



UNIVERSITI PUTRA MALAYSIA

***SYNTHESIS AND CHARACTERIZATION OF EGUSI MELON METHYL
ESTER AS DIESEL FUEL SUBSTITUTE***

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**SYNTHESIS AND CHARACTERIZATION OF EGUSI MELON METHYL
ESTER AS DIESEL FUEL SUBSTITUTE**

By

GIWA SOLOMON OLANREWaju

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Master of Science**

December 2009

DEDICATED TO

God Almighty, the Alpha and Omega of life. Also, to my beloved father Late Chief D. A. Giwa who thoughtfully laid the foundation of sound and quality education, and unknowingly sowed the seed of greatness.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in
fulfilment of the requirement for the degree of Master of Science

**SYNTHESIS AND CHARACTERIZATION OF EGUSI MELON METHYL
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December 2009

Chairman: Associate Professor Ir. Nor Mariah Adam, PhD

Faculty: Engineering

Biodiesel is a monoalkyl esters of vegetable oils (VOs), animal fats and waste oil widely accepted as substitute for fossil-derived diesel fuel. It is a renewable and sustainable energy source that is environmentally friendly. Food-fuel strain of conventional VOs has renewed research interest in exploring 350 alternative oil-bearing crops that can be harnessed as diesel fuel substitute, but with less than 100 investigated. *Colocynthis citrullus Lanatus*, 'egusi', has been studied for the first time as a potential biodiesel feedstock. Crude oil from the seeds have been characterized and transesterified using methanol in the presence of sodium methoxide as catalyst. The design of experiment for the optimization of the reaction conditions was conducted using response surface methodology (RSM). A three-level-three-factors face centered central composite design was employed. Catalyst amount (0.25 - 1.8% wt.), reaction temperature (45 – 65 °C) and oil-methanol molar ratio (4 – 10) were studied as important factors influencing the reaction. Fuel properties of egusi melon methyl ester (EMME) were determined in

accordance to ASTM D 6751 and EN 14214 standard test methods. The fatty acid profile of EMME was analyzed using gas chromatograph. Also, rheological behaviors of EMME and its blends (B2, B5, B10) in relation to viscosity were studied.

The amount of catalyst and reaction temperature was the most significant ($P < 0.0001$) factors affecting the yield of EMME. Multiple regression analysis was used to develop an empirical mathematical model for predicting methyl ester yield of EMME. The optimum reaction conditions obtained from the model for EMME synthesis were 1:6.54 oil-to-methanol molar ratio, 1.22% catalyst amounts, and 65 °C reaction temperature resulting in a yield of 84.01%. Under experimental conditions, methyl esters yield of $84.46 \pm 0.075\%$ was obtained on an average with the optimal values. This yield value is well within the range predicted by the model. RSM was found to be a suitable technique for optimizing the transesterification of egusi melon seed oil. The quality and fuel properties of EMME determined were found to satisfy prescribed ASTM (D 6751) and EN 14214 specifications. The viscosity behavior of EMME and its blends with diesel fuel (pseudoplastic and Newtonian in nature) was found to agree with those of other biodiesels reported in literature.

From this present study, it was discovered that fuel properties and fatty ester profile of egusi melon biodiesel resemble those of sunflower, soybean and safflower. The kinematic viscosity (KV) of EMME was found to be 3.51 mm²/s (at 40 °C), a value remarkably lower than most biodiesels (above 4.0 mm²/s at 40 °C) reported. In addition,

its cloud point is relatively low compared to soybean, rapeseed and sunflower biodiesels. Comparisons of egusi melon biodiesel with Malaysian palm biodiesel were satisfactory with the former offering better cloud point and significantly lower KV than the latter. In this work, the probable potential of *Colocynthis citrullus* L. seed oil for biodiesel production is clearly presented.



