THE SYNTHESIS OF BIODIESEL AND LUBRICANTS FROM PURGING NUT OIL

JARUWAT THONGMOOL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE IN PETROCHEMICALS AND HYDROCARBON CHEMISTRY
SCHOOL OF GRADUATE STUDIES
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
2004

ISBN 974-15-1353-4

หัวข้อวิทยานิพนธ์	**การสังเคราะห์น้ำมันไบโอดีเซลและผลิตภัณฑ์หล่อลื่นจากน้ำมันสบู่ดำ**
นักศึกษา	**นางสาวจารุวัฒก์ ทองมูล**
รหัสประจำตัว	43065706
ปริญญา	**วิทยาศาสตรมหาบัณฑิต**
สาขาวิชา	**ปิโตรเคมีและเคมีของไฮโดรคาร์บอน**
พ.ศ.	2547
อาจารย์ผู้ควบคุมวิทยานิพนธ์	**ผศ.ดร. วันฉัตร ชื่นชม**

บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้ คือ การสังเคราะห์น้ำมันไบโอดีเซลและผลิตภัณฑ์หล่อลื่นจากน้ำมันสบู่ดำ น้ำมันสบู่ดำซึ่งมีโครงสร้างเป็นไตรกลีเซอไรด์จะถูกเปลี่ยนให้มีโครงสร้างเป็นเอสเทอร์เดี่ยว โดยปฏิกิริยาทรานส์เอสเทอริฟิเคชันกับแอลกอฮอล์ 6 ชนิด คือ เมทานอล เอทานอล 1-บิวทานอล 1-เฮกซานอล 1-ออกตานอล และ 1-เดคานอล ตามลำดับโดยใช้กรดซัลฟูริกเข้มข้นและโซเดียมเมทอกไซด์เป็นตัวเร่งปฏิกิริยา พบว่าเมื่อเพิ่มอัตราส่วนโมลของแอลกอฮอล์ต่อน้ำมันสบู่ดำ ปริมาณตัวเร่งปฏิกิริยา เวลาและอุณหภูมิที่ใช้ในการทำปฏิกิริยา ทำให้ปฏิกิริยาเกิดได้รวดเร็วขึ้น และได้ผลิตภัณฑ์มากขึ้นไม่ว่าจะใช้กรดหรือเบสเป็นตัวเร่งปฏิกิริยา และพบว่าเมื่อใช้กรดซัลฟูริกเข้มข้นกับโซเดียมเมทอกไซด์ในปริมาณที่เท่ากัน ตัวเร่งปฏิกิริยาเบสนั้นมีประสิทธิภาพที่ดีกว่า โดยสภาวะที่เหมาะสมในการสังเคราะห์เมทิลเอสเทอร์ในงานวิจัยนี้คือ ใช้อัตราส่วนโมลของเมทานอลต่อน้ำมันสบู่ดำเท่ากับ 40:1 ที่อุณหภูมิรีฟลักซ์ เป็นเวลา 6 ชม. โดยใช้โซเดียมเมทอกไซด์เป็นตัวเร่งปฏิกิริยาในปริมาณ 18.63% โดยน้ำหนักเทียบกับน้ำมันสบู่ดำ และได้เปอร์เซ็นต์ของผลิตภัณฑ์เมทิลเอสเทอร์เท่ากับ 93.33% สภาวะที่เหมาะสมในการสังเคราะห์เอทิลเอสเทอร์คือ ใช้อัตราส่วนโมลของเอทานอลต่อน้ำมันสบู่ดำเท่ากับ 9:1 ที่อุณหภูมิรีฟลักซ์ เป็นเวลา 6 ชม. โดยใช้กรดซัลฟูริกเข้มข้นเป็นตัวเร่งปฏิกิริยาในปริมาณ 7% โดยปริมาตรเทียบกับแอลกอฮอล์ และได้เปอร์เซ็นต์ของผลิตภัณฑ์เอทิลเอสเทอร์มากที่สุดคือ 100% และสภาวะที่เหมาะสมในการสังเคราะห์บิวทิลเอสเทอร์ เฮกซิลเอสเทอร์ ออกติลเอสเทอร์ และเดคซิลเอสเทอร์คือ ใช้อัตราส่วนโมลของบิวทานอล เฮกซานอล ออกตานอล และเดคานอลต่อน้ำมันสบู่ดำเท่ากับ 6:1 ที่อุณหภูมิ 90^{o}ซ เป็นเวลา 5 ชม. โดยใช้กรดซัลฟูริกเข้มข้นเป็นตัวเร่งปฏิกิริยาในปริมาณ 5 % โดยปริมาตรเทียบกับแอลกอฮอล์ และได้เปอร์เซ็นต์ของผลิตภัณฑ์บิวทิลเอสเทอร์ เฮกซิลเอสเทอร์ ออกติลเอสเทอร์ และ เดคซิลเอสเทอร์มากที่สุดเท่ากับ 98.67% 97.33% 96.67% และ 93.33% ตามลำดับ จากการนำน้ำมันสบู่ดำ และสารประกอบประเภท

เอสเทอร์ที่สังเคราะห์ได้ไปวิเคราะห์คุณสมบัติทางเคมีและทางกายภาพ ได้แก่ ความถ่วงจำเพาะ ความหนืด จุดไหลเท จุดวาบไฟ ความเสถียรทางความร้อน และค่าความร้อน โดยเปรียบเทียบคุณสมบัติต่างๆ กับน้ำมันดีเซลและน้ำมันหล่อลื่นพื้นฐานที่ได้จากปิโตรเลียม พบว่าเอสเทอร์ที่น่าจะมีความเหมาะสมกับการนำมาใช้แทนน้ำมันดีเซลมากที่สุดคือ เอทิลเอสเทอร์ ในแง่ของการใช้เป็นสารหล่อลื่นพบว่าไม่มีเอสเทอร์ ชนิดใดสามารถนำมาใช้แทนน้ำมันหล่อลื่นพื้นฐานได้โดยตรง แต่อาจจะนำมาใช้ผสมกับน้ำมันหล่อลื่นพื้นฐานในปริมาณที่ไม่เกิน 10% โดยปริมาตร เพื่อเพิ่มดัชนีความหนืดให้กับน้ำมันหล่อลื่นพื้นฐานได้ ซึ่งก็พบว่าเอสเทอร์ชนิดที่เหมาะสมที่สุดคือ เฮกซิลเอสเทอร์ และจากการทดสอบสมบัติของน้ำมันสบู่ดำในการนำมาใช้เป็นเชื้อเพลิง และสารหล่อลื่น พบว่าน้ำมันสบู่ดำไม่สามารถนำมาใช้ได้โดยตรง แต่สามารถใช้ผสมกับน้ำมันหล่อลื่นพื้นฐานเกรด SN150 จากปิโตรเลียมได้ในปริมาณที่มากกว่า 10% โดยปริมาตร เพื่อเพิ่มดัชนีความหนืด ในขณะที่คุณสมบัติอื่นๆ ยังใกล้เคียงกับน้ำมันหล่อลื่นพื้นฐานก่อนผสม

Thesis Title	The Synthesis of Biodiesel and Lubricants from Purging Nut Oil
Student	Miss. Jaruwat Thongmool
Student ID.	43065706
Degree	Master of Science
Programme	Petrochemicals and Hydrocarbon Chemistry
Year	2004
Thesis Advisor	Asst. Prof. Dr. Vanchat Chuenchom

ABSTRACT

The aim of this research was to synthesise biodiesel and lubricants from purging nut oil. Purging nut oil, which had a triglyceride structure, was changed into a monoester structure by transesterification reactions with six alcohols which were methanol, ethanol, 1-butanol, 1-hexanol, 1-octanol and 1-decanol, respectively, in the presence of concentrated sulfuric acid and sodium methoxide as catalyst. It was found that, with an increase in the mole ratio of alcohol/oil, the amount of catalyst, reaction temperature and reaction time, the reaction rate was raised and gave the higher percent yield of ester products. Moreover, that base catalyst was shown to be more effective than acid catalyst as the same amount of catalyst was used. The transesterification reaction of purging nut oil with methanol was completed in 6 hours at the reflux temperature using the methanol/oil mole ratio of 40:1 and $NaOCH_3$ as catalyst (18.63% weight of oil). The yield of methyl ester was 93.33%. The transesterification reaction of purging nut oil with ethanol was completed in 6 hours at the reflux temperature using the ethanol/oil mole ratio of 9:1 and concentrated sulfuric acid as catalyst (7% volume of ethanol). The maximum yield of ethyl ester was 100%. The transesterification reaction of purging nut oil with butanol, hexanol, octanol and decanol were completed in 5 hours at 90 $^{\circ}C$ using the alcohol/oil mole ratio of 6:1 and concentrated sulfuric acid as catalyst (5% volume of alcohol). The maximum yield of butyl, hexyl, octyl and decyl ester were 98.67, 97.33, 96.67 and 93.33%, respectively. The chemical and physical properties of purging nut oil and ester products which were the specific gravity, viscosity, pour point, flash point, thermal stability and gross heat of combustion were tested to compare with those of

diesel oil and lubricants base oil from petroleum. It was found that ethyl ester was suitable to be used as the diesel oil replacement more than other ester products. When considering the use of ester products as the lube base oil substitutes, the results showed that they were unlikely to be used directly. However, they could be used as an additive to improve the viscosity index of lube base oil, if the blending ratio was not exceed 10%v/v. Hexyl ester was shown to be the most appropriate one in this aspect. From the properties of purging nut oil, the results showed that it was not suitable for use directly as diesel oil and lube base oil substitute. However, it could be used as an additive in lube base oil to improve the properties of lube base oil SN 150. Purging nut oil could be blended with lube base oil SN 150 by more than 10%v/v. This improved the viscosity index while the other properties were still close to those of the lube base oil.

ACKNOWLEDGEMENT

The author would like to express her profound gratitude to her advisor, Asst. Prof. Dr. Vanchat Chuenchom for encouraging guidance, advice, discussion and helpful suggestion throughout this thesis. She is also grateful to Asst. Prof. Dr. Tawan Sooknoi, Asst. Prof. Dr. Patchanee Charoenying and Asst. Prof. Dr. Pramoch Rangsunvigit for serving as the chairman of committee and the committees, and their valuable comments.

Special thanks are also due to National Metal and Materials Technology Center (MTEC) for financial support. She also appreciates the supports from the Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang and PTT Research and Technology Institute for the equipment, chemicals and facilities.

The author would like to extend her sincere appreciation to Mr.Nares Rangsimantasiri, Mr.Narong Panya, Mr.Prasit Phoyee and Mr.Suchart Klintonglang of Department of Agricultural Extension for their helpful suggestion and supporting of the purging nut oil.

The author would like to extend her sincere appreciation to all of her friends for their support and encouragement.

Finally, the author dedicates her work to her beloved parents and sister for their moral support.

JARUWAT THONGMOOL

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

ABBREVIATIONS

°F	: degree Fahrenheit
°C	: degree Celsius
ASTM	: American Society for Testing and Materials
%vol	: percent by volume
mm^2/s	: square millimeter per second
ppm	: parts per million
%wt	: percent by weight
kPa	: kilopascal
cSt	: centistokes
mm	: millimeter
kcl/kg	: kilocalorie per kilogram
MJ/kg	: megajoule per kilogram
g	: gram
hrs	: hours
N	: normality
%wt/wt	: percent by weight per weight
%vol/weight	: percent by volume per weight
ml	: milliliter
%v/v	: percent by volume per volume
TGA	: Thermogravimetric Analyzer
FTNMR	: Fourier-Transfrom NMR spectrometer
δ	: chemical shift

CHAPTER 1
INTRODUCTION

1.1 Motivation

1.1.1 Biodiesel

With exception of hydroelectricity and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted by the end of the next century. Thus, looking for alternative sources of energy is of vital importance.

Vegetable oils are a renewable and potentially inexhaustible source of energy with an energetic content closed to diesel fuel. Historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oils as fuel for diesel engines. In the following decades, the studies became more systematic and nowadays, much is known about its use as fuel. Despite energetically favorable, the direct use of vegetable oils in fuel engines is problematic. Due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. Furthermore, acrolein (a highly toxic substance) is formed through thermal decomposition of glycerol. [1]

Of the several methods available for producing biodiesel, transesterification of natural oils and fats is currently the method of choice although blending of oils and other solvents and microemulsions of vegetable oils lowers the viscosity, engine performance problems, such as carbon deposit and lubricating oil contamination. Pyrolysis produces more biogasoline than biodiesel fuel. Transesterification is basically a sequential reaction. The purpose of the process is to lower the viscosity of the oil or fat. Triglycerides are first reduced to diglycerides. The diglycerides are subsequently reduced to monoglycerides. The monoglycerides are finally reduced to fatty acid ester [2]. The physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel, and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation [1].

1.1.2 The synthetic ester lubricants.

Historically, it has been found from the earliest times that animal and vegetable oils were used as lubricants in general transportation or machinery to reduce friction and wear. These lubricants, while still useful, are not adequate for our industrialized society, either in volume or in desirable properties. Two major problems with vegetable oils as based lubricants are low resistance to thermal stability and poor low temperature properties. However, with the addition of additives, these properties can sometimes be improved, but only at the sacrifice of biodegradability, toxicity and cost.

We can solve this problem by transesterification vegetable oils to synthetic ester lubricants. Synthetic ester lubricants show superior biodegradability, viscosity indices and lubricating properties compared with mineral oils. Ester are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils and grease formulations. The inherent biodegradability of ester molecules offers additional benefits to their performance [3].

Due to the fact that Thailand is an agricultural country that appropriate for the research of synthetic esters produced from plants. The purging nut oil will be used as the sample in this case due to its rapid growth, easy propagation, resistant to drought. Furthermore, all parts of the plant have traditional medicinal uses. For example, leaves is used to relieve coughing and as an antiseptic after birth. Latex from stem is used to arrest bleeding of wounds. The oil has a strong purgative action, and is also widely used for skin diseases, and to relieve the pain such as that caused by rheumatism [4]. Chemically, it is defined as the ester of fatty acids with the trihydric alcohol glycerol. The linoleic and oleic acid are about 30 and 40 percent of the fatty acids present, respectively [5].

1.2 Objectives

1.2.1 To synthesise biodiesel and ester lubricants from purging nut oil by transesterification reaction with alcohols, namely methanol, ethanol, 1-butanol, 1-hexanol, 1-octanol and 1-decanol, using concentrated sulfuric acid and sodium methoxide as catalyst.

1.2.2 Compare the physical and chemical properties of biodiesel and ester lubricants with diesel oil and lubricating base oil.

1.2.3 To study the possibility of using the ester products as a replacement or as an additive in diesel oil and lubricating base oil.

1.3 Scope of study

1.3.1 Synthesis of biodiesel and ester lubricants products from purging nut oil.

1.3.2 Investigation of the reaction conditions for transesterification of purging nut oil with alcohols to obtain the highest ester yield.

1.3.3 Characterization of biodiesel and ester lubricants products.

1.3.4 Study the properties of biodiesel and ester lubricants products.

1.3.5 Blending of ester products with lubricating base oil.

1.3.6 Study the properties of blending mixture.

1.4 Expected results

1.4.1 Obtain synthetic biodiesel and ester lubricants from purging nut oil that can be used in car engine.

1.4.2 Decrease the quantity of high performance diesel and lubricating base oil that are imported from abroad.

1.4.3 Decrease the environmental problems due to the use of petroleum fuels.

1.4.4 Increase the value and application of purging nut oil.

CHAPTER 2

THEORITICAL AND LITERATURE REVIEW

2.1 Diesel fuel

2.1.1 Description of diesel fuel

Liquid fuel for use in internal-combustion engines are extracted and refined from crude oil. The less volatile middle distillate fractions of crude oil boiling in the range of 250 to 370 ^{0}C are suitable as diesel fuels. The hydrocarbons present in the diesel fuels include paraffins, naphthenes, olefins and aromatics. Carbon numbers of these hydrocarbons ranges from 12 to 18. Since straight-run diesel fraction from a given crude oil is fixed, varying amounts of selected cracked distillates from conversion processes such as fluid catalytic cracking, hydrocracking units are used to increase the volume available for meeting the growing demand of diesel fuels [6].

The diesel engine uses a method of ignition which requires that the fuel ignite spontaneously and quickly (within 1 to 2 milliseconds in a high-speed engine). The time lag between the initiation of fuel injection and the initiation of combustion is called ignition delay characterized by two major factors: a mechanical factor which is influenced by such things as compression ratio, motion of the charge air during injection, and ability of the injector to atomize the fuel; and a chemical factor which is influenced by such things as the fuel's autoignition temperature, specific heat, density, thermal conductivity, surface tension, and coefficient of friction.

The fuel's effect on the chemical portion of ignition delay is expressed by a quantity called the cetane number. n-Cetane is a hydrocarbon, which has a high-ignition quality (short chemical ignition delay), has arbitrarily been assigned a cetane number of 100, whereas heptamethylnonane has been assigned a cetane number of 0. The cetane number of diesel fuel is determined by comparing it to a blend of cetane and heptamethylnonane which has the same ignition quality. The cetane number is the percentage by volume of cetane in the blend which has an ignition quality equal to the test fuel [7].

2.1.2 Categories

The American Society for Testing and Materials (ASTM) has categories diesel fuel into five grades. The need to categories these fuels results from the varied uses of diesel engines, which are designed to operate efficiency on one of the standard diesel fuels. Use of a fuel which does not meet the designated specifications could have a detrimental effect on engine efficiency and life, and could cause increased emissions and noise (low cetane number), engine wear, and corrosion (high sulfur, high ash, and high sediment). These grades are described as follows:

2.1.2.1 Grade low sulfur No. 1-D

Grade low sulfur No. 1-D comprises the class of low-sulfur, volatile fuel oils from kerosene to the intermediate distillates. Fuels within this grade are applicable for use in high-speed engines that require low sulfur fuel and in services involving frequent and relatively wide variations in loads and speeds, and also for use in cases where abnormally low fuel temperatures are encountered.

2.1.2.2 Grade low sulfur No. 2-D

Grade low sulfur No. 2-D includes the class of low-sulfur, distillate gas oils of lower volatility than Grade low sulfur No. 1-D. These fuels are applicable for use in high-speed engines that require low sulfur fuel and in services involving relatively high loads and uniform speeds, or in engines not requiring fuels having the higher volatility or other properties specified for Grade low sulfur No. 1-D.

2.1.2.3 Grade No. 1-D

Grade No. 1-D comprises the class of volatile fuel oils from kerosene to the intermediate distillates. Fuels within this grade are applicable for use in high-speed engines in services involving frequent and relative wide variations in loads and speeds, and also for use in cases where abnormally low fuel temperatures are encountered.

2.1.2.4 Grade No. 2-D

Grade No. 2-D includes the class of distillate gas oils of lower volatility. These fuels are applicable for use in high-speed engines in services involving relatively high loads and uniform speeds, or in engines not requiring fuels having the higher volatility or other properties specified for Grade No. 1-D.

2.1.2.5 Grade No. 4-D

Grade No. 4-D covers the class of more viscous distillates and blends of these distillates with residual fuel oils. These fuels are applicable for use in low- and medium-speed engines employed in services involving sustained loads at substantially constant speed [8].

The specification for Diesel fuels as shown in Table 2.1.

