of refinement, which means the most refined castor oil is close to colorless. Castor beans consists of almost 50% of oil, and are harvested mostly in China and India. There are also other countries which have castor plant plantation such as Indonesia and Malaysia.

Table 2.1(a) : Production volume of castor oil by major producers

Major producers	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
	'000 t	000 t	'000 t	'000 t	'000 t	'000 t	'000 t	'000 t	'000 t	'000 t	'000 t
India	192	239	232	242	271	333	344	278	304	294	324
China, PR	77	86	93	97	97	82	73	83	80	91	105
Brazil	77	73	54	28	28	22	21	43	21	19	52
Thailand	18	18	19	18	16	14	10	9	9	7	5
E.U.[B]	20	16	14	12	14	11	9	10	7	8	8
Others	54	52	49	41	20	21	22	19	20	23	23
Total	438	484	461	438	446	483	479	442	441	442	517

A : *Source*—http://www.ciara.com.ar/estadize.htm.

B :E.U.—European Union.

Source : (Ogunniyi D.S., 2006)

According to Scholz and Da Silva, castor is originally a tree or a shrub that can grow up to 10 meters high and reach up to 4 years of age. Currently, the cultivated varieties grow to a height of 60 to 120 centimeters in a year, and several meters in a perennial cultivation. Castor is known to grow in the humid tropics to the sub-tropical dry zones (optimal precipitation 750–1000mm, temperature15–38°C). Castor can also be cultivated in the southern Europe (Scholz, V., & da Silva, J. N., 2008).

Castor oil is difficult and dangerous to harvest as it contains dangerous toxic compounds which are inherent all over the castor beans. This toxic compound is called ricin. This chemical found on the plant surface is known to cause nerve damage, if exposed in a large quantity. During exposure to this compound, only 0.18g/kg of body mass can result in death (Scholz, V., & da Silva, J. N., 2008). However, some researches are conducting research in genetically modifying the castor plant to prevent the synthesis of ricin. Castor seeds are usually cleaned and sorted out by machines. The oil is obtained by pressing the seeds one to three times and extracting it. There are two methods of pressing which is the cold pressing and the warm pressing. During cold pressing, which is usually applied for pharmaceutical and cosmetic use, the yield of oil is 30 to 36% of the mass of seeds. However, during warm pressing (temperature > 70 °C), the yield of oil is 38 to 48% of the mass of the seeds. The remaining oil can be recovered by using solvent extraction process (Scholz, V., & da Silva, J. N., 2008).

Castor oil is a triglyceride that almost 90% of it consists of ricinoleic acid, while oleic and linoleic acids are other significant components. Castor oil consists mainly of esters of 12-hydroxy-9-octadecenoic acid, or in other words known as ricinoleic acid. The abundance of this compound may contribute to the characteristic of the castor oil, which is high viscosity. This is caused by the hydrogen bonding by the hydroxyl groups of the compound ricinoleic acid, although this is highly unnatural for vegetable oils (Santana et al, 2010).

Table 2.1(b) : Oil composition of castor oil

Fatty acid	% Of Oil
Ricinoleic ($C18H34O3$)	87
Oleic (C18:1)	7.4
Linoleic (C18:2)	3.1
Lauric (C12:0) } Myristic (C14:0) } Palmitic (C16:0) } Stearic (C18:0) }	2.4

Source : Journal of American Oil Chemists Society (1988). Vol. 65 (12)

No other vegetable oil is known to contain such high a proportion of fatty hydroxyacids. Castor oils unsaturated bonds, high molecular weight (298), low melting point (5 °C) and very low solidification point (-12 to -18 °C) makes it industrially useful and, highest and most stable viscosity of any vegetable oil (Bonjean, 1991)

Table 2.1(c) : Properties of castor oil

Density (20 oC)	0.956 - 0.963 g/ml
Viscosity (20 oC)	9.5 – 10.0 dPa.s
Refraction index n2d	1.477 – 1.479
Saponification value	177 – 187
Iodine value	82 – 88
Unsaponifiable matter	0.3 – 0.5%
Hydroxlys	160 minimum

Source : Journal of American Oil Chemists Society (1988). Vol. 65 (12)

Castor oil has benefited mankind in numerous ways. There are many uses of castor oil. For an example, castor oil is used in the synthesis of polyurethane. Castor oil is used as a bio based polyol as its functionality is 2.7. Castor oil is also used in food industry as additives, flavorings and mold inhibitor (Wilson R, Van Schie BJ, Howes.D 1998). Eventhough castor oil is not edible, it is more useful than other vegetable oils. It is used as starting material in the manufacturing of coatings, paints, lubricants and wide variety of other products (Ogunniyi D.S. 2006).

Castor oil has been considered as a major feedstock for biofuel and biodiesel production in many nations. The Brazilian government has emphasized on utilizing castor oil as one of the major feedstock for their biodiesel production. There may be several reasons for the Brazilian government to choose castor oil over other vegetable oil such as peanut oil, corn oil, jatropha oil, soya oil and also rapeseed oil. The castor oil has received more emphasis due to the low production cost and also because it is easily grown. The castor bean plant can be easily grown, even in Brazil's vast, semi-arid areas. These areas are known to have frequent draughts which more often than not, decrease the agricultural production rate. In the area with extreme conditions such as the Brazil, castor oil is the best way to produce biofuel and biodiesel. Besides the ability to withstand harsh weather condition and draught, castor seeds has an oil content about almost 45 to 50%. This can produce 470kg of castor oil per hectare. In addition, since castor beans are not suitable for human consumption, its use as an energy source does not overlap compete with the food production (Santana et al, 2010).

2.2 Biofuel and Biodiesel

Biofuels are referred to liquid or gaseous fuels that are produced from renewable sources, such as vegetable oils, biomass and algae. There are a few types of fuels that can be produced from renewable resources, such as ethanol, methanol, biodiesel, and Fischer-Tropsch gas oil. Renewable resources can also be used to produce gaseous fuels such as hydrogen and methane. Liquid biofuels are mainly used to fuel transportation vehicles, but they can also be used to power engines and cells for electricity generation (Ong, Y. K., & Bhatia, S., 2010).

Biofuel can be used in pure state in any conventional fuel engines, and can be distributed in any fueling infrastructure. This is because, the properties of biofuel match the properties of fossil fuel. Biofuel can be obtained by few process such as deoxygenation, cracking, aromatizing, and isomerizing of triglycerides. Biofuel has a higher octane level, and matches the chemical, kinetic and combustion characteristic of petroleum based gasoline. For renewable fuel such as biofuel to be successful, they need to have similar properties as the conventional fuel (Maher, Bressler 2007).

Biofuel is a form of renewable energy. It is also known to emit less sulphur compared petroleum based fuel. The carbon monoxide emission is also considerably lower than of petroleum derived fuel. This is in return beneficial to our environment, and reduces the emission of harmful gases to the atmosphere (Ong, Y. K., & Bhatia, S., 2010).

Biofuel can be produced from vegetable oil such as palm oil, soya oil, canola oil and castor oil. However, statistics show that biofuel are reasonably more expensive than of petroleum derived fuel. This is due to the fact that most vegetable