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

**SINTESIS DAN PENGAMBARAN SIFAT ESTER MINYAK EGUSI MELON
SEBAGAI PENGGANTI KEPADA MINYAK DIESEL**

Oleh

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Biodiesel merupakan monoalkyl ester minyak sayuran (VOs), lemak haiwan dan minyak sisa diterima pakai secara meluas sebagai bahan ganti bahanapi diesel terbitan fosil. Ia adalah punca tenaga boleh diperbaharui dan berterusan (sustainable) yang mesra alam. Strain makanan-bahanapi VO biasa telah mencetus penyelidikan untuk menerokai 350 tanaman alternatif yang mampu diguna sebagai alternatif gantian diesel, tetapi hanya 100 sahaja yang telah diselidik. *Colocynthis citrillus lanatus* 'egusi' telah pertama kalinya dikaji sebagai bahan gantian diesel yang berpotensi. Minyak mentah dari biji benih telah dicirikan dan ditransesterifikasi menggunakan methanol dengan sodium methoxide sebagai pemangkin. Rekabentuk eksperimen untuk pengoptimuman keadaan tindakbalas telah dijalankan dengan kaedah tindakbalas permukaan (RSM). Rekabentuk komposit permukaan tengah berfaktorkan tiga aras telah digunakan. Amaun pemangkin (0.25 - 1.8% berat), suhu tindakbalas (45 - 65 °C) dan nisbah minyak-methanol (4 - 10)

telah dikaji sebagai faktor penting yang mempengaruhi tindakbalas. Sifat bahanapi minyak egusi melon methyl ester (EMME) telah ditentukan mengikut kaedah standard ASTM D 6751 dan EN 14214. Profil asid lemak EMME telah diuji menggunakan gas kromatograf. Pelakuan reologi EMME dan campuran (B2, B5, B10) berkaitan kelikatan juga telah dikaji.

Amaun pemangkin dan suhu tindakbalas adalah faktor paling signifikan ($P < 0.0001$) mempengaruhi hasil EMME. Analisis pelbagai regresi telah digunakan untuk membangun model empirical matematik untuk meramal hasil EMME. Keadaan optimum tindakbalas yang didapati dari model sintesis EMME adalah 1:6.54 nisbah molar minyak:methanol, 1.22% amaun pemangkin dan suhu tindakbalas 65 °C mengeluarkan hasil sebanyak 84.01%. Dalam keadaan eksperimen, methyl ester menghasilkan $84.46 \pm 0.075\%$ secara purata dengan nilai optimum. Nilai hasil ini adalah dalam julat ramalan model. RSM merupakan kaedah yang sesuai untuk pengoptimuman transesterifikasi minyak melon egusi. Kualiti dan sifat bahanapi EMME memenuhi kehendak ASTM (D 6751) dan EN 14214. Kelakuan kelikatan EMME dan campuranya adalah hamper menyerupai biodiesel lain yang dilaporkan dalam literature.

Dalam kajian ini, sifat bahanapi dan profil lemak ester minyak egusi melon menyerupai minyak bunga matahari, kacang soya dan safflower. Kelikatan kinematic (KV) EMME didapati jauh lebih rendah daripada kebanyakan biodiesel lain. Tambahan pula titik kabus EMME adalah lebih rendah berbanding biodiesel kacang soya, rapeseed dan bunga

matahari. Perbandingan minyak melon egusi dengan minyak sawit adalah memuaskan dengan EMME mempunyai titik kabus yang lebih bagus dan nilai KV jauh lebih rendah dari minyak sawit. Dalam kajian ini, potensi *Colocynthis citrullus Lanatus* sebagai biodiesel adah cerah.



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I certify that a Thesis Examination Committee has met on 4th December 2009 to conduct the final examination of Giwa Solomon Olanrewaju on his thesis entitled “Synthesis and Characterization of Egusi Melon Methyl Ester As Diesel Fuel Substitute” 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 Master of Science degree.

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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 Universiti Putra Malaysia or other institution.