Table 2.1 Detailed requirements for diesel fuel oils

Properties	ASTM Test Method	Grade Low Sulfur No. 1-D	Grade Low Sulfur No. 2-D	Grade No. 1-D	Grade No. 2-D	Grade No. 4-D
1. Flash Point, °C, min.	D 93	38	52	38	52	55
2. Water and Sediment, % vol, max	D 2709	0.05	0.05	0.05	0.05	-
	D 1796	-	-	-	-	0.50
3. Distillation Temperature, °C, 90% Recovered	D 86					
min		-	282	-	282	-
max		288	338	288	338	-
4. Kinematic Viscosity, mm^2/s at 40 °C	D 445					
min		1.3	1.9	1.3	1.9	5.5
max		2.4	4.1	2.4	4.1	24.0
5. Ash, % mass, max	D 482	0.01	0.01	0.01	0.01	0.10
6. Sulfur, % mass, max	D 2622	0.05	0.05	-	-	-
	D 129	-	-	0.50	0.50	2.00
7. Copper strip corrosion rating max 3 h at 50 °C	D 130	No. 3	No.3	No.3	No.3	-
8. Cetane number, min	D 613	40	40	40	40	30
9. Cetane index, min	D 976	40	40	-	-	-
10. Ramsbottom carbon residue on 10% distillation residue, % mass, max	D 524	0.15	0.35	0.15	0.35	-

2.2 Biodiesel

2.2.1 What is biodiesel

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. "Bio" represents its renewable and biological source in

contrast to traditional petroleum-based diesel fuel; "diesel" refers to its use in diesel engines. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel [9]. The American Society for Testing and Materials (ASTM) has categories biodiesel into two grades. These grades are described as follows:

2.2.1.1 Grade S15 B100

Grade S15 B100 is a grade of biodiesel meeting ASTM specification D 6751 and having a sulfur specification of 15 ppm maximum.

2.2.1.2 Grade S500 B100

Grade S500 B100 is a grade of biodiesel meeting ASTM specification D 6751 and having a sulfur specification of 500 ppm maximum [10].

2.2.2 Properties of biodiesel

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines. The specification of biodiesel is shown in Table 2.2.

Table 2.2 The specification for biodiesel [10]

Properties	ASTM Method	Grade S15 Limits	Grade S500 Limits
1. Flash point, °C	D93	130.0 min	130.0 min
2. Water & sediment, %vol	D2709	0.050 max	0.050 max
3. Kinematic Viscosity, at 40 °C, mm^2/s	D445	1.9-6.0	1.9-6.0
4. Sulfate ash, %mass	D 874	0.020 max	0.020 max
5. Sulfur, % mass (ppm)	D 5453	0.0015 max	0.05 max
6. Copper Strip Corrosion	D130	No.3 max	No.3 max
7. Cetane number	D613	47 min	47 min
8. Cloud Point, °C	D2500	Report	Report
9. Carbon Residue, %mass	D4530	0.050 max	0.050 max
10. Acid number, mg KOH/g	D 664	0.80 max	0.80 max
11. Atmospheric equivalent temperature, 90% recovered, °C	D 1160	360 max	360 max

Table 2.3 Examples of biodiesel from various vegetable oils [6]

Properties	Vegetable oil methyl ester				
	Peanut	Soy bean	Palm	Sunflower	Tallow
1. Kinematic viscosity at 37.8 ^{0}C , mm^{2}/s	4.9	4.5	5.7	4.6	-
2. Cetane number	54	45	62	49	-
3. Lower heating value, MJ/l	33.6	33.5	33.5	33.5	-
4. Cloud Point , ^{0}C	5	1	13	1	12
5. Pour Point, ^{0}C	-	-7	-	-	9
6. Flash Point, ^{0}C	176	178	164	183	96
7. Density, gm/ml	0.883	0.885	0.880	0.860	-
8. Carbon residue, %wt.	-	1.74	-	-	1.83
9. Copper Strip Corrosion	-	1a	-	-	1a

The characteristics of biodiesel are close to diesel fuels, and therefore biodiesel becomes a strong candidate to replace the diesel fuels if the need arises. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third of that of the triglyceride, reduces the viscosity by a factor of about eight and increases the volatility marginally. Biodiesel has viscosity close to diesel fuels. These esters contain 10 to 11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel fuels in an engine. The cetane number of biodiesel is around 50. The use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the finished diesel fuel without having any negative effect on its cold flow properties. Since the volatility increases marginally, the starting problem persists in cold conditions. Biodiesel has lower volumetric heating values (about 12%) than diesel fuels but has a high cetane number and flash point. The esters have cloud point and pour points that are 15 to 25 ^{0}C higher than those of diesel fuels [6].

2.2.3 The production of biodiesel from transesterification reaction

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (Figure 2.1). The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the

adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess or to remove one of the products from the reaction mixture.

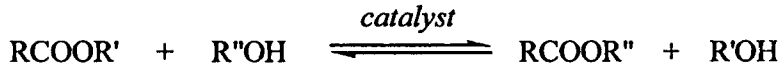


Figure 2.1 General equation for a transesterification reaction.

2.2.3.1 Transesterification of vegetable oils

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol (Figure 2.2). The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed [1].

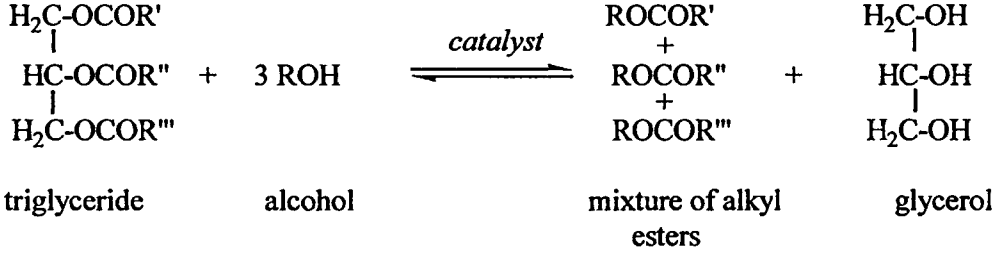


Figure 2.2 Transesterification of vegetable oils.

2.2.3.2 Process variables

The most important variables that influence transesterification reaction time and conversion are:

A) Reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (60 to 70 ^{0}C) at atmospheric pressure. These mild reaction conditions, however, require the removal of free fatty acids from the oil by refining or pre-esterification. The pretreatment is not required if the reaction is carried out under high pressure (9000 kPa)

and high temperature (240 ^{0}C). Usually, the maximum yield of esters occurs at temperature ranging from 60-80 ^{0}C at a molar ratio (alcohol to oil) of 6:1. The butanolysis and methanolysis of soy bean oil were studied at different temperatures in the presence of acidic and alkaline catalysts. These studies indicated that, given enough time, trasnsesterification can proceed satisfactorily at ambient temperatures in the case of the alkaline catalyst [6].

B) Ratio of alcohol to oil

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichemistry of the transesterification reaction requires 3 mol of alcohol per mole of triglyceride to yield 3 mol of fatty esters and 1 mol of glycerol. To shift the transesterification reaction to the right, it is necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. The second option is preferred wherever feasible, since in this way, the reaction can be driven to completion. Although, the conversion is increased when increasing the molar ratio of alcohols to vegetable oil, but higher molar ratio of alcohols to oil interferes in the separation of glycerol. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight [6].

C) Catalysts type and concentration

Acid-catalyzed processes

The transesterification process is catalyzed by Brønsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 ^{0}C and more than 3 hours to reach complete conversion.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.3, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+.

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order

to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

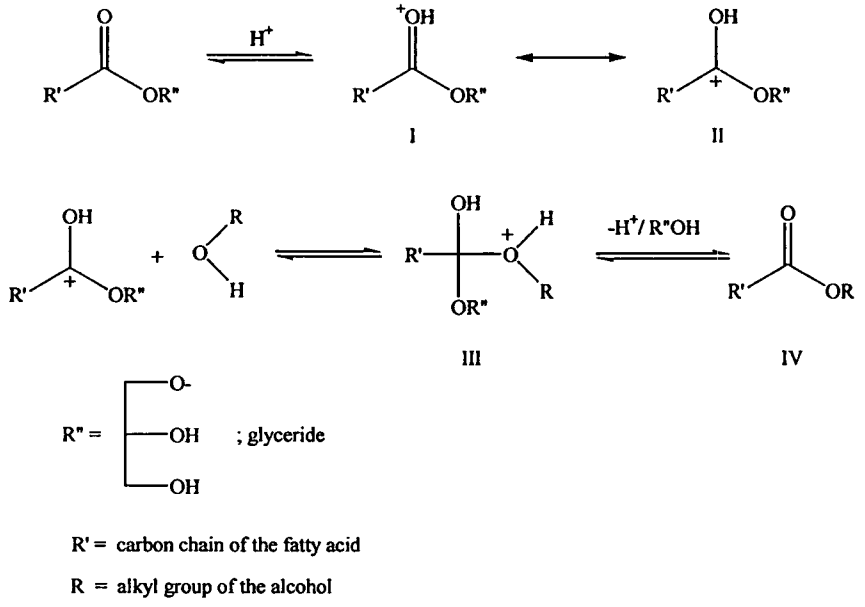


Figure 2.3 Mechanism of the acid-catalyzed transesterification of vegetable oils.

Base-catalyzed processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Sodium alkoxides are among the most efficient catalysts used for this purpose, although KOH and NaOH can also be used. Transmethylations occur approximately 4000 times faster in the presence of alkaline catalysts than those catalysed by the same amount of acidic catalyst. Due to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 2.4. The first step (Eq.1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq.2), from which the alkyl ester and the corresponding anion of the diglyceride are

formed (Eq.3). The latter deprotonates the catalyst, thus regenerating the active species (Eq.4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

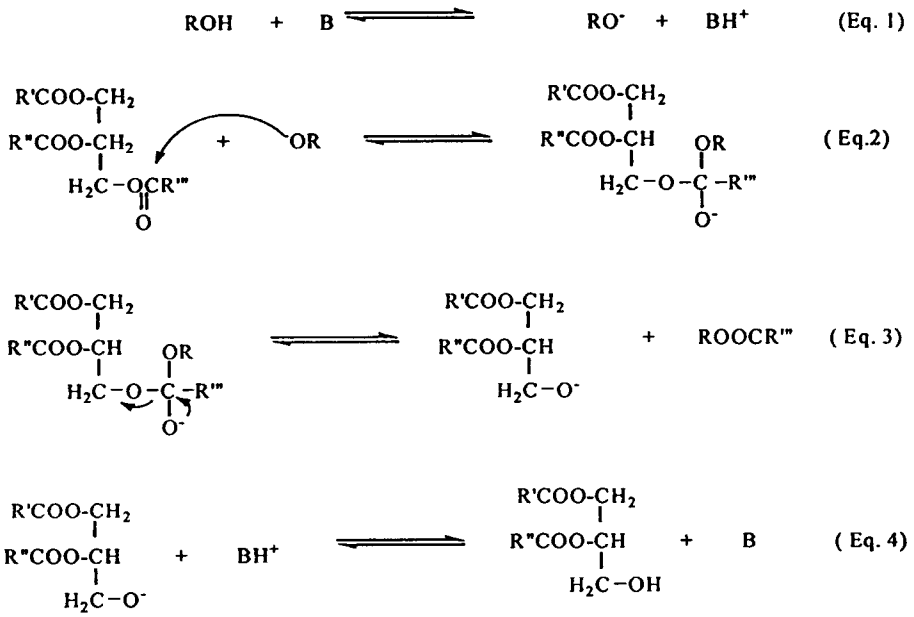


Figure 2.4 Mechanism of the base-catalyzed transesterification of vegetable oils.

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 minutes) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation (Figure 2.5). This undesirable saponification reaction reduces the ester yields

and considerably difficult the recovery of the glycerol due to the formation of emulsions [1].

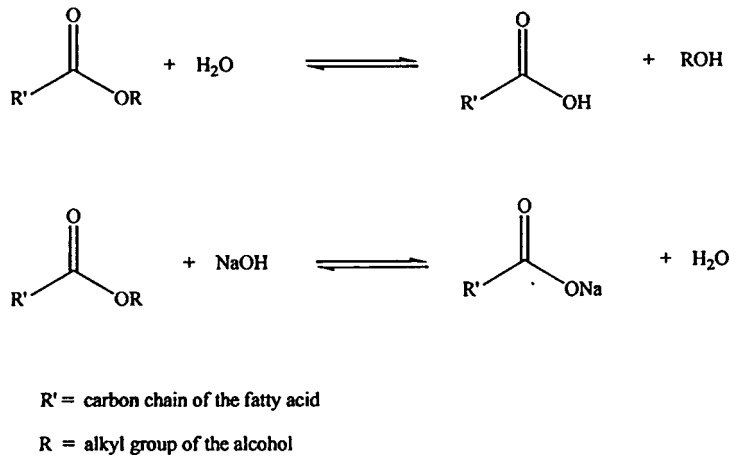


Figure 2.5 Saponification reaction of the produced fatty acid alkyl esters

2.2.4. Advantages of biodiesel

2.2.4.1 Biodiesel is safer to use than petroleum diesel. The flash point for biodiesel in its pure form is more than 149 ^{0}C versus about 52 ^{0}C for regular diesel.

2.2.4.2 Just like petroleum diesel, biodiesel can be used in conventional diesel engines. Essentially, no engines modification are required.

2.2.4.3 Biodiesel exhaust is less offensive, when compared with diesel oil, and does not require special storage. In fact, in its pure form or in blends, biodiesl can be stored wherever petroleum diesel is stored [11].

2.2.4.4 The use of biodiesel in conventional diesel engines results in substantial reduction of un-burnt hydrocarbons, carbon monoxide and particulate matter. Biodiesel is considered a clean fuel since it has almost no sulfur, no aromatics and has about 10% built-in oxygen, which helps it to burn fully. Its higher cetane number improves the ignition quality even when blended in the petroleum diesel.

2.2.4.5 Neat biodiesel fuel is non-toxic and biodegradable [12].

2.2.4.6 Biodiesel provides significant lubricity improvement over petroleum diesel fuel [13]

2.2.5. Disadvantages of biodiesel

2.2.5.1 In general, biodiesel will soften and degrade certain types of elastomers and natural rubber compounds over time. Using high percent blends can impact fuel system components (primary fuel hoses and fuel pump seals), that contain elastomer compounds incompatible with biodiesel.

2.2.5.2 Neat biodiesel will gel faster than petrodiesel in cold weather operation.

2.2.5.3 Biodiesel is more expensive to produce than petroleum diesel [13].

2.2.5.4 The viscosity of biodiesel is higher (1.9 to 6.0 cSt) and reported to result in gum formation on injector, cylinder liner etc if used in neat form. However, blends of up to 20% should not give any problem [12].

2.3 Synthetic esters

The ester is an organic, oxygen-containing material resulting from the reaction of an alcohol and an organic acid. In the past, the main lubricants were natural ester contained in animal fat or in vegetable oils; but , due to the reason of low stability and easy to decompose during use, esters of long chain alcohols and acids were proved to be excellent for low temperature lubricants. However, at present, the esters which excellent physical properties, such as low volatility, low pour point, and good low-temperature fluidity can be synthesised. They also excel in certain chemical characteristics, such as oxidative and thermal stability. The high solvency of esters also is an advantage. They readily dissolve most additives and help retain deposit precursors in solution. Esters are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils and greases formulations. The inherent biodegradability of ester molecules offers added benefits to those of performance.

The superiority of ester fluids is shown very clearly by comparing the physical properties of an ester with those of a conventional 150-s neutral mineral oil stock (Table 2.4). The ester and the mineral oil have similar viscosities at 100 ^{0}C. However, the ester, with very low pour point, retains its fluidity to much lower temperatures and has a much higher viscosity index, which is indicative of its excellent viscosity-temperature characteristics. The ester also has very low volatility and high flash point [14].

Table 2.4 Organic esters physical properties [14]

Properties	Ester	Mineral Oil
1. Viscosity, (cSt.)		
at 100 ^{0}C	4.6	5.2
at 40 ^{0}C	21.0	29.5
at –17.8 ^{0}C	474	-
at –40 ^{0}C	5,465	-
2. Viscosity index	140	102
3. Pour point (^{0}C)	-57	-18$^+$
4. Flash point (^{0}C)	243	218
5. Distillation		
% Overhead at 400 ^{0}C	3	20

+ Using pour point depressants

An example of the synthetic esters are as the following:

Monoesters

Monoesters are made by reacting a monofunctional acid (e.g. oleic, stearic) with a monofunctional alcohol (usually between 8 and 13 carbon atoms in length). Monoesters are characterized by their relatively low viscosity. Examples of commercially available monooleate esters with their physical properties are given in Table 2.5 [15].

Table 2.5 Summary of monooleate physical properties

Monooleate esters	Viscosity (cSt)		Viscosity index	Pour point (^{0}C)
	at 40 ^{0}C	at 100 ^{0}C		
Methyl	4.4	1.7	-	-12
Isobutyl	6.0	2.2	219	-50
2-Ethylhexyl	8.0	2.8	238	-35
Isooctyl	9.1	2.9	192	-
Decyl	10.2	3.4	246	-3

2.4 The basic function of lubricant

2.4.1 The reduction of friction

Simple stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important properties of a lubricating oil is its viscosity. It forms lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearing, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils and the rate of oil consumption. It determines that machines may be started under varying of equipment, satisfactory results are obtained only with the use of an oil of proper viscosity under the operated condition.

2.4.2 Heat removal

Another important function of a lubricants is to act as a coolant, removing heat generated either by friction or other sources such as via combustion process or transfer by contacting with substances at a higher temperatures. In performing this function, it is important that the lubricant remain in a relatively unchanged condition. Changes in thermal and oxidation stability which affect its ability to reach the areas involved will materially decreases its efficiency in this respect.

2.4.3 Containment of contaminants

The ability of a lubricant to remain effective in the presence of outside contaminants is quite important. These contaminants are water, acidic combustion products, particular matter, etc., which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives [16].

2.5 Standard test method for properties

2.5.1 Density, ASTM D4052

1) Density is mass per unit volume at a specified temperature.

2) This test method covers the determination of the density or relative density of petroleum distillates and viscous oils that can be handled in a normal fashion as liquids at test temperatures between 15 and 35 ^{0}C. Its application is restricted to liquids with vapor pressures below 600 mm Hg (80 kPa) and viscosities below about 15,000 cSt (mm^{2}/s) at the temperature of test. The accepted units of measure for density are grams per millilitre or kilograms per cubic metre.

2.5.2 Kinematic viscosity, ASTM D445

1) Kinematic viscosity is the resistance to flow of a fluid under gravity.

2) This test method specified a procedure for the determination of the kinematic viscosity, ν, of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The range of kinematic viscosities covered by this test method is from 0.2 to 300,000 mm^{2}/s, at all temperatures.

2.5.3 Viscosity Index, ASTM D2270

1) Viscosity index is an arbitrary number used to characterize the variation of the kinematic viscosity of a petroleum product with temperature.

2) This practice specifies the procedures for calculating the viscosity index of petroleum products, such as lubricating oils, and related materials from their kinematic viscosities at 40 and 100 ^{0}C.

3) The Viscosity Index is a widely used and accepted measure of the variation in kinematic viscosity due to changes in the temperature of a petroleum product between 40 and 100 ^{0}C. A higher viscosity index indicates a smaller decrease in kinematic viscosity with increasing temperature of the lubricant.

2.5.4 Pour point, ASTM D97

1) Pour point is the lowest temperature at which movement of the test specimen is observed under prescribed conditions of test.

2) This test method is intended for use on any petroleum product. It is used for testing the fluidity of a residual fuel oil at a specified temperature.

3) The pour point of a petroleum specimen is an index of the lowest temperature of its utility for certain applications.

2.5.5 Flash point, ASTM D92

1) Flash point is the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mmHg), at which application of an ignition source causes the vapors of a specimen of the sample to ignite under specified conditions of test.

2) This test method describes the determination of the flash and fire points of all petroleum products with flash points above 79 °C (175 °F) and below 400 °C (752 °F) except fuel oils.

3) The flash point is one measures of the tendency of the test specimen to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties that should be considered in assessing the overall flammability hazard of a material.

2.5.6 Copper strip corrosion, ASTM D 130

1) This test method covers the detection of the corrosiveness to copper of aviation gasoline, aviation turbine fuel, automotive gasoline, natural gasoline, kerosine, diesel fuel, distillate fuel oil, lubricating oil, and certain other petroleum products.

2) Crude petroleum contains sulfur compounds, most of which are removed during refining. However, of the sulfur compounds remaining in the petroleum product, some can have a corroding action on various metals and this corrosivity is not necessarily related directly to the total sulfur content. The effect can vary according to the chemical types of sulfur compounds present. The copper strip corrosive test is designed to assess the relative degree of corrosivity of a petroleum product.

2.5.7 Acid number, ASTM D 664

1) Acid number is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point.

2) This test covers procedures for the determination of acidic constituents in petroleum products.

2.5.8 Heat of combustion, ASTM D 240

1) Gross heat of combustion is the quantity of energy released when a unit mass of fuel is burned in a constant volume enclosure, with the products being gaseous, other than water that is condensed to the liquid state.

2) This test method covers the determination of the heat of combustion of liquid hydrocarbon fuels ranging in volatility from that of light distillates to that of residual fuels.

3) The heat of combustion is a measure of the energy available from a fuel. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat [17].

2.6 Purging nut (Jatropha curcas Linn.)

Jatropha curcas Linn. belongs to the family Euphorbiaceae. It is also commonly called physic nut or purging nut. It is a multipurpose tree of Mexican and Central American origin with a long history of cultivation in tropical America, Africa and Asia. The purging nut tree is of significant economic importance because of its numerous industrial and medicinal uses. Purging nut grows throughout most of the tropics and survives on poor, stony soils while being resistant to drought. The plant requires a minimum of 250 mm. rainfall per year but grows best on 900 to 1200 mm. Purging nut starts producing seeds within 12 months but reaches its maximum productivity level after 4 to 5 years and can live for up to 50 years [18].

2.6.1 Yield and description of purging nut

Purging nut is a large shrub, with a milky juice, and leaves that are heart-shaped, smooth, 5-lobed, and borne on leaf-stalks 2 or 3 inches long. The flowers are small, green, monoecious and in axillary, stalked cymes. The corolla and calyx are 5-parted, and the male flowers have 10 stamens. The ovary is 3-lobed, 3 – celled, and has a 3-parted style. The fruit is a fleshy black berry, and contains 3 seeds, about an inch in length. The kernel is oily, inodorous, sweetish to the taste, followed by acridity. The seeds are about 1 inch long, oval, flattish on one surface, rounded on the opposite, each side presentating a slight elevation, running lengthwise [19].

Purging nut can easily be propagated from seeds or cuttings. It reaches a height of up to 8 m. and is cultivated mainly for the production of seeds with an oil content of 55-60%. The oil is pale yellow to brown in color [18].

Figure 2.6 Purging nut

Figure 2.7 Purging nut seeds

2.6.2 Composition and properties of the oil

The composition of fatty acid of purging nut oil are shown in Table 2.6 and the properties of purging nut oil are shown in Table 2.7

Table 2.6 The major fatty acid composition of purging nut oil [5]

Fatty Acids	%
Saturated	
Palmitic acid	16.17
Stearic acid	5.11
Total saturated fatty acid	21.28
Unsaturated	
Oleic acid	44.89
Linoleic acid	33.83
Total unsaturated fatty acid	78.72

Table 2.7 Properties of purging nut oil [5]

Properties	Value
1. Specific gravity, at 25 °C/25 °C	0.9136
2. Refractive index, at 25 °C	1.4670
3. Total acid number, mg KOH/g	4.80
4. Saponification value	197.13
5. Iodine value	97.08
6. Water & volatile matter, at 105 °C, %	0.107
7. Flash point, °C	240
8. Carbon residue,%	0.64
9. Cetane value	51.0
10. Distillation, 90% recovered, °C	295
11. Kinematic viscosity , cSt	50.73
12. Sulfur,%	0.13
13. Calorific value , kcl/kg	9.470

2.6.3 Purging nut oil for diesel substitute

About one-third of the energy in the fruit of purging nut can be extracted as an oil that has a similar energy value to diesel fuel. Purging nut oil can be used directly in diesel engines, added to diesel fuel as an extender or trans-esterised to a bio-diesel fuel. In theory, a diesel substitute can be produced from locally grown purging nut plants, thus providing these areas with the possibility of becoming self sufficient in fuel for motive power. There are technical problems to using straight purging nut oil in diesel engines that have yet to be completely overcome. Moreover, the cost of producing purging nut oil as a diesel substitute is currently higher than the cost of diesel itself that is either subsidized or not priced at "full cost" because of misconceived and distorted national energy policies. Nevertheless the environmental benefits of substituting plant oils for diesels provides for highly desirable goals [20].

Purging nut oil has physical and chemical properties that give its potential as a petroleum-substituting fuel. Research on this oil was first initiated during the Second World War to study its use as a liquid, renewable fuel substitute for diesel oil. In recent years, research has continued to assess the oil's application as a fuel substitute. The greatest differences between purging nut oil and No. 2 diesel oil occur in viscosity, solidifying point, flash point, carbon residue and sulfur content. The high viscosity of purging nut oil contributes to the formation of carbon deposits in the engines, incomplete fuel combustion (particularly under low loads), and results in a reduction in the life of an engine. The higher solidifying point of purging nut oil limits usage in cooler climates and the higher flash point leads to ignition problems. The carbon residue value and sulfur content in purging nut oil have resulted in hydrocarbon and carbon monoxide emissions which exceed those of diesel oil under certain conditions, but sulfur emissions remain negligible when compared with diesel.

Polymerization is a serious engine problem encountered with purging nut oil. This problem can be avoided simply through the addition of an antioxidant to the oil, frequent changes of the engine oil, or through hydrogenation of the oil.

Technically, the easiest method to overcome engine problems involves blending purging nut oil with diesel. Problems with viscosity, sticking and gumming are usually

avoided or significantly reduced through blending, although generally only 10-20 percent of crude vegetable oil can be blended with diesel to obtain reasonable results.

Transesterification of purging nut oil is one of the choices to solves many engine problems from the use of purging nut oil directly in diesel engines. Due to transesterification, triglyceride is transformed into monoester which has viscosity lower than that of triglyceride [21].

The comparison of the properties of diesel fuel and purging nut oil are shown in Table 2.8

Table 2.8 Some properties of diesel fuel and purging nut oil [22]

Properties	Diesel	Purging nut oil
1. Energy content (MJ/kg)	42.6-45.0	39.6-41.8
2. Spec.weight (15/40 ^{0}C)	0.84-0.85	0.91-0.92
3. Solidifying point (^{0}C)	-14.0	2.0
4. Flash point (^{0}C)	80	110-240
5. Cetane value	47.8	51.0
6. Sulphur (%)	1.0-1.2	0.13

2.7 Literature review of biodiesel

In 1986, Prayoon Houngnikorn studied the transesterification reaction of purging nut oil with methanol, using sodium hydroxide as a catalyst. The operation conditions were the oil mass of 100 g(0.11 mole), the reaction temperature of 70 ^{0}C , the catalyst amounts of 1.17%wt of oil, methanol/oil mole ratio of 4.5:1, 6:1, 7.5:1 and 9:1, reaction time of 5,15,30,60 and 90 min. It was found that the biodiesel with the maximum yields was obtained using methanol/oil mole ratio of 7.5:1, the reaction time of 60 min. The yield of methyl ester was 91.94% [23].

In 1996, N. Foidl et al. studied the transesterification reaction of purging nut oil with methanol and ethanol, using potassium hydroxide as a catalyst. In preparation of methyl esters, 2,000 g (2.3 mol) of purging nut oil were transesterified with a solution of 30 g KOH (0.53 mol, 1.5% wt of oil) in 331 g of methanol (10.34 mol, 4.5:1 methanol/oil mole ratio). The reaction was carried out in two steps at 30 ^{0}C. First, the oil was mixed with two-third of

methanolic KOH solution and the reaction mixture was stirred for 30 min. After the separation of glycerol layer, the organic layer was mixed with the rest of the methanolic KOH solution and stirred for a further 30 min. After separation of glycerol layer, the organic layer was washed with warm water and dried over sodium sulfate anhydrous to obtain pure methyl ester. The yield of methyl ester was 92%.

For the preparation of ethyl esters, 1,000 g (1.14 mole) of purging nut oil was transesterified with a solution of 30 g KOH (0.53 mole, 3% wt of oil) in 317.7 g of ethanol (6.9 mole, 6:1 ethanol/oil mole ratio). The reaction mixtures were stirred at 75 °C for 90 min. before it was transferred to a separation funnel, and two liquid layers were formed. The separated glycerol layer was evaporized to remove excess alcohol, and acidified with 50% H_2SO_4 to pH = 5.0. The solid material was filtered, and two liquid layers were formed. After separation glycerol layer, the organic layer was mixed with 5.8 g of concentrated sulfuric acid and 69.0 g of ethanol to carry out the esterification of free fatty acids. The reaction mixture was stirred at 80 °C for 6 hrs. After cooling and separating of glycerol layer, the organic layer was combined with the ester phase from the first step, and was washed with 1 N HCl. Then, it was washed with warm water and 1 N Na_2CO_3 solution to remove free fatty acids. The product was dried over sodium sulfate anhydrous to obtain ethyl ester. The yield of ethyl ester was 88.4%. The density at 15 °C, viscosity at 30 °C, total acid number and cetane number of methyl and ethyl ester were 0.879 and 0.886 g/cm^3, 4.84 and 5.54 cSt, 0.24 and 0.08 mg KOH/g, and 51 and 59, respectively [24].

In 1999, Milford A. Hanna et al. wrote a review of biodiesel production. There are four primary ways to make biodiesel which are direct use and blending, microemulsions, pyrolysis and transesterification. The most commonly used method is transesterification of vegetable oils and animal fats. The transesterification reaction is affected by molar ratio of glycerides to alcohol, catalysts, reaction temperature, reaction time, and free fatty acids and water content of oils or fats. The commonly accepted mole ratio of alcohol to glycerides is 6:1. Base catalysts are more effective than acid catalysts and enzymes. The recommended amount of base used is between 0.1 and 1% w/w of oils and fats. Higher reaction temperatures speed up the reaction and shorten the reaction time. Base catalyzed transesterifications are basically finished within one hour. The oils or fats used

in transesterification should be substantially anhydrous ($\leq$ 0.06% w/w) and free fatty acids (< 0.5% w/w) [2].

In 1999, O.E. Ikuagwu et al. studied the transesterification reaction of crude rubber seed oil with methanol, using sodium hydroxide as a catalyst (1%wt of oil). The mole ratio of methanol/oil was 6:1. The reaction temperature and time were 60 °C and 1 hrs. The yield of methyl ester was 74.64%. The specific gravity at 30 °C/30 °C, viscosity at 30 °C, cloud point, flash point, heat of combustion and acid value of rubber seed methyl ester were 0.885, 6.29 cSt, 0.4 °C, 235 °C, 38.65 KJ/g and 0.9 mg KOH/g, respectively [25].

In 2001, J.M.Encinar et al. studied the transesterification reaction of Cynara cardunculus L. oil with ethanol, using sodium hydroxide and potassium hydroxide as catalysts. The operation variables employed were reaction temperature (25-75 °C), catatyst type (sodium hydroxide and potassium hydroxide), amount of catalyst (0.25-1.5%wt of oil), and ethanol/oil mole ratio (3:1-15:1). Oil mass of 200 g and reaction time of 120 min were fixed as common parameters in all the experiments. It was found that the biodiesel with the best properties and the maximised yields was obtained using an ethanol/oil mole ratio of 12:1, sodium hydroxide as catalyst (1%wt of oil) at 75 °C. The yield of ethyl ester was 94.5%. The density at 25 °C, viscosity at 40 °C, pour point, flash point and cetane index of Cynara ethyl ester were 0.870 g/cm^3, 4.58 cSt, -7 °C, 190 °C and 48.4, respectively [26].

In 2001, Ayaaki Ishizaki et al. studied the transesterification reaction of crude palm oil with methanol, using sulfuric acid as catalyst. The operation variables employed were the amount of acid (1 to 5% volume of H_2SO_4 by weight of oil), the mole ratio of methanol to oil (3:1 to 40:1), reaction temperature (70, 80 and 95 °C) and reaction time (3, 6, 9,12 and 24 hrs.). It was found that the methyl ester with the maximum yields was obtained using methanol/oil mole ratio of 40:1 with 5% H_2SO_4 (vol/wt) and at 95 °C for 9 hrs. The yield of methyl ester was 97%. The density at 15 °C, cetane number and flash point of crude palm methyl ester were 0.8587 g/cm^3, 49 and 27 °C minimum, respectively [27].

In 2003, A.V. Tomasevic et al. studied the transesterification reaction of used frying oil with methanol, using potassium hydroxide as catalyst. The operation conditions were the oil mass of 30 g, the reaction temperature of 25 °C for 30 min., amount of catalyst (0.5-1.5 %wt of oil) and methanol/oil mole ratio (4.5:1, 6:1 and 9:1). It was found that the biodiesel

with the maximum yields was obtained using methanol/oil mole ratio of 6:1 with 1% potassium hydroxide at 25 °C for 30 min [28].

2.8 Literature review of synthetic ester lubricants.

In 1995, Kawin Phattanaphakdee synthesized lubricating base oils from palm oil by transesterification reactions with 1-butanol and 1-hexanol, using concentrated sulfuric acid as catalyst (5% by volume of alcohols). The mole ratio of alcohol/oil was 6:1. The reaction temperature was varied from 70, 80 and 90 °C, respectively. The reaction time was varied from 1-4 hours. The reactions with 1-butanol and 1-hexanol were completed at 80 °C within 1 and 1.5 hours, respectively. The yield of butyl ester and hexyl ester products were 92.57% and 90.57%. The kinematic viscosity at 40 °C and 100 °C, viscosity index, pour point and flash point of butyl ester were 6.04 and 2.26 cSt, 197.04, -6 °C and 215 °C, respectively. The kinematic viscosity at 40 °C and 100 °C, viscosity index, pour point and flash point of hexyl ester were 7.12 and 2.40 cSt, 183.88, -6 °C and 230 °C, respectively [16].

In 1996, Naiyachan Vatanaputi synthesized lubricating oils from coconut oil by transesterification reactions with 1-hexanol and 1-octanol, using concentrated sulfuric acid as catalyst (5% by volume of alcohols). The reaction temperature was varied from 70, 80 and 90 °C, respectively. The reaction time was varied from 3-6 hours. The reactions with 1-hexanol and 1-octanol were completed at 80 °C within 3 hours. The yield of hexyl ester and octyl ester products were 87.56% and 85.02%. The kinematic viscosity at 40 °C and 100 °C, viscosity index, pour point and flash point of hexyl ester were 4.98 and 1.86 cSt, 192.5, -8 °C and 195 °C, respectively. The kinematic viscosity at 40 °C and 100 °C, viscosity index, pour point and flash point of octyl ester were 6.33 and 2.20 cSt, 183.1, -1 °C and 198 °C, respectively [29].

In 1996, Thongjuta Suwanprasert synthesized lubricating oils from soybean oil by transesterification reactions with 1-butanol and 1-hexanol, using concentrated sulfuric acid as catalyst (5% by volume of alcohols). The reaction temperature was varied from 70, 80 and 90 °C, respectively. The reaction time was varied from 1-4 hours. The reactions with 1-butanol and 1-hexanol were completed at 80 °C within 3 hours. The yield of butyl ester and hexyl ester products were 92.41% and 93.60%. The kinematic viscosity at 40 °C

and 100 °C, viscosity index, pour point and flash point of butyl ester were 5.29 and 2.04 cSt, 245.04, -11 °C and 214 °C, respectively. The kinematic viscosity at 40 °C and 100 °C, viscosity index, pour point and flash point of hexyl ester were 5.95 and 2.15 cSt, 204.92, -12 °C and 214 °C, respectively [30].

In 1999, Kachane Eiamsupasawat synthesized lubricating base oils from rice bran oil by transesterification reactions with 1-butanol, 1-hexanol and 1-octanol in toluene, using concentrated sulfuric acid as catalyst. These reaction mixtures were heated at reflux for 2, 3 and 4 hours, respectively. The reactions with 1-butanol, 1-hexanol and 1-octanol were completed in 2 hours at 84, 86 and 90 °C, respectively. The yield of butyl ester, hexyl ester and octyl ester products were 92.57%, 91.54% and 90.84%. The kinematic viscosity at 40 °C and 100 °C, viscosity index, pour point and flash point of butyl ester were 10.47 and 3.15 cSt, 182, +6 °C and 208 °C, respectively. The kinematic viscosity at 40 °C and 100 °C, viscosity index, pour point and flash point of hexyl ester were 11.53 and 3.36 cSt, 181, 0 °C and 230 °C, respectively. The kinematic viscosity at 40 °C and 100 °C, viscosity index, pour point and flash point of octyl ester were 13.60 and 3.72 cSt, 174, +6 °C and 220 °C, respectively [14].

In 2001, Onnapa Khumkratok and Areeya Tabbai synthesized decyl stearate from the esterification reaction of stearic acid and decanol in the presence of toluene with concentrated sulfuric acid as catalyst. The mole ratio of decanol/stearic acid was 2:1. The amount of concentrated sulfuric acid was 1% by mole of stearic acid. The reaction temperature and time were 130 °C and 3 hours. The yield of product was 92.57% [31].

In 2003, S. Gryglewicz, W. Piechocki and G. Gryglewicz, the preparation of neopentyl glycol and trimethylol propane esters by transesterification of triglyceride such as rape seed oil, olive oil and lard with neopentyl glycol(NPG) and trimethylol propane(TMP) using calcium methoxide as a catalyst.The method consists of a two-stage transesterification. The first stage, triglycerides are subjected to alcoholysis with methanol using sodium hydroxide as a catalyst to obtain fatty acid methyl esters. The operation condition were 450 g of the oil mass (0.5 mole), 0.11%wt of NaOH, 35 g of MeOH (1.09 mole), 65-70 °C of reaction temperature and 30 min of reaction time. After purified the yield of methyl ester was 46%. The second stage, took the fatty acid methyl esters from the first stage to transesterification with neopentyl glycol and trimethylol propane using

calcium methoxide as a catalyst. The operation condition were 50 g of FAME (0.17 mole), 8.0 g of NPG (0.07 mole) or 6.7 g of TMP(0.05 mole) and 0.3 g of $Ca(OCH_3)_2$ (0.6%wt of FAME) as a catalyst at boiling point of the reaction mixture for 20 hrs. The products yield of 85-90%. The viscosity at 40 ^{o}C, pour point and viscosity indices of NPG and TMP esters were in the range of 13.5 – 37.6 cSt, between -10.5 and -17.5 ^{o}C and between 208.7 and 234.7, respectively [31].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemicals

3.1.1 Purging nut oil.

3.1.2 Lubricating Base Oil (grade 150 SN) from PTT.

3.1.3 Methanol (analytical grade) from Fluka.

3.1.4 Ethanol (analytical grade) from Carlo Erba.

3.1.5 1-Butanol (analytical grade) from Carlo Erba.

3.1.6 1-Hexanol (analytical grade) from Fluka.

3.1.7 1-Octanol (analytical grade) from Carlo Erba.

3.1.8 1-Decanol (analytical grade) from Fluka.

3.1.9 Silicone oil from Fluka.

3.1.10 Sulfuric acid (analytical grade) from Merck.

3.1.11 Sodium sulfate anhydrous from Carlo Erba.

3.1.12 Diethyl ether from Carlo Erba.

3.1.13 Acetone (commercial grade) from Merck.

3.1.14 Sodium methoxide from Carlo Erba.

3.2 Apparatus and instruments

3.2.1 Fourier-Transfrom NMR spectrometer : Model Advanced 300 Ultra Shield (300 MHz), Spectrospin

3.2.2 Thermogravimetric Analyzer : Model Pyris 1 TGA, Perkin Elmer

3.2.3 Rotary Vacuum Evaporator : Model Rotary vacuum evaporator N- 1N series, EYELA

3.2.4 Thermostat and hot plate stirrer

3.2.5 Three necked round bottomed flask 250 ml

3.2.6 Thermometer 100, 200 and 300 ^{0}C.

3.2.7 Condenser

3.2.8 Beaker 50, 100, 250 and 500 ml

3.3 Experimental procedure

3.3.1. Synthesis of biodiesel using acid-catalyst

1) Pour 43.50 g (0.05 mole) of purging nut oil into a 250-ml three necked round bottomed flask.

2) Pipette 12.15 ml of methanol (0.3 mole, 100% alcohol excess) and 0.61 ml of concentrated sulfuric acid (5% by volume of alcohol) into the flask in 1).