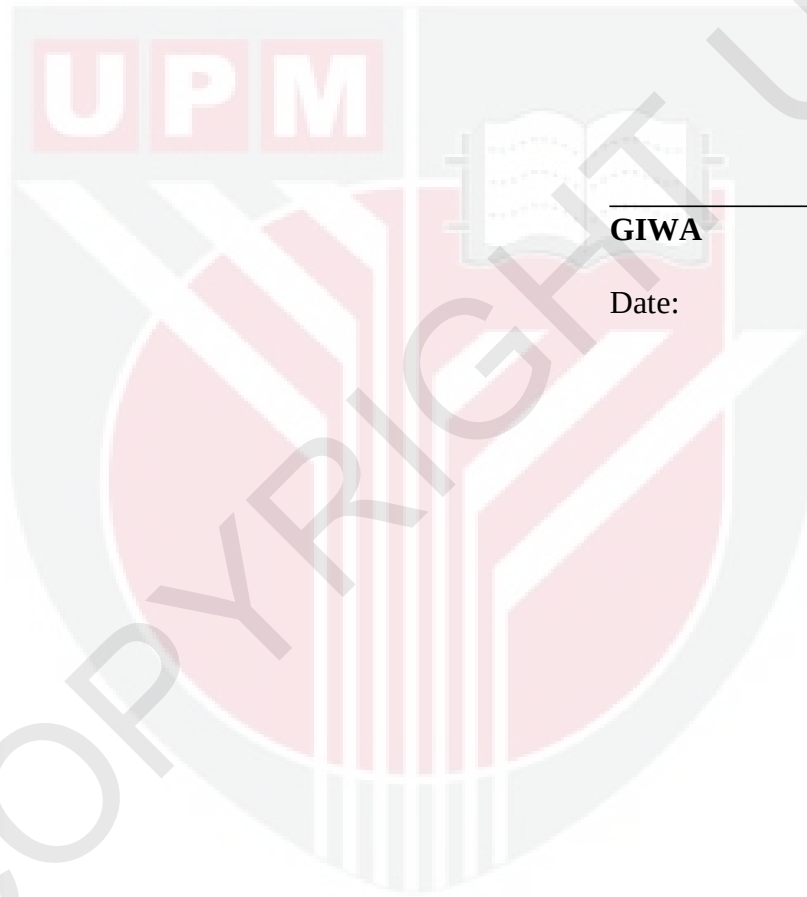


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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Material
CaO	Calcium Oxide
CCD	Central Composite Design
CCRD	Central Composite Rotatable Design
CEMSO	Crude Egusi Melon Seed Oil
CN	Cetane Number
CO	Carbon Monoxide
COST	Changed One Separate Factor at a Time
CO₂	Carbon Dioxide
CP	Cloud Point
D2	No. 2 Diesel
DG	Diglyceride
EMA	Engine Manufacturers Association
EMME	Egusi Melon Methyl Ester
EN 14214	European Standard
EU	European Union
FA	Fatty Acid
FFA	Free Fatty Acid
FID	Flame Ionization Detection
GC	Gas Chromatography
GL	Glycerol
H₂O	Water

H₂SO₄	Sulphuric Acid
HHV	Higher Heating Value
HPLC	High Performance Liquid Chromatography
KOH	Potassium Hydroxide
KV	Kinematic Viscosity
MeOH	Methanol
MG	Monoglyceride
MgO	Magnesium Oxide
MPa	mega Pascal (Pressure)
MPOB	Malaysian Palm Oil Board
NaOCH₂CH₃	Sodium Ethoxide
NaOCH₃	Sodium Methoxide
NaOH	Sodium Hydroxide
PORIM	Palm Oil Research Institute Malaysia
PP	Pour Point
RSM	Response Surface Methodology
SCM	Supercritical Methanol
SiO₂	Silicon Dioxide
SO₂	Sulphur Dioxide
TG	Triglyceride
VO	Vegetable Oil
vol	volume
wt	weight

g	gram
rpm	revolution per minute
s⁻¹	shear rate
Pa	pascal (shear stress)
Pas	viscosity (dynamic)
min	minutes
mol	mole
max	maximum
K	kelvin (temperature)
h	hour
cSt	centistokes
ml	millilitre
ppm	part per million
μl	microlitre

CHAPTER 1

INTRODUCTION

1.1 Background

Energy has been an indispensable and important issue of world concern. Major energy supply have been from fossil sources; petroleum, coal and gas. The scarcity of traditional fossil fuels, growing emissions of combustion-generated pollutants, and their increasing costs will make biomass sources more attractive (Sensoz *et al.*, 2000). Petroleum-based fuels have limited reserves concentrated in certain regions of the world and these sources are on the verge of declining off their peak production. The fossil fuel resources are depleting day by day. Known petroleum reserves are scarce and have made renewable energy sources more attractive, especially in very near future. Transportation and energy generation is reported to consume an estimated 90% of petroleum fuels (Crabbe *et al.*, 2001 and Demirbas, 2007).

Biodiesel refers to a diesel-equivalent processed fuel derived from biological sources which makes it a renewable form of energy. Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. Biodiesel, as an alternative fuel for internal combustion engines, is defined as a mixture of monoalkyl esters of long chain fatty acids (FAME) derived from a renewable lipid feedstock, such as vegetable oil, animal fat and waste oil. Biodiesel

typically comprises alkyl fatty acid (chain length C_{14} - C_{22}) esters of short-chain alcohols, primarily; methanol or ethanol. Biodiesel is the best candidate for diesel fuels in diesel engines. An alternative fuel to petrodiesel is expected to be technically feasible, economically competitive, environmentally acceptable, and easily available (Pinto *et al.*, 2005).

Biodiesel can offer benefits including reduction of greenhouse gas emissions, regional development and social structure, especially to developing countries (Demirbas and Demirbas, 2007). Biodiesel improve the lubrication properties of diesel fuel and also reduce long term engine wear in diesel engines when used as blend. It is a good lubricant which is about 66% better than petrodiesel (Demirbas, 2009). Recently, biodiesel fuels have received significant attention both as a possible renewable alternative fuel and as an additive to existing petroleum-derived fuels. Besides an additional fuel supply, biodiesel presents several advantages when compared to existing fossil-based fuel. Numerous researchers have shown that exhaust particulate matter, unburned hydrocarbons, carbon monoxide, and sulfur levels are all significantly reduced when using biodiesel fuels (Graboski and McCormick, 1998; Murugesan *et al.*, 2009). Research in this field has also shown increase in the levels of oxides of nitrogen, primarily as a result of advanced injection timing with biodiesel. Considerable research has been undertaken to understand the performance characteristics of biodiesel fuels as well as the production methods (Chang and Gerpen, 1997; Shahid and Jamal, 2007). Additional advantage of biodiesel is that it can be distributed using today's infrastructure, and its use and production are on rapid increase. Biodiesel raw materials

are basically from three sources; vegetable oils (VOs), animal fats, and waste oils. VOs of rapeseed, canola, soybean, sunflower and palm have been investigated (Ma and Hanna, 1999) and used for biodiesel production both on small and large scales in different countries of the world. Other oil-bearing crops, especially the non edible ones (jatropha, neem oil, castor oil) have also been studied (Murugesan *et al.*, 2009; Meher *et al.*, 2006a; Demirbas, 2009).

There are various other biodiesel sources: almond, andiroba (*Carapa guianensis*), babassu (*Orbignia sp.*), barley, camelina (*Camelina sativa*), coconut, copra, cumaru (*Dipteryx odorata*), *Cynara cardunculus*, fish oil, groundnut, *Jatropha curcas*, karanja (*Pongamia glabra*), laurel, *Lesquerella fendleri*, *Madhuca indica*, microalgae (*Chlorella vulgaris*), oat, piqui (*Caryocar sp.*), poppy seed, rice, rubber seed, sesame, sorghum, tobacco seed, and wheat (Pinto *et al.*, 2005).

Because it has similar properties to petroleum diesel fuel, biodiesel can be used alone (known as B100) or mixed in any proportion with petroleum diesel fuel. Biodiesel has slightly less energy content and a higher cetane number than the average diesel fuel. When biodiesel is blended with conventional diesel in proportions of 20% or less, any difference in engine performance is nearly imperceptible (Anonymous, 2001). Malaysia biodiesel policy also encourages the use of 5% palm biodiesel blend with diesel to reduce emission related environmental problem and over-dependence on fossil fuel due to declining petroleum reserves.

1.2 Problem Statement

Conventional oils (soybean, palm, sunflower, rapeseed oils etc.) mostly used for food purposes have been recently used as fuel (biodiesel) due to the rekindled interest in alternative fuel for diesel (Balat and Balat, 2008; Demirbas, 2007). In spite of this, biodiesel production from these oils has progressively strained food uses, price, production and availability of these oils (Rashid *et al.*, 2008a). In addition, this has precipitated a demand-driven competition between food and non-food uses of these VOs at the expense of their relatively constant supply. Consequently, this has ignited the search for additional regional biodiesel raw material. The increasing need of biorenewable energy sources to substitute petroleum-derived diesel has driven research for other oil crops to meet biodiesel production needs without strain to food uses of VOs.

Various oils have been in used different countries as raw materials for biodiesel production owing to their availability. Soybean oil is commonly used in United States and rapeseed oil is used in many European countries for biodiesel production, whereas, coconut oil and palm oils are used in Malaysia and Indonesia for biodiesel production (Ghadge and Raheman, 2005; Srivastava and Verma, 2008; Sarin *et al.*, 2007; Demirbas, 2006).