3) The flask was fitted with a condenser and a thermometer, and was then placed in an oil-bath which was set on a hot plate with magnetic stirrer.

4) Heat the mixture at reflux for 6 hours.

5) After the reaction was finished, the reaction mixture was allowed to cool to room temperature. Diethyl ether was then added into the mixture to dissolve the organic layer.

6) The mixture was placed into a 500 ml separatory funnel, and was then washed several times with distilled water to remove excess acid and glycerol.

7) After the removal of aqueous layer, the organic layer was dried by using sodium sulfate anhydrous, and was filtered through a Buchner funnel.

8) Next, the organic layer was heated using the rotary vacuum evaporator to remove diethyl ether and excess alcohol. The yield of methyl ester product was determined by weighting.

9) Repeat 1) to 8) by changing the type of alcohol (ethanol), the mole ratio of alcohol and oil (3:1, 6:1, 9:1, 20:1and 40:1), concentration of catalyst (1, 5, 7 and 10% by volume of alcohol) to obtain the highest yield of monoester products.

3.3.2 Synthesis of biodiesel using base-catalyst

1) Pour 43.50 g (0.05 mole) of purging nut oil into a 250- ml three necked round bottomed flask.

2) Place 0.87 g of sodium methoxide (2% by weight of purging nut oil) and pipette 12.15 ml of methanol (0.3 mole, 100% alcohol excess) into the flask in 1).

3) The flask was fitted with a condenser and a thermometer, and was then placed in an oil-bath which was set on a hot plate with magnetic stirrer.

4) Heat the mixture at reflux for 6 hours.

5) After the reaction was finished, the mixture was allowed to cool to room temperature.

6) The mixture was then neutralized with concentrated hydrochloric acid. Diethyl ether was then added into the mixture to dissolve the organic layer.

7) The mixture was placed into a 500 ml separatory funnel, and was then washed several times with distilled water to remove excess acid and glycerol.

8) After the removal of aqueous layer, the organic layer was dried by using sodium sulfate anhydrous, and was filtered through a Buchner funnel.

9) Next, the organic layer was heated using the rotary vacuum evaporator to remove diethyl ether and excess alcohol. The yield of methyl ester product was determined by weighting.

10) Repeat 1) to 9) by changing the mole ratio of alcohol and oil (6:1 and 40:1), the amounts of catalyst (2 and 18.63% by weight of purging nut oil) to obtain the highest yield of methyl ester product.

3.3.3. Synthesis of ester lubricant using acid-catalyst

1) Pour 43.5 g of purging nut oil (0.05 mole) into a 250-ml three necked round bottomed flask.

2) Pipette 27.5 ml of butanol (0.3 mole, 100% alcohol excess) and 1.37 ml of concentrated sulfuric acid (5% by volume of alcohol) into the flask in 1).

3) The flask was fitted with a condenser and a thermometer, and was then placed in an oil-bath which was set on a hot plate with magnetic stirrer.

4) Heat the mixture at 90 $^{\circ}$C for 5 hours.

5) After the reaction was finished, the reaction mixture was allowed to cool to room temperature. Diethyl ether was then added into the mixture to dissolve the organic layer.

6) The mixture was placed into a 500 ml separatory funnel, and was then washed several times with distilled water to remove excess acid and glycerol.

7) After the removal of aqueous layer, the organic layer was dried by using sodium sulfate anhydrous, and was filtered through a Buchner funnel.

8) Next, the organic layer was heated using the rotary vacuum evaporator to remove diethyl ether, and was distilled under reduced pressure to remove excess alcohol. The yield of butyl ester product was determined by weighing.

9) Repeat 1) to 8) by changing the type of alcohol to 1-hexanol, 1-octanol, and 1-decanol, respectively.

3.3.4 Determination of the physical and chemical properties of pure purging nut oil, biodiesel and lubricant products

3.3.4.1 Determination of the physical properties of pure purging nut oil and biodiesel product

1) Kinematic viscosity @ 40 °C	by ASTM D 445
2) Specific gravity @ 25 °C	by ASTM D 4052
3) Pour point	by ASTM D 97
4) Flash point	by ASTM D 93
5) Gross heat of combustion	by ASTM D 240

3.3.4.2 Determination of the physical properties of pure purging nut oil and lubricant products

1) Viscosity @ 40 °C	by ASTM D 445
2) Viscosity @ 100 °C	by ASTM D 445
3) Viscosity Index	by ASTM D 2270
4) Pour point	by ASTM D 97
5) Flash point	by ASTM D 93
6) Copper strip corrosion	by ASTM D 130
7) Total acid number, mg KOH/g	by ASTM D 664

3.3.4.3 Determination of the chemical properties of pure purging nut oil, biodiesel and lubricant products

Determination of the purity and structure analysis of pure purging nut oil, biodiesel and lubricant product by FTNMR (Fourier-Transfrom NMR spectrometer) and TGA (Thermogravimetric Analyzer).

3.3.5 Blending

3.3.5.1 Blending lubricating base oil with pure purging nut oil and hexyl ester

1) Pipette 30 ml of hexyl ester (10 % by volume of lubricating base oil) into 270 ml of lubricating base oil (grade 150 SN) in a 500 ml-beaker, and stirred the mixture with magnetic stirrer until mixed well.

2) Then, the mixture was transferred into the bottle. The physical and chemical properties of the blending products were determined using the same method as with pure purging nut oil and lubricant products.

3) Repeat 1) to 2) by changing the ratio of hexyl ester to lubricating base oil to 7% by volume of lubricating base oil.

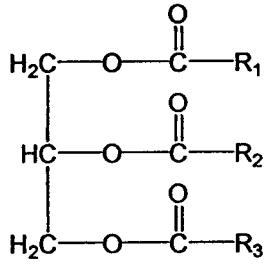
4) Repeat 1) to 2) by changing the ester to purging nut oil, and with the blending ratio of 10 and 13% by volume of lubricating base oil, respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of purging nut oil

The main composition of fatty acids in purging nut oil are palmitic acid, stearic acid, oleic acid and linoleic acid which have general structure as shown in Figure 4.1. Its structure was characterized using NMR spectroscopy and its stability was tested using TGA analysis.



R_1 R_2 and R_3 = CH_3-$(CH_2)_{14}$- (palmitic acid) , CH_3-$(CH_2)_{16}$- (stearic acid)

CH_3-$(CH_2)_7$- CH=CH-$(CH_2)_7$- (oleic acid)

or CH_3-$(CH_2)_4$- CH=CH-CH_2- CH=CH-$(CH_2)_7$- (linoleic acid)

Figure 4.1 The general structure of fatty acids in purging nut oil

^{1}H-NMR spectrum (Figure 4.2) showed the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.85-0.88 and 1.25-1.30 ppm, respectively. The signal of –CH_2-C-COO-C- appeared at δ 1.61 ppm. The signal of –CH_2-C=C appeared at δ 2.01-2.05 ppm. The signal of –CH_2-COO-C- appeared at δ 2.28-2.33 ppm. The signal of –C=C-CH_2-C=C- appeared at δ 2.74-2.76 ppm. The signal of –CH_2-OOC-R and >CH-OOC-R appeared at δ 4.11-4.17 and 4.27-4.32 ppm, respectively. The signal of –CH=CH- appeared at δ 5.26-5.35 ppm.

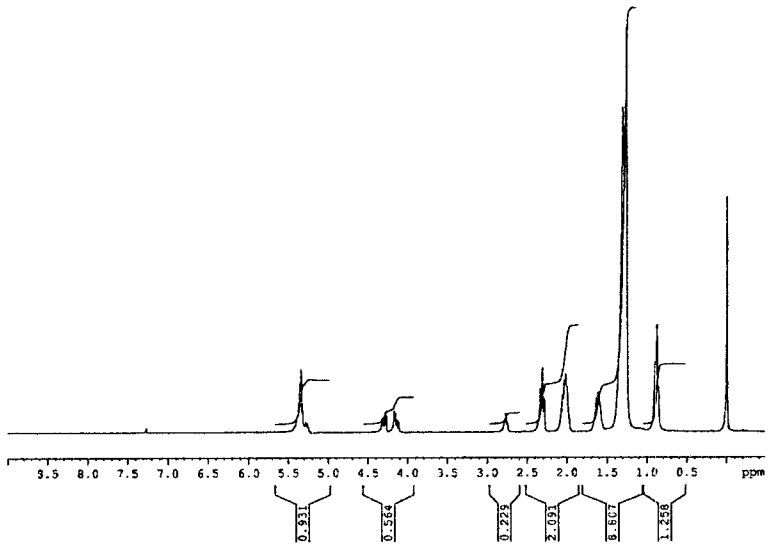


Figure 4.2 ^{1}H-NMR spectrum of purging nut oil

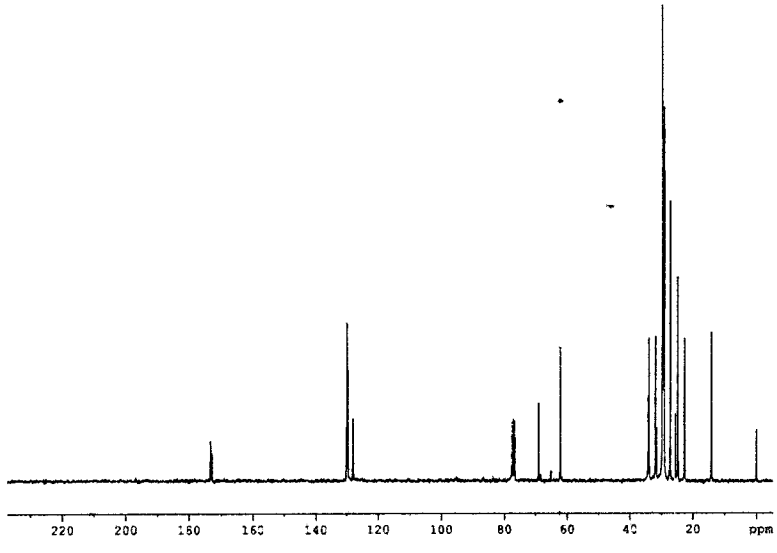


Figure 4.3 ^{13}C-NMR spectrum of purging nut oil

^{13}C-NMR spectrum (Figure 4.3) showed the signals for triglyceride of purging nut oil, the signals of methyl carbons (-CH_3) and methylene carbons (-CH_2-) at δ 14.13 and 22.61-34.22 ppm, respectively. The signals of -CH_2-O- and >CH-O- appeared at δ 62.13 and 68.93 ppm, respectively. The signal of C=O was shown at δ 172.86 and

173.27 ppm. The signals of unsaturated group appeared between δ 127.92 and 130.22 ppm.

TGA thermogram (Figure 4.4) indicated that purging nut oil changed rapidly from liquid to vapor at 339.19 °C.

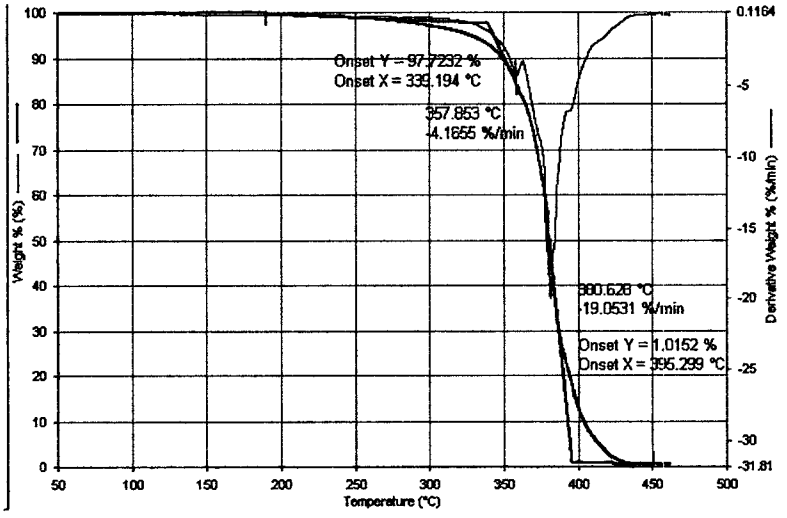


Figure 4.4 TGA thermogram of purging nut oil

The physical and chemical properties of purging nut oil, biodiesel, diesel oil and lube base oil SN 150 are listed in Table 4.1. The results showed that purging nut oil was not suitable to be used directly as diesel and lube base oil SN 150 substitute because the viscosity at 40 and 100 °C, the pour point, the flash point and total acid number of purging nut oil are higher than those of biodiesel(B100), diesel oil and lube base oil SN 150. The high viscosity causes some problems in atomization of injector systems and combustion in cylinders of diesel engines. In long term operations, high viscosity of purging nut oil may also lead to ring sticking, formation of injector deposits, development of gumming, as well as incompatibility with lubricating oils. In addition, the flash point of purging nut oil is higher than diesel oil and biodiesel(B100) which causes the problem with engines starting because purging nut oil has the lower volatility than diesel oil and biodisel(B100) thus the temperatures required for oils to give off ignitable vapors are higher. Moreover, the high amount of free fatty acids in purging nut oil can cause damage to injector and also results in deposits in fuel system and affect life of

pumps and filters. Different techniques have been developed to solve their high viscosity, low volatility and high free fatty acids problems of purging nut oil, such as preheating oils, blending or dilution with other fuels, transesterification and thermal cracking. Transesterification appears to be the most promising technique which is chemical process of converting purging nut oil into alkyl ester.

Table 4.1 The physical and chemical properties of purging nut oil, biodiesel, diesel oil and lube base oil SN 150

Properties	Purging nut oil	Biodiesel (B100) Grade S15 and S500	Diesel oil		Lube base oil SN 150
			Automotive diesel oil	Industrial diesel oil	
1. Viscosity @ 40 °C, cSt	34.98	1.9-6.0	1.8-4.1	8.0 max	30.31
2. Viscosity @ 100 °C, cSt	7.8	-	-	-	5.23
3. Viscosity Index	203.5	-	-	-	103
4. Pour point, °C	-3	-	10 max	16 max	-12
5. Cloud point	-	Report	-	-	-
6. Copper strip corrosion	1a	No.3 max	No.1 max	-	1b
7. Specific gravity @ 15.6/15.6 °C	-	-	0.81-0.87	0.920 max	-
8. Specific gravity @ 25 °C	0.9125	-	-	-	-
9. Flash point, °C	247	130.0 min	52 min	52 min	224
10. Total acid number, mg KOH/g	7.04	0.80 max	-	-	0.01

4.2 Transesterification of purging nut oil

4.2.1 Transesterification of purging nut oil with methanol

The transesterification reaction of purging nut oil with methanol was carried out by varying the mole ratio of methanol/oil (6:1, 20:1 and 40:1), the type of catalyst (concentrated sulfuric acid and sodium methoxide) and the amount of catalyst (5 and 10% of concentrated sulfuric acid by volume of methanol, and 2 and 18.63% of sodium methoxide by weight of oil) to obtain the highest yield of methyl ester product. The factors affecting the transesterification reaction are as follows:

4.2.1.1 The effect of the amount of catalyst

The effect of the amount of catalyst using acid and base as catalyst are shown in Table 4.2 and Table 4.3, respectively.

From the mechanism of the acid and base catalyzed transesterification of vegetable oils shown in Figure 2.3 and 2.4, transesterification is a three-step reversible reaction. Each of these steps starts with an attack of the carbonyl group of the triglyceride, diglyceride or monoglyceride molecule by the CH_3O^- and H^+ from the base and acid catalyst, respectively. The amount of the CH_3O^- and H^+ from the base and acid catalyst depends on the catalyst concentration. Consequently, when the amount of both acid and base catalyst were increased, the percent yield of methyl ester products was also increased. However, using excess amount of concentrated sulfuric acid gave the products which had dark brown color instead of yellow. Furthermore, using excess amount of sodium methoxide gave rise to the formation of an emulsion, which increased the viscosity and led to the formation of gels, and the problems associated with glycerol separation, and loss in ester yield.

Table 4.2 The effect of the amount of catalyst using concentrated sulfuric acid as catalyst for methyl ester synthesis

Experiments	Mole ratio of alcohol to oil (mol/mol)	Concentration of catalyst (% v/v)	Reaction temperature (°C)	Reaction time (hrs.)	Approximate yield (%)
1	6:1	5	Reflux	6	25.44
2	6:1	10	Reflux	6	70.06

Table 4.3 The effect of the amount of catalyst using sodium methoxide as catalyst for methyl ester synthesis

Experiments	Mole ratio of alcohol to oil (mol/mol)	The amount of catalyst (% wt/wt)	Reaction temperature (°C)	Reaction time (hrs.)	Approximate yield (%)
1	40:1	2	Reflux	6	19.82
2	40:1	18.63	Reflux	6	93.33

4.2.1.2 The effect of mole ratio of methanol/oil

One of the most important variables affecting the yield of ester is the mole ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three mole of fatty acid ester and one mole of glycerol. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to products.

The effect of mole ratio of methanol/oil using acid and base catalyst are shown in Table 4.4 and 4.5

Table 4.4 The effect of mole ratio of methanol/oil using concentrated sulfuric acid as catalyst for methyl ester synthesis

Experiments	Mole ratio of alcohol to oil (mol/mol)	Concentration of catalyst (% v/v)	Reaction temperature (°C)	Reaction time (hrs.)	Approximate yield (%)
1	6:1	10	Reflux	6	70.06
2	20:1	10	Reflux	6	79.17
3	40:1	10	Reflux	6	84.73

For acid and base catalyst, it was found that using the higher mole ratios of methanol/oil gave the higher percent yield of methyl ester products. When a 40:1 mole ratio of methanol/oil was used, the yield of methyl ester using 10%v/v acid and 2%wt/wt base as catalyst were 84.73 and 19.82% whereas the yield of methyl ester using a methanol/oil mole ratio of 6:1 with the same acid and base catalyst concentration were 70.06 and 17.30%. This perhaps due to the increased possibility of contact between the molecules of methanol and triglycerides. Furthermore, from the collision theory of reaction rates, the rate of a reaction is directly proportional to the number of molecular collision per unit time, or to the frequency of molecular collision. So the increased concentration of reacting species result in the greater numbers of collisions per unit time and the reaction rate is speeded up.

However, the percent yield of methyl ester was slightly changed when 2 percent of sodium methoxide by weight of oil was used because the amount of catalyst was too small. Moreover, the higher mole ratio of methanol/oil led to an extra

consumption of alcohol, which increased the production cost. This created more difficulties in the remove of glycerol and excess alcohol.

Table 4.5 The effect of mole ratio of methanol/oil using sodium methoxide as catalyst for methyl ester synthesis

Experiments	Mole ratio of alcohol to oil (mol/mol)	The amount of catalyst (% wt/wt)	Reaction temperature (°C)	Reaction time (hrs.)	Approximate yield (%)
1	6:1	2	Reflux	6	17.30
2	40:1	2	Reflux	6	19.82

4.2.1.3 The effect of the type of catalyst

The effect of the type of catalyst using acid and base as catalyst are shown in Table 4.6

Table 4.6 The effect of type of catalyst using concentrated sulfuric acid and sodium methoxide as catalyst for methyl ester synthesis

Type of catalyst	Mole ratio of catalyst to oil (mol/mol)	Mole ratio of alcohol to oil (mol/mol)	Reaction temperature (°C)	Reaction time (hrs.)	Approximate yield (%)
H_2SO_4	3:1	40:1	Reflux	6	89.27
$NaOCH_3$	3:1	40:1	Reflux	6	93.33

It was found that sodium methoxide was more effective than concentrated sulfuric acid as the same amount of catalyst was used due to the reaction rate constants for the alkali-catalyzed reaction were much higher than those for the acid catalyzed reactions [Ref.2]. Thus, the rate of alkali-catalyzed reaction is faster than acid catalyzed reactions.

However, because purging nut oil had the high amount of free fatty acids which deactivates base catalyst and the addition of excess amount of base catalyst also gave rise to the formation of emulsion that led to the problems associated with glycerol separation, the later reactions only used concentrated sulfuric acid as catalyst.

The results indicated that the transesterification reaction of purging nut oil with methanol was completed in 6 hours at the reflux temperature using the methanol/oil mole ratio of 40:1 and 0.15 mole of $NaOCH_3$ as catalyst (18.63% weight of oil, 300% mole of oil). The yield of methyl ester was 93.33%.

The methyl ester product was characterized by NMR spectroscopy. ^{1}H-NMR spectrum (Figure 4.5) showed the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.83-0.85 and 1.23-1.27 ppm, respectively. The signal of –CH_2-C-COO-C- was shown at δ 1.59 ppm. The signal of –CH_2-C=C appeared at δ 1.97-2.03 ppm. The signal of –CH_2-COO-C- appeared at δ 2.25-2.33 ppm. The signal of –C=C-CH_2-C=C- appeared at δ 2.72-2.76 ppm. The signal of R-COO-CH_3 of the methyl ester product appeared at δ 3.63 ppm. The signal of –CH=CH- appeared at δ 5.29-5.33 ppm.

^{13}C-NMR spectrum (Figure 4.6) showed the signals of methyl carbons (-CH_3) and methylene carbons (-CH_2-) at δ 13.30 and 21.80-33.32 ppm, respectively. The signals of -O-CH_3 and C=O of methyl ester product appeared at δ 50.63 and 173.58 ppm, respectively. The signals of C=O of free fatty acid appeared at 178.75 ppm which was produced from the hydrolysis of methyl ester with moisture from the air when kept the methyl ester product for a long time. The signals of unsaturated group appeared between δ 128.94 and 129.39 ppm.

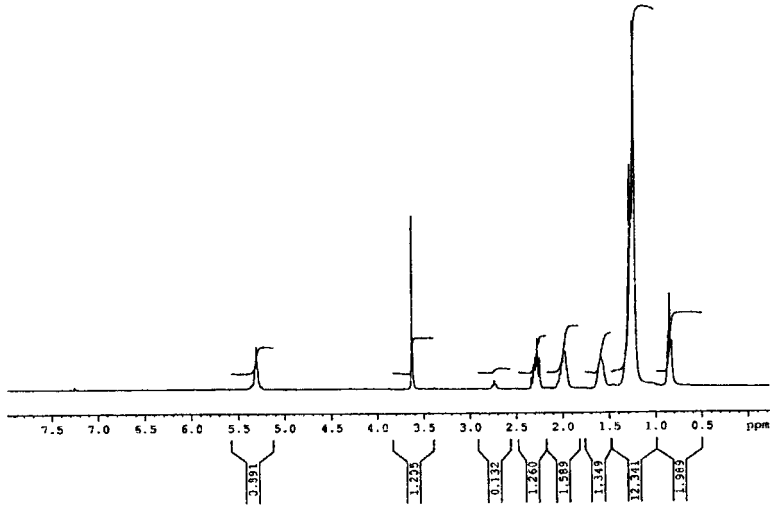


Figure 4.5 ^{1}H-NMR spectrum of methyl ester

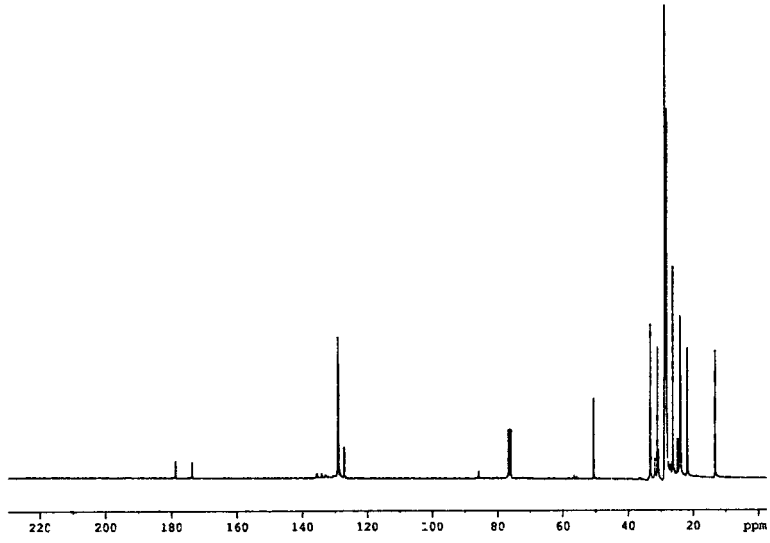


Figure 4.6 ^{13}C-NMR spectrum of methyl ester

4.2.2 Transesterification of purging nut oil with ethanol

Currently, methanol is the most appropriate alcohol to be used commercially due to its low cost. However, methanol is highly toxic, miscible with water and can be absorbed through the skin. Therefore, spills present a serious problem to aquatic life. Due to the environmental concerns, it is being replaced by ethanol, as ethanol is generally recognized as being more environmentally compatible and safer processing material than methanol. Ethanol is the most widely used renewable fuel in the world and is commonly derived from crops (sugar cane, sugar beet, wheat or cellulose source). Because Thailand is an agricultural country, so that it is suitable for the research involving the use of ethanol. The next attempt was to synthesise biodiesel using ethanol as reagent.

The transesterification reaction of purging nut oil with ethanol was carried out by varying the mole ratio of ethanol/oil (3:1, 6:1, 9:1 and 20:1) and the amount of catalyst (1 and 7% of concentrated sulfuric acid by volume of ethanol) to obtain the highest yield of ethyl ester product. The factors affecting the transesterification reaction are as follows:

4.2.2.1 The effect of the amount of catalyst

The effect of the amount of catalyst using acid catalyst are shown in Table 4.7

Table 4.7 The effect of the amount of catalyst using concentrated sulfuric acid as catalyst for ethyl ester synthesis

Experiments	Mole ratio of alcohol to oil (mol/mol)	Concentration of catalyst (% v/v)	Reaction temperature (°C)	Reaction time (hrs.)	Approximate yield (%)
1	20:1	1	Reflux	6	97.38
2	20:1	7	Reflux	6	100

It was found that when the amount of catalyst was increased from 1 to 7%, the percent yield of ethyl ester products was also raised as same as the results from the methyl ester product. The transesterification reaction of purging nut oil with ethanol was completed in 6 hours at the reflux temperature using the ethanol/oil mole ratio of 20:1 and 0.075 mole of concentrated sulfuric acid as catalyst (7% v/v of ethanol, 150% mole by mole of oil). The yield of ethyl ester was 100%. To find the optimized condition for the transesterification reaction of purging nut oil with ethanol using 7% v/v of acid, the mole ratio of ethanol/oil was changed from 20:1 to 9:1 and 3:1, respectively. The results are shown in 4.2.2.2.

4.2.2.2 The effect of mole ratio of ethanol/oil

The effect of mole ratio of ethanol/oil using acid catalyst are shown in Table 4.8

Table 4.8 The effect of mole ratio of ethanol/oil using concentrated sulfuric acid as catalyst for ethyl ester synthesis

Experiments	Mole ratio of alcohol to oil (mol/mol)	Concentration of catalyst (%v/v)	Reaction temperature (°C)	Reaction time (hrs.)	Approximate yield (%)
1	20:1	7	Reflux	6	100
2	9:1	7	Reflux	6	100
3	3:1	7	Reflux	6	93.33

It was found that the use of ethanol/oil mole ratio of 20:1 and 9:1 both gave a 100 percent yield of ethyl ester products. However, when the mole ratio of ethanol/oil was 3:1, the percent yield of ethyl ester products was 93.33%. So that the optimized condition for the transesterification reaction of purging nut oil with ethanol in this work was 6 hours at the reflux temperature using the ethanol/oil mole ratio of 9:1 and 0.035 mole of concentrated sulfuric acid as catalyst (7% v/v of ethanol, 70% mole by mole of oil). The yield of ethyl ester was 100%.

The ethyl ester product was characterized by NMR spectroscopy and its thermal stability was tested by TGA analysis, respectively.

^{1}H-NMR spectrum (Figure 4.7) showed the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.78-0.81 and 1.15-1.23 ppm, respectively. The signal of –CH_2-C-COO-C- appeared at δ 1.52-1.54 ppm. The signal of –CH_2-C=C appeared at δ 1.92 -1.98 ppm. The signal of –CH_2-COO-C- appeared at δ 2.18-2.23 ppm. The signal of –C=C-CH_2-C=C- appeared at δ 2.67-2.71 ppm. The signal of R-COO-CH_2- of the ethyl ester product appeared at δ 4.01-4.08 ppm. The signal of –CH=CH- appeared at δ 5.24-5.28 ppm.

^{13}C-NMR spectrum (Figure 4.8) showed the signals of methyl carbons (-CH_3) and methylene carbons (-CH_2-) at δ 13.41-13.57 and 21.92-33.69 ppm, respectively. The signals of -O-CH_2- and C=O of ethyl ester product appeared at δ 59.43 and 173.13 ppm, respectively. The signals of unsaturated group appeared between δ 127.26 and 129.47 ppm.

TGA thermogram (Figure 4.9) showed that ethyl ester was quickly evaporated at 271.44 °C.

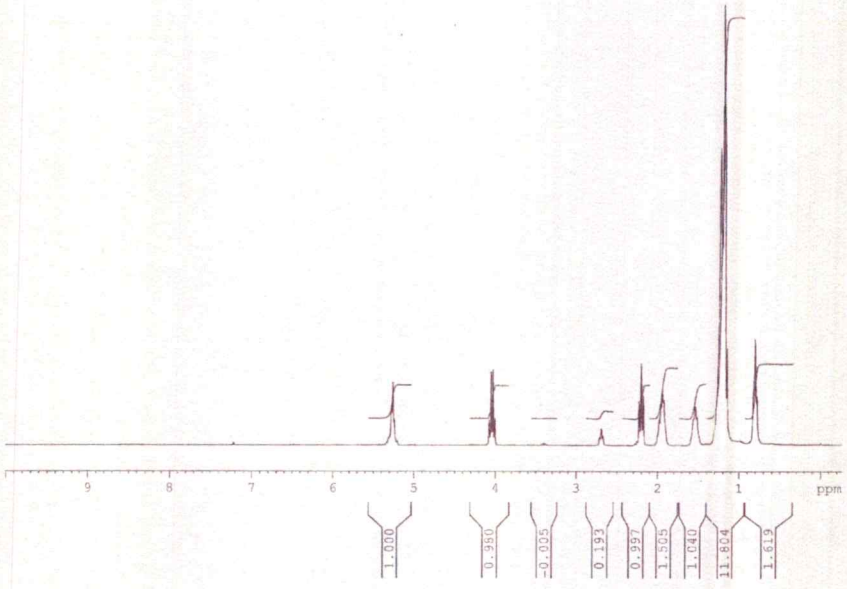


Figure 4.7 ^{1}H-NMR spectrum of ethyl ester

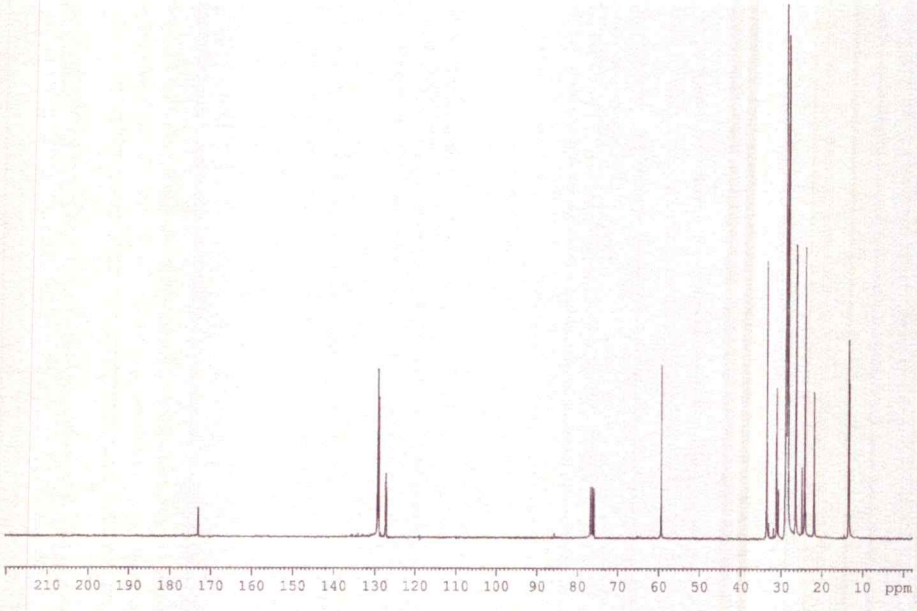


Figure 4.8 ^{13}C-NMR spectrum of ethyl ester

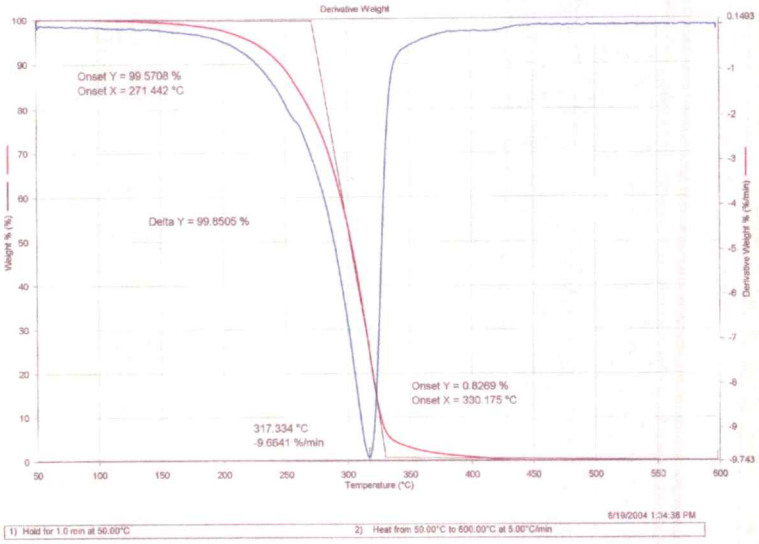


Figure 4.9 TGA thermogram of ethyl ester

4.2.3 Transesterification of purging nut oil with 1-butanol

The transesterification reaction of purging nut oil with 1-butanol was completed in 5 hours at 90 °C using the butanol/oil mole ratio of 6:1 and 0.026 mole of concentrated sulfuric acid as catalyst (5% volume of butanol, 52% mole of oil). The yields of butyl ester were in the range of 97.65 to 98.67 %.

The butyl ester product was characterized by NMR spectroscopy and its thermal stability was tested by TGA analysis, respectively.

^{1}H-NMR spectrum (Figure 4.10) showed the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.88-0.95 and 1.26-1.41 ppm, respectively. The signal of –CH_2-C-COO-C- appeared at δ 1.55-1.63 ppm. The signal of –CH_2-C=C appeared at δ 2.01-2.03 ppm. The signal of –CH_2-COO-C- appeared at δ 2.26-2.31 ppm. The signal of –C=C-CH_2-C=C- appeared at δ 2.75-2.77 ppm. The signal of R-COO-CH_2- of the butyl ester product appeared at δ 4.04-4.08 ppm. The signal of –CH=CH- appeared at δ 5.33-5.36 ppm.

^{13}C-NMR spectrum (Figure 4.11) showed the signals of methyl carbons (-CH_3) and methylene carbons (-CH_2-) at δ 13.72-14.12 and 19.21-34.43 ppm, respectively. The signals of -O-CH_2- and C=O of butyl ester product appeared at δ 64.10 and 173.95

ppm, respectively. The signals of unsaturated group appeared between δ 127.97 and 130.19 ppm.

TGA thermogram (Figure 4.12) showed that butyl ester was quickly evaporated at 284.04 ^{o}C

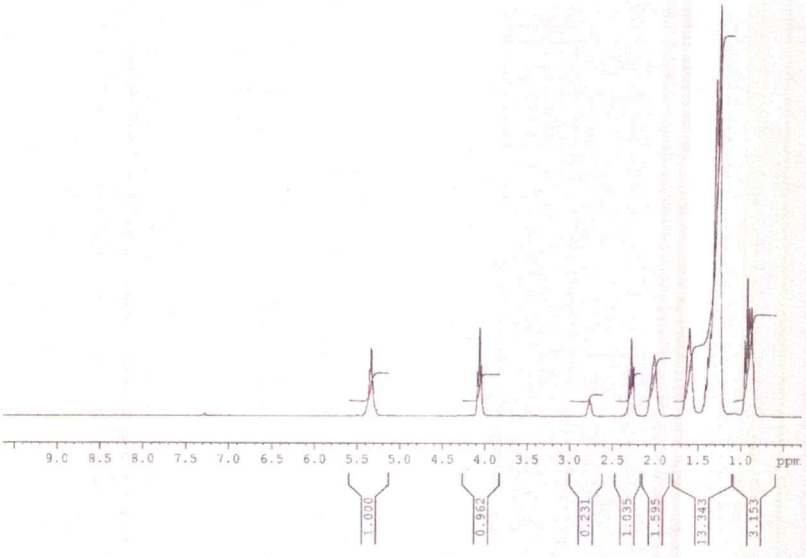


Figure 4.10 ^{1}H-NMR spectrum of butyl ester

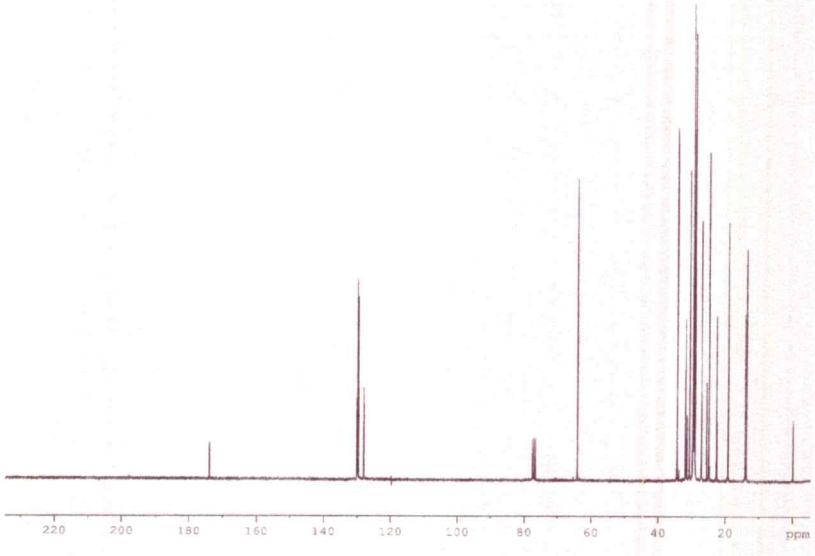


Figure 4.11 ^{13}C-NMR spectrum of butyl ester

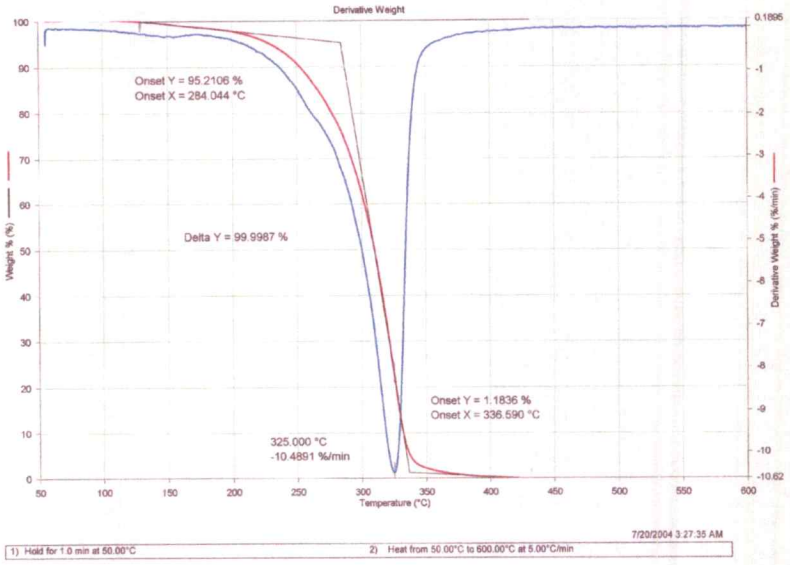


Figure 4.12 TGA thermogram of butyl ester

4.2.4 Transesterification of purging nut oil with 1-hexanol

The transesterification reaction of purging nut oil with 1-hexanol was completed in 5 hours at 90 °C using the hexanol/oil mole ratio of 6:1 and 0.035 mole of concentrated sulfuric acid as catalyst (5% volume of hexanol, 70% mole of oil). The yields of hexyl ester were in the range of 93.33 to 97.33 %.