With over 350 oil crops identified (Demirbas, 2007; 2009; Balat and Balat, 2008) and their availability in different geographical locations (Pinto *et al.*, 2005), there is the need

to explore these oil-bearing crops' potential as biodiesel feedstock apart from the conventional VOs. Low quality underused raw materials have been reported used for biodiesel production (Pinto *et al.*, 2005). Moreso, recent studies showed the investigation of lesser known, under-utilized and neglected oil crops in various parts of the world as potential feedstocks for biodiesel production. Schinas *et al.* (2009), Kansedo *et al.* (2009), Rashid *et al.* (2008a), Hosamani *et al.* (2009), Yang *et al.* (2009), Chapagain *et al.* (2009) and Li *et al.* (2009) investigated pumpkin (*Cucurbita pepo* L), sea mango (*Cerbera odollam*), *moringa oleifera* oil, *michelia champaca* and *garcinia indica* seed oils, *idesia polycarpa* var. *vestita* fruit oil, desert date (*Balanites aegyptiaca*) and *eruca sativa* gars vegetable oil, respectively and reported their potential as biodiesel fuels. Also, Schinas *et al.* (2009) studied pumpkin melon oil, first of curcubit family to be investigated for its biodiesel potential and found its fuel properties in good agreement with European (EN 14214) biodiesel standard.

Cucurbitaceae is a large plant family which consists of nearly 100 genera and 750 species (Ng, 1993). This plant family is known for its enormous genetic diversity and wide range adaptation which includes tropical and subtropical regions, arid deserts and temperate locations (Achu *et al.*, 2006). Seeds of cucurbits are sources of oil and protein (Ng, 1993, Achu *et al.*, 2005) and contain about 50% oil with up to 35% proteins (Achu *et al.*, 2005) and are cultivated and consumed for these reasons world over. Egusi melon belongs to the species of the genus *Citrullus* of cucurbitaceae family, which usually consist of a large number of varieties that are generally known as melons (Mabaleha *et al.*, 2007). Egusi melon is among the 300 species of melon found in tropical Africa (Ntui *et al.*, 2009). It is cultivated for its seeds, which are rich in oil (53%) and protein (28%)

(Ntui *et al.*, 2009). It is cultivated in regions of Middle East, West Africa, especially, Nigeria, Ghana, Togo, Benin and Cameroon for the foods in the seeds and as a crop interplanted with maize, cassava and yam (Uruakpa and Aluko, 2004). In Nigeria only, “egusi” is cultivated over an area of 361,000 ha with a production figure of 347,000 tonnes (seeds) in 2002 (Federal Ministry of Agriculture and Rural Development, 2005) with harvest period of three to four months. It is used both as local condiment and soup thickener and the industrial scale production of the oil yet to be utilized despite the huge potential (Uruakpa and Aluko, 2004). The crude oil from the seed was investigated as potential feedstock for biodiesel production.

1.3 Purpose and Objectives

The main purpose of this work was to investigate egusi melon oil as a potential fuel substitute for petrodiesel. Biodiesel is a regional issue of energy security since the raw materials used in various countries have to do with its availability in those countries in question. Egusi melon was chosen for this study due to its high oil content (52% based on preliminary work conducted), less food use, availability (in region where it is cultivated), less competition for food use and commercial VO production potential yet to be harnessed. Response surface methodology (RSM) was used to design the experiment in order to optimize selected reaction variables. The three most important variables (reaction temperature, catalyst amount and molar ratio of oil to methanol) affecting the yield of esters during transesterification process were selected for investigation. The optimum conditions for the transesterification of egusi seed oil to produce egusi melon

biodiesel were determined based on the yield of egusi melon methyl ester (EMME). The quality and selected key fuel properties of EMME as fossil-diesel fuel substitute were measured in accordance with biodiesel standards. In addition, the rheological behavior of EMME and its blends with diesel fuel was investigated. The specific objectives of this study were as follows;

1. To synthesize egusi melon methyl ester (EMME) and optimize the reaction variables.
2. To characterize EMME and study its rheological behavior including its blends with diesel fuel.

1.4 Scope and Limitation

The scope of this research focuses on the investigation of a new, lesser-known and under-utilized oil crop of curcubit family called 'egusi' melon (*Colocynthis citrullus* L.) as fuel substitute for petrodiesel. This entails the transesterification of crude egusi melon seed oil using methanol and sodium methoxide (NaOCH_3) as alcohol and catalyst, respectively. The choice of NaOCH_3 as catalyst over NaOH and KOH was informed by the high yield of EMME during preliminary study. Important transesterification reaction variables (reaction temperature, catalyst amount and oil/methanol molar ratio) were optimized. The characterization of the raw oil and the resulting methyl ester and the rheological study on the methyl ester product (including its blend with diesel fuel) were carried out.

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