The hexyl ester product was characterized by NMR spectroscopy and its thermal stability was tested by TGA analysis, respectively.

^{1}H-NMR spectrum (Figure 4.13) showed the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.89 and 1.26-1.30 ppm, respectively. The signal of –CH_2-C-COO-C- appeared at δ 1.59-1.61 ppm. The signal of –CH_2-C=C appeared at δ 2.01-2.05 ppm. The signal of –CH_2-COO-C- appeared at δ 2.26-2.31 ppm. The signal of –C=C-CH_2-C=C- appeared at δ 2.75-2.77 ppm. The signal of R-COO-CH_2- of the hexyl ester product appeared at δ 4.03-4.07 ppm. The signal of –CH=CH- appeared at δ 5.33-5.35 ppm.

^{13}C-NMR spectrum (Figure 4.14) showed the signals of methyl carbons (-CH_3) and methylene carbons (-CH_2-) at δ 14.01-14.13 and 22.60-34.44 ppm, respectively. The signals of -O-CH_2- and C=O of hexyl ester product appeared at δ 64.41 and 173.93

ppm, respectively. The signals of unsaturated group appeared between δ 127.98 and 130.22 ppm.

TGA thermogram (Figure 4.15) showed that hexyl ester was quickly evaporated at 295.84 °C

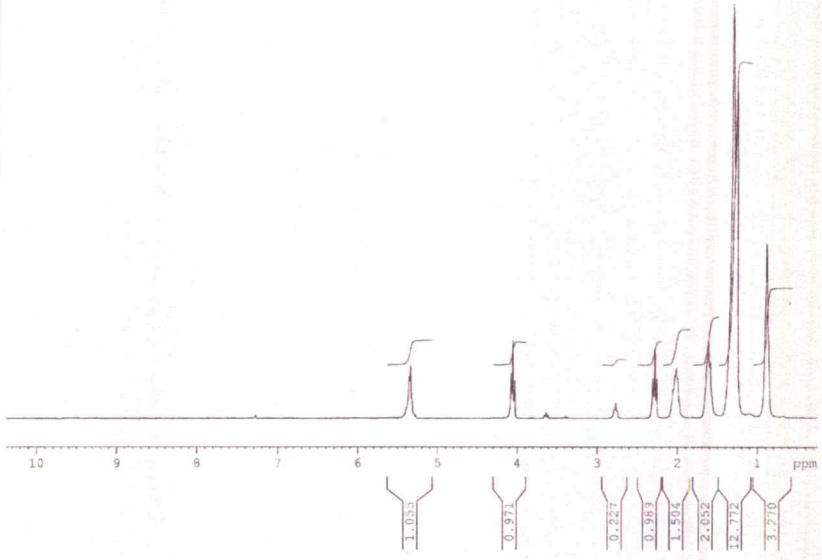


Figure 4.13 ^{1}H-NMR spectrum of hexyl ester

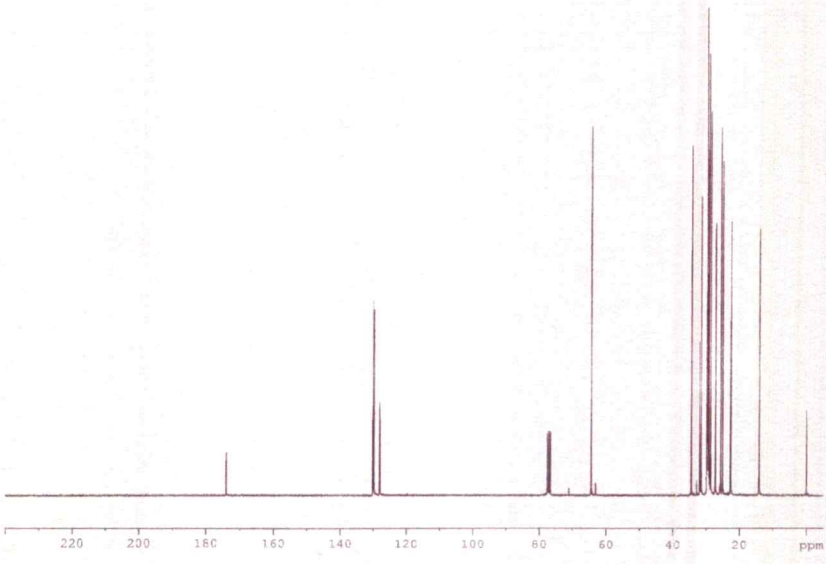


Figure 4.14 ^{13}C-NMR spectrum of hexyl ester

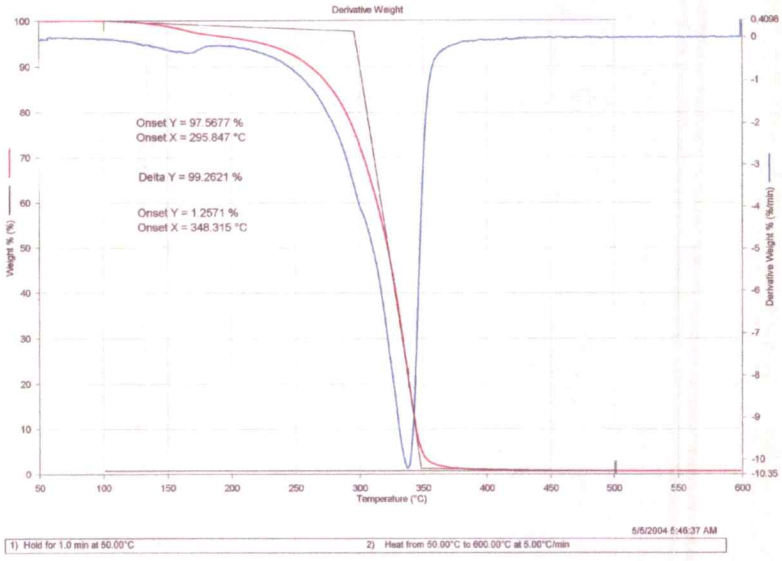


Figure 4.15 TGA thermogram of hexyl ester

4.2.5 Transesterification of purging nut oil with 1-octanol

The transesterification reaction of purging nut oil with 1-octanol was completed in 5 hours at 90 °C using the octanol/oil mole of 6:1 and 0.044 mole of concentrated sulfuric acid as catalyst (5% volume of octanol, 88% mole of oil). The yields of octyl ester were in the range of 95.67 to 96.67 %.

The octyl ester product was characterized by NMR spectroscopy and its thermal stability was tested by TGA analysis, respectively.

^{1}H-NMR spectrum (Figure 4.16) showed the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.85-0.87 and 1.25-1.29 ppm, respectively. The signal of –CH_2-C-COO-C- appeared at δ 1.58-1.60 ppm. The signal of –CH_2-C=C appeared at δ 2.01 ppm. The signal of –CH_2-COO-C- appeared at δ 2.25-2.30 ppm. The signal of –C=C-CH_2-C=C- appeared at δ 2.76 ppm. The signal of R-COO-CH_2- of the octyl ester product appeared at δ 4.02-4.07 ppm. The signal of –CH=CH- appeared at δ 5.32 ppm.

^{13}C-NMR spectrum (Figure 4.17) showed the signals of methyl carbons (-CH_3) and methylene carbons (-CH_2-) appeared at δ 14.37 and 22.97-34.70 ppm, respectively. The signals of -O-CH_2- and C=O of octyl ester product appeared at δ 64.67 and 174.16

ppm, respectively. The signals of unsaturated group appeared between δ 128.26 and 130.46 ppm.

TGA thermogram (Figure 4.18) showed that octyl ester was quickly evaporated at 311.92 °C

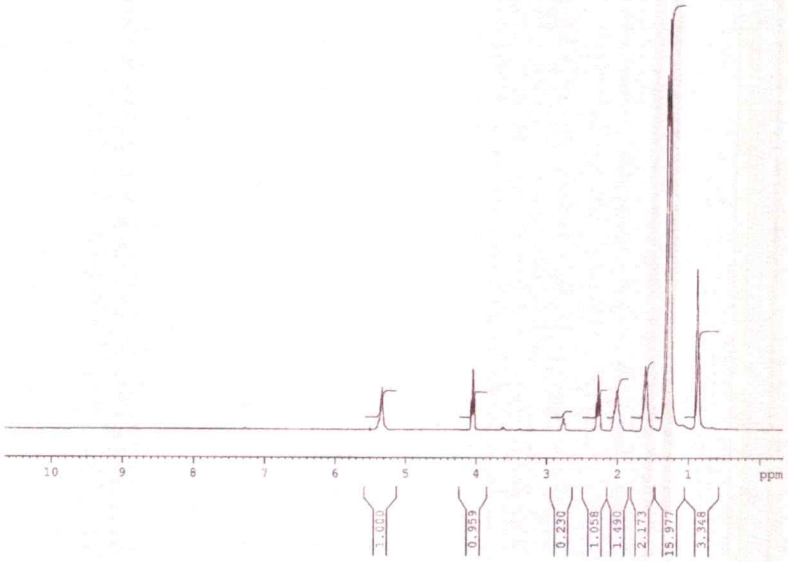


Figure 4.16 ^{1}H-NMR spectrum of octyl ester

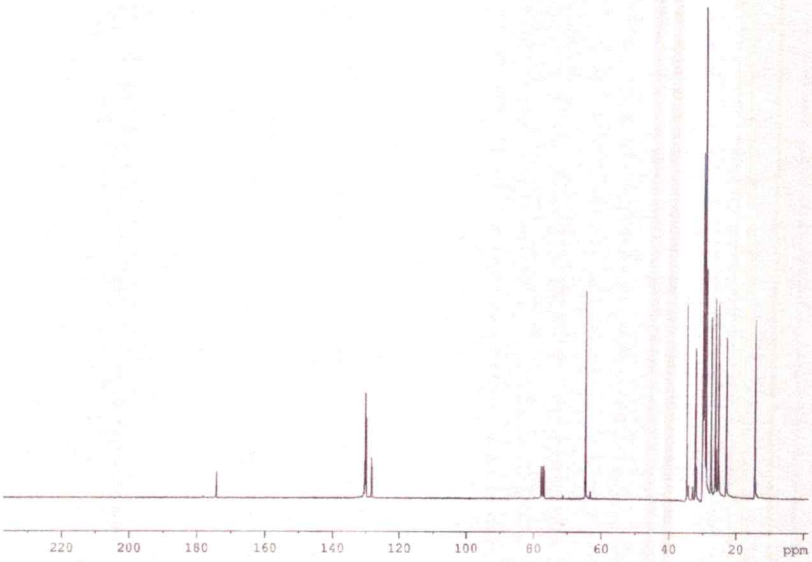


Figure 4.17 ^{13}C-NMR spectrum of octyl ester

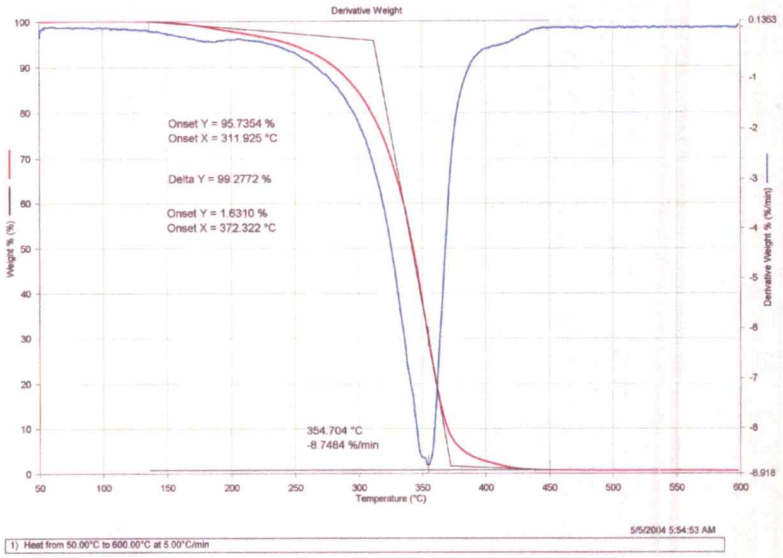


Figure 4.18 TGA thermogram of octyl ester

4.2.6 Transesterification of purging nut oil with 1-decanol

The transesterification reaction of purging nut oil with 1-decanol was completed in 5 hours at 90 ^{o}C using the decanol/oil mole ratio of 6:1 and 0.054 mole of concentrated sulfuric acid as catalyst (5% volume of decanol, 108% mole of oil). The yields of decyl ester were in the range of 90 to 93.33 %. The decyl ester product was then characterized by NMR spectroscopy, and its thermal stability was tested by TGA analysis.

^{1}H-NMR spectrum (Figure 4.19) showed the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.86-0.88 and 1.27-1.31 ppm, respectively. The signal of –CH_2-C-COO-C- appeared at δ 1.59-1.61 ppm. The signal of –CH_2-C=C appeared at δ 2.02-2.04 ppm. The signal of –CH_2-COO-C- appeared at δ 2.26-2.31 ppm. The signal of –C=C-CH_2-C=C- appeared at δ 2.75-2.77 ppm. The signal of R-COO-CH_2- of the decyl ester product appeared at δ 4.03-4.08 ppm. The signal of –CH=CH- appeared at δ 5.28-5.36 ppm.

^{13}C-NMR spectrum (Figure 4.20) showed the signals of methyl carbons (-CH_3) and methylene carbons (-CH_2-) appeared at δ 14.43 and 22.94-34.75 ppm, respectively. The signals of -O-CH_2- and C=O of decyl ester product appeared at δ 64.73 and 174.24

ppm, respectively. The signals of unsaturated group appeared between δ 128.29 and 130.52 ppm.

TGA thermogram (Figure 4.21) showed that decyl ester was quickly evaporated at 324.39 ^{o}C

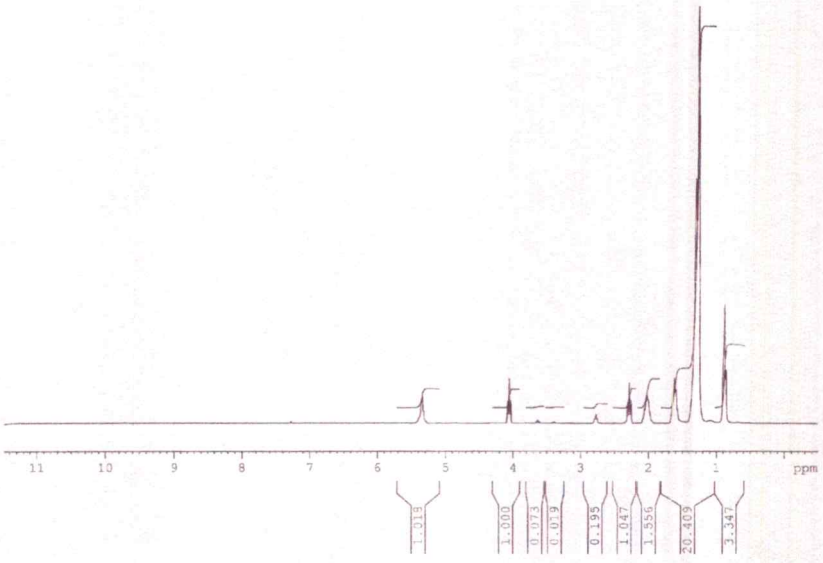


Figure 4.19 ^{1}H-NMR spectrum of decyl ester

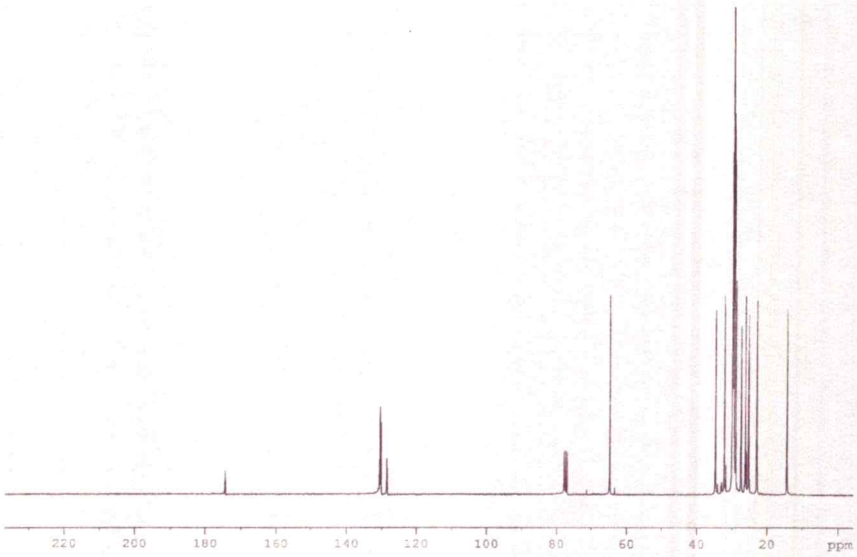


Figure 4.20 ^{13}C-NMR spectrum of decyl ester

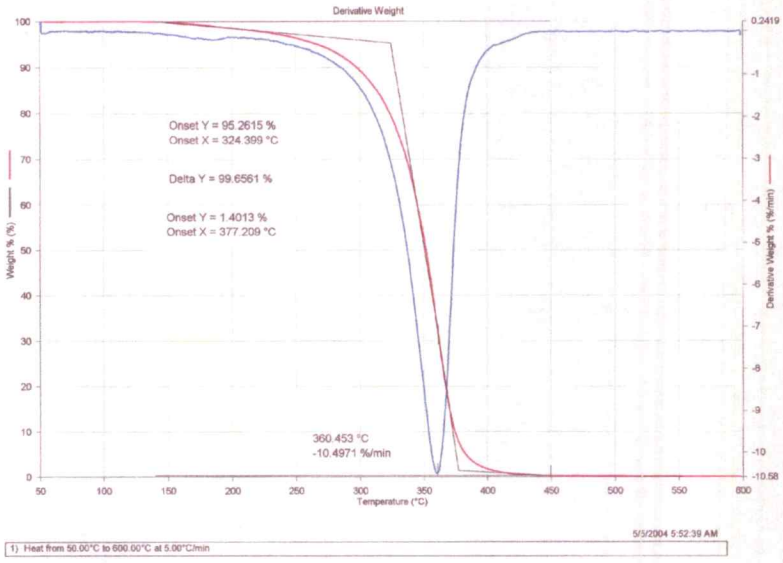


Figure 4.21 TGA thermogram of decyl ester

4.3 Application of monoesters as diesel oil and lubricating base oil substitute

4.3.1 Monoesters as diesel substitute

The properties of monoesters comparing with purging nut oil, biodiesel (B100), diesel oil and lube base oil SN 150 are shown in Table 4.9.

It was found that the gross heat of combustion of purging nut oil was close to that of diesel oil. However, its direct use in diesel engines is restricted by some unfavorable physical properties, such as viscosity, flash point and total acid number. The viscosities of purging nut oil is approximately 9 times higher than automotive diesel oil, 4 times higher than industrial diesel oil and 6 times higher than biodiesel (B100). Thus, use of purging nut oil in direct injection diesel engines may create poor atomization of the fuel spray, incomplete combustion, carbon deposition on the injector, and fuel build up in the lubricants oil resulting in serious engine fouling. In addition, the flash point of purging nut oil is higher than diesel oil and biodiesel (B100) so that it is safer than diesel oil, however, high flash point causes the problem with engines starting because purging nut oil has the lower volatility than diesel oil and biodiesel(B100) thus the temperatures required for oils to give off ignitable vapors are higher.

Table 4.9 The physical and chemical properties of monoesters, purging nut oil, biodiesel(B100) and lube base oil SN 150

Properties	ASTM Methods	Ethyl Ester	Butyl Ester	Hexyl Ester	Octyl Ester	Decyl Ester	Purging Nut Oil	Lube Base Oil SN 150	Diesel Oil		Biodiesel (B100) Grade S15 and S500
									Limits		Limits
									Automotive Diesel Oil	Industrial Diesel Oil	
1.Viscosity @ 40 °C, cSt	D 445	6.61	6.42	6.41	8.73	10.84	34.98	30.31	1.8-4.1	8.0 max	1.9-6.0
2. Viscosity @ 100 °C, cSt	D 445	-	2.28	2.39	2.99	3.34	7.8	5.23	-	-	-
3. Viscosity Index	D 2270	-	205.5	253.2	237.8	202.9	203.5	103	-	-	-
4. Pour Point, °C	D 97	0	-3	-3	+6	+15	-3	-12	10 max	16 max	-
5. Copper Strip Corrosion	D 130	-	-	1a	-	-	1a	1b	No.1 max	No.1 max	No.3 max
6. API Gravity, API	D 4052	-	-	-	-	-	-	30.8	-	-	-
7. Specific Gravity @ 25 °C	D 4052	-	-	-	-	-	0.9125	-	-	-	-
8. Specific Gravity @ 15.6/15.6°C	D 1298	0.8873	0.8754	-	-	-	-	-	0.81-0.87	0.920 max	-
9. Flash Point, °C	D 93	103	110	-	-	-	247	224	52 min	52 min	130.0 min
10. Total Acid Number, mg KOH/g	D 664	-	-	4.21	-	-	7.04	0.01	-	-	0.80 max
11. Gross Heat of Combustion, J/g	D 240	39,519	40,435	-	-	-	41,800**	-	45,782*	-	-
12. TGA Analysis, °C	-	271.44	284.04	295.84	311.92	324.39	357.32	311.70	-	-	-

Moreover, the high amount of free fatty acids in purging nut oil can cause damage to injector and also results in deposits in fuel system and affect life of pumps and filters. In order to use purging nut oil in diesel engines, they should be modified by installing the oil pre-heat system (pre-combustion chamber) and improving the pump and injection system. Besides, purging nut oil can be blended with diesel oil or alcohols. Blending can reduce the viscosity of oil. Moreover, transesterification can be used to reduce the viscosity and the amount of free fatty acid in oil

It was found that the viscosity, pour point, flash point and gross heat of combustion of ester products, namely ethyl, butyl, hexyl, octyl and decyl ester were increased when the size of alkyl group increased from ethyl to decyl. The volatility of ester products was, on the other hand, decreased with the size of alkyl group. Considering the viscosity at 40 °C, it was found that ethyl, butyl and hexyl ester had the viscosity lower than the maximum limits of industrial diesel oil. It was also found that ethyl, butyl, hexyl and octyl ester had the pour point lower than the maximum limits of diesel oil. Furthermore, ethyl and butyl ester had the specific gravity lower than the maximum limits of industrial diesel oil. Considering the gross heat of combustion, it was found that butyl ester was more suitable for use as diesel oil substitute than ethyl ester due to the higher gross heat of combustion. Nevertheless, ethyl ester had lower flash point than butyl ester-hence its high volatility. Ethyl ester also had lower production cost than butyl ester because ethanol was cheaper than butanol. Moreover, comparing the properties of ethyl ester from purging nut oil in this experiment with ethyl ester from purging nut oil from the previous work [24], it was found that ethyl ester in this work had the specific gravity at 15.6 °C/15.6 °C of 0.8873 and the viscosity at 40 °C of 6.61 cSt which were higher than those of ethyl ester from previous work (0.8867, 4.41 cSt) [33]. This was because the major fatty acid in purging nut oil from this work was oleic acid, whereas in the previous work linoleic acid was predominant, thus ethyl ester in this work was less unsaturate. As the results, the viscosity and density of ester product in this work were higher than those from previous work. Besides, when compare the properties of ethyl ester from purging nut oil in this work with Cynara ethyl ester [26], it was found that ethyl ester from purging nut oil had the viscosity at 40 °C (6.61 cSt) and the pour point (0 °C) higher than the viscosity at 40 °C (4.58 cSt) and the pour point (-7 °C) of

Cynara ethyl ester. This was because purging nut oil had more saturated fatty acid than Cynara cardunculas L. oil which increased viscosity and pour point of ester product.

4.3.2 Monoesters as lubricant

It was found that purging nut oil was not suitable to be used directly as a lube base oil SN 150 substitute due to its higher viscosity, pour point and total acid number. However, the viscosity index, flash point and thermal stability of purging nut oil were higher than those of lube base oil SN 150, thus, it could be used directly as lube base oil if the free fatty acid was eradicated prior to use. Transesterification of purging nut oil to monoester products is an appropriate way to reduce the viscosity and the amount of free fatty acid in oil.

Comparing the properties of monoester products with lube base oil SN150, it was found that the viscosity of ethyl, butyl, hexyl, octyl and decyl ester were lower than that of lube base oil SN150, while the pour point of ester products were higher, so that ester products were not suitable to be used directly as lube base oil SN 150 substitute. However, the viscosity index of ester products was much higher than that of lube base oil SN 150. Therefore, ester products could be used an additive to improve viscosity index of lube base oil SN 150.

When compare the properties of hexyl and octyl ester from purging nut oil with hexyl and octyl ester from coconut oil [29], it was found that hexyl and octyl ester from purging nut oil had the viscosity, viscosity index and pour point higher than those hexyl and octyl ester from coconut oil. Hexyl ester in this work had the viscosity at 40 °C and 100 °C of 6.41cSt and 2.39 cSt, the viscosity index of 253.2 and the pour point of -3 °C. Octyl ester in this work had the viscosity at 40 °C and 100 °C of 8.73 cSt and 2.99 cSt, the viscosity index of 237.8 and the pour point of +6 °C. Whereas hexyl ester from coconut oil had the viscosity at 40 °C and 100 °C of 4.98 and 1.86 cSt, the viscosity index of 192.5 and the pour point of -8 °C. Octyl ester from coconut oil had the viscosity at 40 °C and 100 °C of 6.33 and 2.20 cSt, the viscosity index of 183.1 and the pour point of -1 °C. This was because purging nut oil had oleic acid as major fatty acid components that had 18 carbon chain length while coconut oil had lauric acid that had 12 carbon chain length as main component, therefore purging nut oil containing

triacyglycerols of higher molecular weight were more viscous than coconut oil. Moreover, purging nut oil had the carbon chain length longer than coconut oil, thus pour point and viscosity index of purging nut oil were higher than coconut oil. When comparing the properties of monoester products with polyol ester of neopentyl glycol (NPG) and trimethylol propane (TMP) esters [32], it was found that NPG and TMP esters had the viscosity at 40 °C in the range of 13.5-37.6 cSt that was higher than the viscosity at 40 °C of monoester products in the range of 6.41-10.84 cSt. This is probably due to the fact that there are three acid groups in the structure of TMP esters and two acid groups in the molecules of NPG esters whereas there is one acid group in the structure of monoester products. NPG and TMP esters had more carbon chains and functional groups in the structure than monoester products. However, the pour point of NPG and TMP esters were between -10.5 and -17.5 °C and viscosity indices were in the range of 208.7- 234.7 that were lower than the pour point (-3 to 15 °C) and viscosity indices (202.9-253.2) of monoester products due to the higher amount of branching in the molecule of NPG and TMP esters.

4.4 Blending lube base oil SN 150 with purging nut oil and hexyl ester

In the study of the ability of monoester as a viscosity index improver, it was found that hexyl ester was suitable for use as a viscosity index improver due to its highest viscosity index. Although the pour point of hexyl ester (-3 °C) was higher than that of lube base oil (-12 °C) but it was still lower than 0 °C. Its thermal stability was slightly lower than lube base oil, which was not a problem when used as an additive. Comparing with butyl ester, it was found that the pour point of butyl ester was equal to hexyl ester, but the viscosity index of butyl ester was lower than hexyl ester. Looking at the properties of octyl and decyl ester, it was found that both esters had the thermal stability close to that of lube base oil but there viscosity indices were lower than hexyl ester. Moreover, the pour points of both esters were very high, therefore they were not suitable to be used directly as lube base oil substitutes or in the blends. As the results, hexyl ester was the most suitable ester for use as an additive to improve the viscosity index of lube base oil.

The properties of lube base oil SN 150 comparing with lube base oil SN 150 blended with hexyl ester and purging nut oil by 10 percent volume of lube base oil SN 150 were shown in Table 4.10.

Table 4.10 The physical and chemical properties of lube base oil SN 150 and the lube base oil blended with of purging nut oil and hexyl ester

Properties	Blended purging nut oil 10%v/v	Blended hexyl ester 10%v/v	Lube base oil SN 150	Specification Limits	
				Min	Max
1. Viscosity @ 40 °C, cSt	28.99	23.32	30.31	29.0	32.0
2. Viscosity @ 100 °C, cSt	5.34	4.61	5.22	-	5.2-5.45
3.Viscosity Index	119.2	113.5	103.0	100.0	-
4. Pour Point, °C	-12	-9	-12	-	-9
5.Total Acid Number, mg KOH/g	0.78	0.12	0.01	-	0.03

It was found that the viscosity index of lube base oil SN 150 blended with hexyl ester by 10 percent volume was higher than lube base oil SN 150 and the specification limits of lube base oil, but the viscosity of the hexyl ester blend was significantly lower and out of specification limit. This was because the viscosity of hexyl ester was much lower than that of the lube base oil. For the pour point, it was found that pour point of the hexyl ester blend was increased from -12 to -9 °C, however, it was equal to the specification limits of lube base oil. In order to adjust the properties of the blend to be as close as possible to the specification limit of lube base oil, the blending ratio of hexyl ester should be decreased.

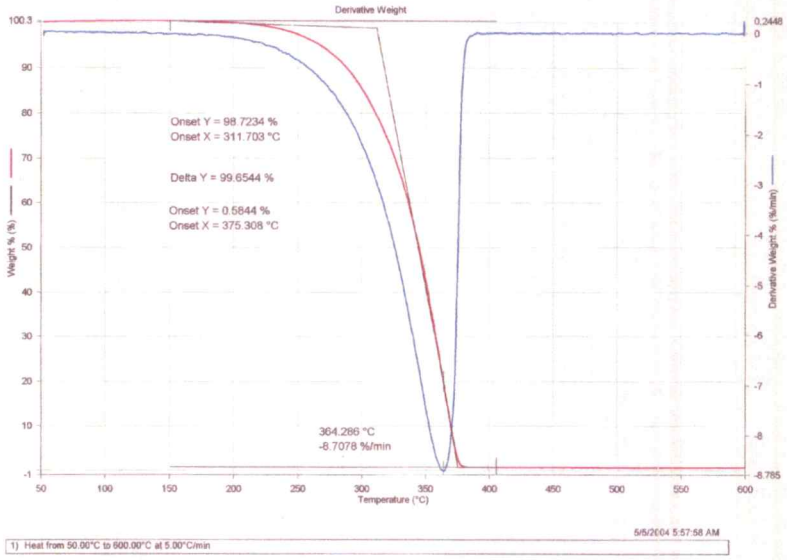


Figure 4.22 TGA thermogram of lube base oil SN 150

For lube base oil SN 150 blended with purging nut oil by 10 percent volume of lube base oil SN 150, it was found that the viscosity of the purging nut oil blend was nearly the same as that of lube base oil SN 150 and close to the specification limit of lube base oil, although the pure purging nut oil had the viscosity higher than the lube base oil SN 150. Moreover, the viscosity index of the blend was raised from 103 to 119.2, which was also better than the specification limits. Because the pour point of the purging nut oil blend was not different from that of lube base oil SN 150, so the ratio of the blend can be further increased. However, due to its high total acid number, an increase in the blending ratio of purging nut oil resulted in an increase of acids in the blends. This was the only disadvantage when using the blending products.

The properties of lube base oil SN 150 comparing with the lube base blended with hexyl ester by 7 and 10 percent volume of lube base oil SN 150 were shown in Table 4.11.

Table 4.11 The physical and chemical properties of the lube base oil SN 150 blended with 7 and 10%v/v of hexyl ester

Properties	Hexyl ester (% v/v)				Specification Limits	
	0%	7%	10%	100%	Min	Max
1. 1. Viscosity @ 40 °C , cSt	30.31	24.88	23.32	6.41	29.0	32.0
2. Viscosity @ 100 °C, cSt	5.22	4.76	4.61	2.99	-	5.2-5.45
3.Viscosity Index	103.0	111.2	113.5	253.2	100.0	-
4. Pour Point, °C	-12	-9	-9	-3	-	-9
5.Total Acid Number, mg KOH/g	0.01	0.09	0.12	-	-	0.03

The results indicated that when the ratio of hexyl ester blended with lube base oil SN 150 was decreased from 10 to 7 percent by volume of lube base oil SN 150, the viscosity index of the blends was also decreased from 113.5 to 111.2. In contrast, the viscosity at 40 and 100 °C of the blends was slightly raised from 23.32 to 24.88 cSt, and 4.61 to 4.76 cSt, respectively. To get closer to the specification limit, the ratio of the blended hexyl ester had to be decreased to less than 7 percent by volume of lube base oil SN 150. However, doing so, the improvement on the viscosity index and the attempted reduction of the quantity of lubricating base oil from petroleum used in present will be minimized. As a result, the lube base blended with 10 percent by volume of hexyl ester was a preferred choice in this study.

The properties of lube base oil SN 150 comparing with the lube base blended with purging nut oil by 10 and 13 percent volume of lube base oil SN 150 were shown in Table 4.12.

In contrast with the hexyl ester blends, it was found that when the ratio of purging nut oil blended with lube base oil SN 150 was increased from 10 to 13 percent by volume of lube base oil SN 150, the viscosity of the blend was in the specification limits of lube base oil. Moreover, the viscosity index was increased from 119.2 to 121.5. However, the total acid number was again increased to much higher than the specification limits of lube base oil. So, if the acids were removed beforehand and the total acid number was not to be considered, the ratio of blended purging nut oil in lube base oil SN 150 could be raised to higher than 13 percent by volume of lube base oil

SN 150. As a result, the viscosity index of the products could be further improved, the quantity of lubricating base oil from petroleum used in present could be reduced.

Table 4.12 The physical and chemical properties of the lube base oil SN 150 blended With 10 and 13%v/v of purging nut oil

Properties	Purging nut oil (% v/v)				Spec Limits	
	0%	10%	13%	100%	Min	Max
1. Viscosity @ 40 °C, cSt	30.31	28.99	29.14	34.98	29.0	32.0
2. Viscosity @ 100 °C, cSt	5.22	5.34	5.40	7.80	-	5.2-5.45
3.Viscosity Index	103.0	119.2	121.5	203.5	100.0	-
4. Pour Point, °C	-12	-12	-12	-3	-	-9
5.Total Acid Number, mg KOH/g	0.01	0.78	1.00	7.04	-	0.03

CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Synthesis of ester products

Transesterification of purging nut oil and alcohols using acid and base as catalyst was affected by many factors. The results indicated that the reaction rate was raised with an increase in the mole ratio of alcohol/oil, the amount of catalyst, and reaction temperature and time, and gave the higher the percent yield of ester products. Moreover, it was found that base catalyst was more effective than acid catalyst as the same amount of catalyst was used. However, purging nut oil had the high amount of free fatty acids which deactivated base catalyst. The addition of excess amount of base catalyst also gave rise to the formation of emulsion and to the problems associated with glycerol separation. The optimized conditions for transesterification of purging nut oil and alcohols, and the percent yield of products are shown in Table 5.1.

Table 5.1 The optimized conditions and the percent yield of products

Type of ester	Mole ratio of alcohol to oil (mol/mol)	Type of catalyst	The amount of catalyst (%)	Reaction temperature (°C)	Reaction time (hrs.)	Approximate yield (%)
1. Methyl ester	40:1	Base	18.63 %w/w	Reflux	6	93.33
2. Ethyl ester	9:1	Acid	7%v/v	Reflux	6	100.00
3. Butyl ester	6:1	Acid	5%v/v	90	5	97.65 - 98.67
4. Hexyl ester	6:1	Acid	5%v/v	90	5	93.33 - 97.33
5. Octyl ester	6:1	Acid	5%v/v	90	5	95.67 – 96.67
6. Decyl ester	6:1	Acid	5%v/v	90	5	90.00 – 93.33

5.2 Properties of purging nut oil and ester products

From tested properties of purging nut oil and ester products for uses as diesel oil and lube base oil substitutes, it was shown that purging nut oil was not suitable for direct use as a diesel oil substitute. Because purging nut oil has high viscosity, when it was used in diesel engines, the high viscosity created poor atomization of the fuel spray, incomplete combustion, carbon deposition on the injector, and fuel build up in the

lubricants oil resulting in serious engine fouling. Besides, the flash point of purging nut oil was higher than diesel oil which caused the problem when starting the engines. This was due to the low volatility of purging nut oil comparing with that of diesel oil, and thus the temperatures required for oils to give off ignitable vapors were also high. Moreover, the high amount of free fatty acids in purging nut oil could cause damages to the injector and also result in the deposits in the fuel system and affect the life of pumps and filters. So the diesel engines have to be modified in order to use purging nut oil directly, or the viscosity of purging nut oil has to be reduced by transesterification reaction into ester products.

The properties of ester products were tested using ASTM Methods. It was found that ethyl, butyl and hexyl ester could be used as diesel oil substitutes because they have the viscosity within the specification limits of diesel oil. However, ethyl ester was more appropriate to be used as a diesel substitute than butyl and hexyl ester because the cost of ethanol was lower than butanol and hexanol. Besides, ethanol can be derived from agricultural products and is renewable. Nevertheless, ethyl ester had a slight disadvantage because it has the lower gross heat of combustion than butyl ester and diesel oil. For octyl and decyl ester, it was shown that their viscosities were higher than the spec limits of diesel oil, so they were not suitable to be used as the diesel oil replacements.

When considering the use of purging nut oil as lube base oil, the results showed that the viscosity of purging nut oil was close to that of lube base oil. However, it was not able to be used directly as lube base oil because the viscosity, the pour point and total acid number of purging nut oil were higher than those of lube base oil. So, in order to use purging nut oil directly, the free fatty acid must be previously eradicated. Moreover, it could be used as an additive in lube base oil to improve the properties of lube base oil SN 150. Purging nut oil could be blended with lube base oil SN 150 by more than 10 percent volume. This improved the viscosity index and the other properties to be close to the lube base oil.

Considering the use of ester products as lube base oil replacements, it was found that they could not be used directly as lube base oil because their viscosities were lower than the specification limits. However, it can be used as an additive in lube base oil to

improve the viscosity index if the small ratio of blending was applied. Hexyl ester was shown to be most suitable in this aspect, due to its highest viscosity index. The pour point of hexyl ester was lower than 0 °C, and its thermal stability was slightly lower than lube base oil.

5.3 Suggestion

The results from this research showed that purging nut oil had high efficiency to be used directly as lube base oil substitute if the free fatty acid in purging nut oil was removed. Esterification reaction is a technique to reduce the free fatty acid content in purging nut oil using an acid-catalyzed pretreatment to esterify the free fatty acid with alcohols for converting the free fatty acid to usable esters before transesterification reaction of triglycerides. Moreover, when compare the properties of monoester products from this work with polyol esters from previous work [32], it was found that monoester products had the viscosity lower than polyol esters. This was because monoester products had the shorter carbon chain length than polyol esters and it had less ester functional group than polyol esters. Besides, polyol esters had the pour point lower than monoester products due to their higher amount of branching. So that, to improve the properties of ester products from transesterification reaction of purging nut oil, we could change the type of alcohol from straight-long chain to branch chain to reduce the pour point of ester products, from the monohydroxy alcohol to polyhydroxy alcohol or from the short carbon chain length to the longer one to increase the viscosity of ester products. In addition, purging nut oil can be used to synthesise biodiesel using homogeneous catalyst such as sulfuric acid and sodium methoxide. However, it has a problem concerning the production cost to synthesise biodiesel which is far more expensive than that of petroleum fuels and a large amount of waste water will be produced to separate and clean the catalyst and the product. Therefore, for the development of an environmentally benign process and the reduction of the production cost, a new process using heterogeneous catalysts should be introduced because heterogeneous catalysts are easy to remove and can be reused without observed loss of activity.

REFERENCES

[1] Vargas, R.M. "Transesterification of Vegetable Oils: a Review." J. Braz. Chem. Soc., vol.9, no.1, 1998. pp.199-210.

[2] Hanna, M.A. et al. "Biodiesel Production: a Review." Bioresource Technology 70, 1999, pp. 1-15.

[3] Tubthim, D. "Synthetic Diester Lubricating Base Oils from Palm Oil." Master Thesis Multidisciplinary Program of Petrochemistry and Polymer Science, Chulalongkorn University, 1996.

[4] Henning, R. "The Jatropha Booklet." [Online]. Available: http://www.jatropha.de/documents/jcl-booklet.pdf. 2003

[5] ระพีพันธ์ ภาสบุตร และสุขสันต์ สุทธิผลไพบูลย์. "**ผลการวิจัยค้นคว้าการใช้น้ำมันสบู่ดำเป็นพลังงานทดแทนเครื่องยนต์ดีเซล.**"กองเกษตรเคมีและกองวิศวกรรม กรมวิชาการการเกษตร,. กรุงเทพฯ. 2525. หน้า 1-42.

[6] Prasad, R. "Triglycerides-Based Diesel Fuels." Renewable & Sustainable Energy Reviews, vol. 4, 2000. pp. 111-133.

[7] Parker, S.P. Encyclopedia of Science & Technology. 4 th ED. New York: McGraw Hill. 1998.

[8] Annual Book of ASTM Standards, Vol. 05.01, 2003

[9] McLean, D.D. "Biodisel Production from Waste Cooking Oil: 1. Process Design and Technological Assessment." [Online]. Available: http://www. Sciencedirect.com. 2003.

[10] Annual Book of ASTM Standards, Vol. 05.04, 2004

[11] Leonardo da Vinci project. "Facts about Biodiesel." [Online]. Available: http://www.koal2.cop.fi/Leonardo/biodiesel-facts.html. 2002.

[12] Advani. L.K. "Report of The Committee on Development of Bio-Fuel." [Online]. Available: http://planning commission.nic.in. 2003

[13] Walsh, P.M. "International Experience on Ultra Low Sulfur Diesel and Biodiesel." [Online]. Available: http:// www.cleanairnet.org. 2000.

[14] Eiamsupasawat, K. "Synthesis of LubricatingBase Oils from Rice Bran Oil." Master Thesis. Multidisciplinary Program of Petrochemistry and Polymer Science,

Chulalongkorn University, 1999.

[15] Rudnick, I.R. and Shubkin, R.L. **Synthetic Lubricants and High-Performance Functional Fluids.** New York, Marcel Dekker, Inc., 1999.

[16] Phatanaphakdee, K. **"Synthesis of Lubricating Base Oils from Palm Oil."** Master Thesis. Multidisciplinary Program of Petrochemistry and Polymer Science, Chulalongkorn University, 1995.

[17] **Annual Book of ASTM Standards,** Vol. 05.01, 2004

[18] Becker, K. and Makkar,H.P.S. **"Jatropha and Moringa."** [Online]. Available: http://www.uni-hohenheim.de/~www480/docs/se990720/jatropha.htm. 1999.

[19] Felter, H.W. and Lloyd, J.U. **"Purging Nut."** [Online]. Available: http://www.ibiblio.org/herbmed/electic/kings/curcas-purg.html. 2002.

[20] Rockefeller Foundation and Scientific & Industrial Research & Development Centre. **"The Potential of Jatropha curcas in Rural Development and Environment Protection an Exploration."** [Online]. Available: http://www.jatropha.org/zimbabwe/rf-conf1.htm .1998.

[21] Appropriate Technology International. **"Energy Corner."** [Online]. Available: file//C:\My Documents/curcas 2.htm.2002.

[22] Schrimpff,E. **"The Jatropha System."** [Online]. Available: http://www.jatropha.org/p-o-engines/svo-bd-characteristics.htm. 2002.

[23] **ประยูร ห่วงนิกร. "การศึกษาการปลูกสบู่ดำแปลงใหญ่ และการเปลี่ยนรูปเอสเทอรของน้ำมันสบู่ดำ."** วิทยานิพนธ์วิทยาศาสตรมหาบัณฑิต(เกษตรศาสตร์), สาขาพืชสวน, ภาควิชาพืชสวน, มหาวิทยาลัยเกษตรศาสตร์, กรุงเทพฯ. 2529.

[24] Foidl, N. et al. "Jatropha curcas L. as a Source for The Production of Biofuel in Nicaragua." **Bioresoucre Technology** 58. 1996. pp. 77-82.

[25] Ikwuagwu, O.E. et al. "Production of Biodiesel using Rubber [*Hevea brasiliensis*] Seed Oil." **Industrial Crops and Products** 12. 2000. pp.57-62.

[26] Encinar, J.M. et al. "Biodiesel Fuels from Vegetable oils : Transesterification of Cynara cardunculus L. Oils with Ethanol." **Energy & Fuels** 16. 2002. pp.443-450.

[27] Ayaaki Ishizaki. et al. " Biodiesel Production from Crude Palm Oil and Evaluation of Butanol Extraction and Fuel Properties." **Process Biochemistry** 37. 2001. pp.65- 71.

[28] Tomasevic, A.V. "Methanolysis of Used Frying Oil." **Fuel Processing Technology** 81. 2003. pp.1-6.

[29] Vatanaputi, N. **"Synthesis of Lubricating Oil from Coconut Oil."** Master Thesis. Multidisciplinary Program of Petrochemistry and Polymer Science, Chulalongkorn University, 1996.

[30] Suwanprasert, T. **"Synthetic Lubricant from Soybean Oil."** Master Thesis. Multidisciplinary Program of Petrochemistry and Polymer Science, Chulalongkorn University, 1996.

[31] Onnapa khumkratok and Areeya Tabbai, **" Synthesis of Esters from Stearic Acid for use as Lubricating Products."** A Special Project., Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, 2001.

[32] Gryglewicz, S. "Preparation of polyol esters based on vegetable and animal fats." **Bioresource Technology** 87. 2003.pp.35-39.

[33] ศ.ดร. ปราโมทย์ ไชยเวท และ ผศ.ดร.นุรักษ์ กฤษดานุรักษ์. **ปิโตรเลียมเทคโนโลยี** พิมพ์ครั้งที่ 1, ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย, กรุงเทพฯ, 2543.

APPENDICES

APPENDIX A

The Molecular Weight of purging nut oil and monoester products

1. The average molecular weight of purging nut oil

Table A-1 The major fatty acid composition of purging nut oil

Fatty Acids	%	M.W. of triglyceride (g/mole)
1. Palmitic acid	16.17	806
2. Stearic acid	5.11	890
3. Oleic acid	44.89	884
4. Linoleic acid	33.83	878

So that the average M.W. of purging nut oil = (0.1617 × 806) + (0.0511× 890) +

(0.4489 ×884) + (0.3383 × 878)

= 869.67 g/mole

≈ 870 g/mole

2. The average molecular weight of methyl ester products

Table A-2 The major fatty acid composition of methyl ester products

Fatty Acids	%	M.W. of methyl ester (g/mole)
1. Palmitic acid	16.17	270
2. Stearic acid	5.11	298
3. Oleic acid	44.89	296
4. Linoleic acid	33.83	294

So that the average M.W. of methyl ester = (0.1617 × 270) + (0.0511× 298) +

(0.4489 ×296) + (0.3383 × 294)

= 291.22 g/mole

3. The average molecular weight of ethyl ester products

Table A-3 The major fatty acid composition of ethyl ester products

Fatty Acids	%	M.W. of ethyl ester (g/mole)
1. Palmitic acid	16.17	284
2. Stearic acid	5.11	312
3. Oleic acid	44.89	310
4. Linoleic acid	33.83	308

So that the average M.W. of ethyl ester = (0.1617 × 284) + (0.0511× 312) + (0.4489 ×310) + (0.3383 × 308)

= 305.21 g/mole

4. The average molecular weight of butyl ester products

Table A-4 The major fatty acid composition of butyl ester products

Fatty Acids	%	M.W. of butyl ester (g/mole)
1. Palmitic acid	16.17	312
2. Stearic acid	5.11	340
3. Oleic acid	44.89	338
4. Linoleic acid	33.83	336

So that the average M.W. of butyl ester = (0.1617 × 312) + (0.0511× 340) + (0.4489 ×338) + (0.3383 × 336)

= 333.22 g/mole

5. The average molecular weight of hexyl ester products

Table A-5 The major fatty acid composition of hexyl ester products

Fatty Acids	%	M.W. of hexyl ester (g/mole)
1. Palmitic acid	16.17	340
2. Stearic acid	5.11	368
3. Oleic acid	44.89	366
4. Linoleic acid	33.83	364

So that the average M.W. of hexyl ester = (0.1617 × 340) + (0.0511× 368) +

(0.4489 ×366) + (0.3383 × 364)

= 361.22 g/mole

6. The average molecular weight of octyl ester products

Table A-6 The major fatty acid composition of octyl ester products

Fatty Acids	%	M.W. of octyl ester (g/mole)
1. Palmitic acid	16.17	368
2. Stearic acid	5.11	396
3. Oleic acid	44.89	394
4. Linoleic acid	33.83	392

So that the average M.W. of octyl ester = (0.1617 × 368) + (0.0511× 396) +

(0.4489 ×394) + (0.3383 × 392)

= 389.23 g/mole

7. The average molecular weight of decyl ester products

Table A-7 The major fatty acid composition of decyl ester products

Fatty Acids	%	M.W. of decyl ester (g/mole)
1. Palmitic acid	16.17	396
2. Stearic acid	5.11	424
3. Oleic acid	44.89	422
4. Linoleic acid	33.83	420

So that the average M.W. of decyl ester = (0.1617 × 396) + (0.0511× 424) +

(0.4489 × 422) + (0.3383 × 420)

= 417.23 g/mole

APPENDIX B

1. % Yield of monoester products from weighting.

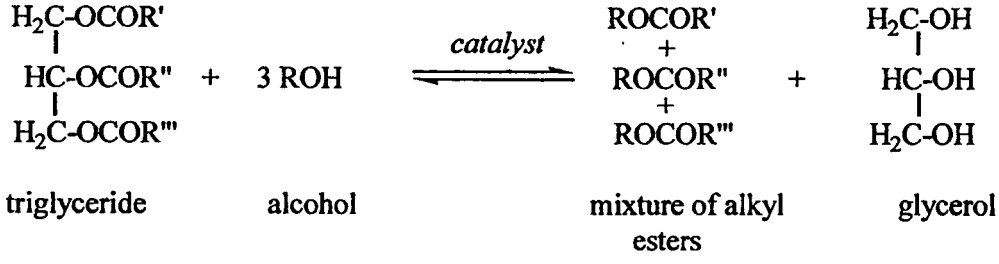


Figure B-1 Transesterification of vegetable oils.

It is shown that the stoichiometric of transesterification reaction requires 1 mol of a triglyceride and 3 mol of the alcohol to produce 3 mol of fatty acids alkyl ester and 1 mol of glycerol. Thus the yield of ester product was determined by percent of mole as following equation (B-1).

$$\%\text{Yield} = \frac{\text{Observed mole of methyl ester}}{\text{Theory mole of methyl ester}} \times 100 \qquad \text{(B-1)}$$

Example1. Determination of the yield of methyl ester when using 43.50 g (0.05 mole) of purging nut oil and observed weight of methyl ester was 41.19 g.

From theory and eq. B-1:

The mole of observed methyl ester (n) can be calculated by

$$n = \frac{m}{M.W.} = \frac{41.19\ g}{291.22\ g/mole} = 0.14\ mole$$

The mole of theory methyl ester = 0.05 mole × 3 = 0.15 mole

$$\therefore \%\text{Yield} = \frac{0.14}{0.15} \times 100 = 93.33\%$$

2. % Yield of monoester products calculated from ^{1}H-NMR spectrum

Example2. From the transesterification of purging nut oil with methanol using 20:1 methanol/oil mole ratio, 10% H_2SO_4, at reflux temperature for 6 hrs. Determination of the yield of methyl ester product was carried out using ^{1}H-NMR spectrum in Figure B-2 and equation (B-2)

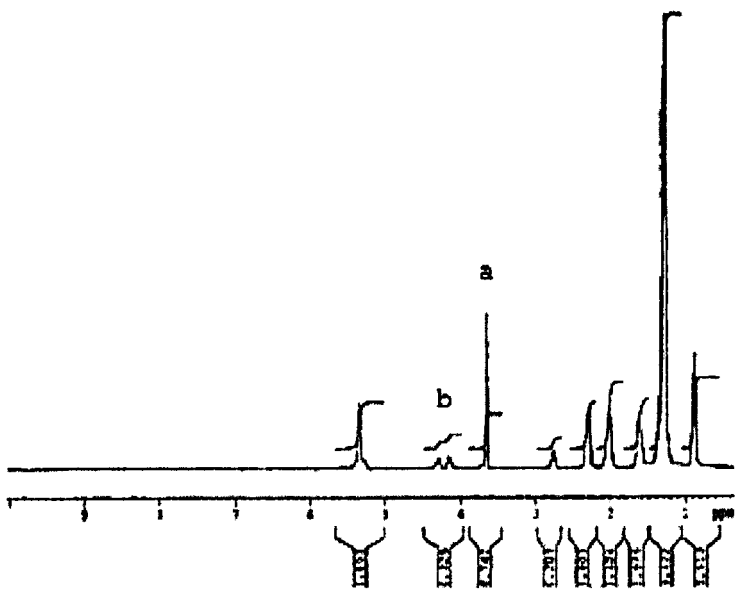


Figure B-2 ^{1}H-NMR spectrum of the product from the incompleted transesterification using methanol

$$Y_{ME} = 100 \times \frac{\frac{I_{ME}}{3}}{\frac{I_{ME}}{3} + \frac{I_{TG}}{5}} \qquad \text{(B-2)}$$

Where Y_{ME} refer to percent yield of methyl ester

I_{ME} refer to integration values of methyl ester

I_{TG} refer to integration values of triglyceride

The factors 3 and 5 were derived from the fact that the CH_3-OOC-R (a) of methyl ester has 3 attached protons and the –CH_2-OOC-R and >CH-OOC-R (b) of triglyceride has 5 attached protons.

So that

$$Y_{ME} = 100 \times \frac{\frac{I_{ME}}{3}}{\frac{I_{ME}}{3} + \frac{I_{TG}}{5}}$$

$$Y_{ME} = 100 \times \frac{\frac{0.742}{3}}{\frac{0.742}{3} + \frac{0.325}{5}}$$

$$Y_{ME} = 100 \times \frac{0.247}{0.247 + 0.065}$$

$$Y_{ME} = 79.17\%$$

APPENDIX C

Figure C-1 Plantation of purging nut

Figure C-2 Purging nut tree

Figure C-3 Immature purging nut fruit

Figure C-4 Purging nut fruit

Figure C-5 Purging nut seeds

Figure C-6 Grinder for the purging nut seeds

Figure C-7 Expeller for the purging nut seeds

Figure C-8 Pouring the purging nut seeds into the expeller

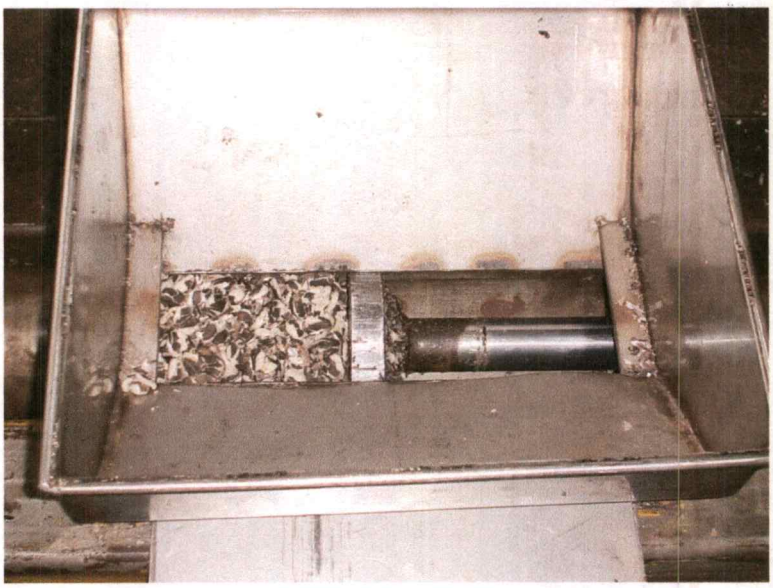


Figure C-9 Pressing the purging nut seeds

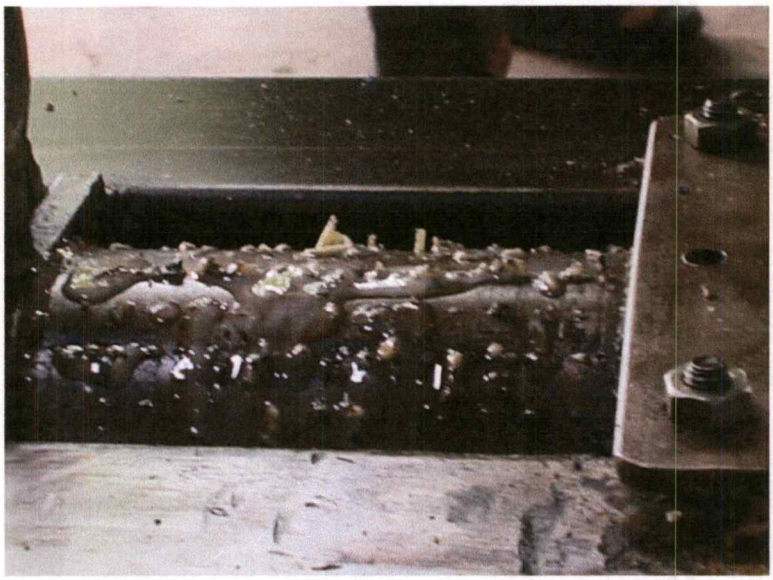


Figure C-10 Purging nut oil was extracted

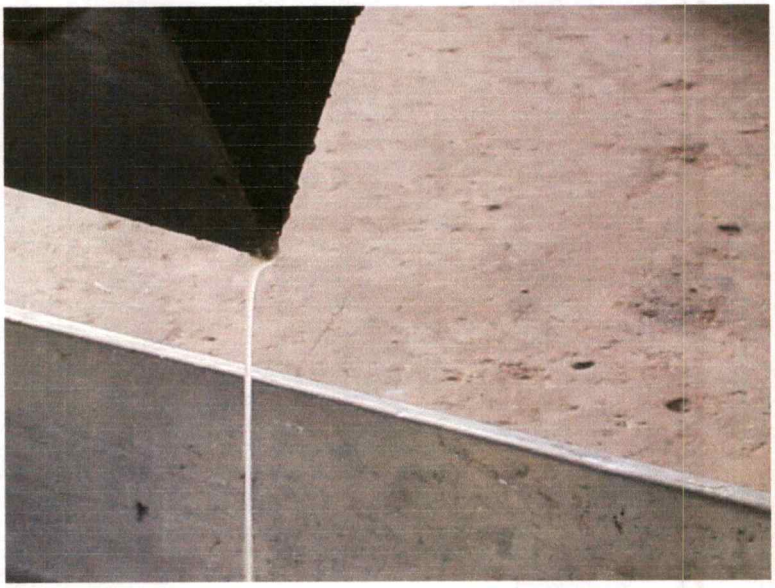


Figure C-11 Purging nut oil from the expeller

Figure C-12 Purging nut oil after filtration

AUTHOR BIOGRAPHY

First Name - Last Name	Miss.Jaruwat Thongmool
Birthdate	4 October 1978
Birthplace	Nakhonphanom Thailand
Address	73 Moo 7 Tumbon Donnanghong Amphur Thatphanom Nakhonphanom Province. 48110
Previous Certificate/Degree	Bachelor degree of Science in Chemistry from Ubon Ratchathani University, Ubon Ratchathani, Thailand in 2000.