ULTRASONICALLY-ASSISTED PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL (WCO)

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Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in
Partial Fulfillment of the Requirement for the
Degree of Bachelor Engineering in Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
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MAY, 2008

I declare that this thesis entitled “Ultrasonically-assisted Production of Biodiesel from Waste Cooking Oil (WCO)” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.

Signature :
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Date :

Special Dedication of This Grateful Feeling to My…

Beloved mother;
Puan. Radziah Abu Bakar

Loving brothers and sisters;
Rozmi, Rozlinda, Firdaus, Raimi

Supportive families;
Atok, Damia Sabrina, Uncles and Aunties

For Their Love, Support and Best Wishes.

ACKNOWLEDGEMENT

Firstly, I want to express gratitude to my mother Puan Radziah Abu Bakar and the rest of family for their unconditional support and encouragement in whatever I do.

I would like to thank my supervisor, Puan Ruwaida Abdul Rasid for her invaluable advice and contributions to this work. Her insights and high standards have definitely helped to shape this work. It is a pleasure to have an advisor being so joyful in her work.

My thank goes to Miss Shalyda binti Md Shaarani @ Md Nawi, Miss Sumaiya binti Zainal Abidin @ Murad, the Undergradute Research Project Coordinator and other lecturers from Faculty of Chemical and Natural Resources Engineering for giving me guidance in completing this thesis. Special thank goes to FKKSA laboratory owner, Mr. Zaki, Mr. Zainal, Miss Hafiza and also our research officer, Miss Siti Fatimah for your guidance, assistance and ideas.

Thanks to former and present colleagues especially Norafliza, Farha, Stephenie, Nurshuhada and PSM biodiesel teammate at Universiti Malaysia Pahang for making an enjoyable working environment and giving me ideas, opinions and advices. Thank you again.

ABSTRACT

The use and research of biodiesel from waste cooking oil as an alternative fuel for the diesel engine started because of the decrease of petroleum production by Organization of the Petroleum Exporting Countries (OPEC) and the resulting in price increase. Waste cooking oil (WCO) was selected as raw material for production of biodiesel because it is inexpensive and can save our environment from pollution. In this study, transesterification process assisted with ultrasonic was chosen as a process to produce biodiesel. It is the reaction of a fat or oil with methanol in presence of sodium hydroxide as catalyst to form methyl esters and glycerol. Effect of using ultrasonic was study on transesterification reaction time. The result, using ultrasonic was proved to be time and energy saving. The process of transesterification in this study is affected by reaction temperature, catalyst (sodium hydroxide) concentration and reaction time. Thin-layer chromatography (TLC) are used to study the formation of methyl esters of waste cooking oil in the reaction and Karl Fisher analyzer are used to study the moisture content in biodiesel. Base on this research, excess amount of catalyst (NaOH) and excess reaction time at higher temperature affects a negative impact on the ester yield, resulted in a reduction of the product yield. The optimum conditions to achieve the highest conversion and yield of biodiesel were using 1.5 wt % sodium hydroxide (NaOH) at reaction temperature 30ºC and reaction time of 20 minutes.

ABSTRAK

Penggunaan dan kajian biodiesel daripada sisa-sisa minyak masak sebagai salah satu sumber alternatif bahan api untuk enjin diesel telah bermula kerana penurunan penghasilan petroleum oleh Organisasi Negara Mengimport Petroleum dan kenaikan harga minyak. Sisa minyak masak dipilih sebagai bahan mentah untuk penghasilan biodiesel kerana ia murah dan dapat mengurangkan alam sekitar daripada tercemar. Dalam kajian ini, proses transesterifikasi dengan bantuan ultrasonik telah dipilih sebagai proses untuk menghasilkan biodiesel. Tindakbalas oleh lemak atau minyak dengan methanol dengan kehadiran natrium hidroksida sebagai mangkin untuk menghasilkan metil ester dan gliserol. Masa tindak balas dalam proses transesterifikasi dengan bantuan ultrasonik dikaji dalam kajian ini. Penggunaan ultrasonik telah terbukti menjimatkan masa dan tenaga. Proses transesterifikasi dalam kajian ini dipengaruhi oleh suhu tindakbalas, kepekatan mangkin (natrium hidroksida) dan masa tindakbalas. *Thin-layer chromatography (TLC)* digunakan untuk mengkaji pembentukkan metil ester daripada sisa minyak di dalam tindak balas transesterifikasi dan *Karl Fisher analyzer* digunakan untuk mengkaji kandungan kelembapan di dalam biodiesel. Berdasarkan kajian ini, penggunaan mangkin (natrium hidroksida) yang berlebihan dan masa tindakbalas yang lebih lama pada suhu yang tinggi memberi kesan yang negatif terhadap penghasilan ester, mengakibatkan pengurangan hasil produk. Keadaan yang terbaik untuk mencapai hasil produk biodiesel yang terbaik adalah meggunakan 1.5 peratus berat mangkin (natrium hidroksida) pada suhu tindakbalas 30ºC dan masa tindakbalas selama 20 minit.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

Dr. Rudolph Diesel, a German engineer, introduced the diesel engine over a century ago (Nitske and Wilson, 1965). Since then, a great deal of research and development has taken place, not only in the design area but also in finding an appropriate fuel. For many years, the ready availability of inexpensive middle-distillate petroleum fuels provided little incentive for experimenting with alternative, renewable fuels for diesel engines. However, since the oil crisis of the 1970s, research interest has expanded in the area of alternative fuels (Mustafa Canakci, 2005).

Biodiesel is an alternative diesel fuel derived from the transesterification of vegetable oils, animal fats, or waste frying oils with alcohols to give the corresponding fatty acid methyl esters. The use and research of biodiesel as an alternative fuel for the diesel engine started because of the reduction of petroleum production by Organization of the Petroleum Exporting Countries (OPEC) and the resulting price rise (Kahn J. *et al.*, 2002).

In Malaysia, biodiesel is also called palm diesel because it produced from reaction of palm oil and methanol to become methyl ester. Methyl esters together with fatty acids, fatty alcohol, fatty amines and glycerol are important basic oleochemical raw materials which are essential building blocks for the oleochemical industry.

The world total biodiesel production was around 1.8 billion liters in 2003 (Fulton *et al*., 2004). Figure 1.1 shows the world biodiesel capacity between 1991 and 2003. World biodiesel capacity was increase from year 1991 to 2003. It is expected that it will continues increase after year 2003 because of the reduction of petroleum production and resulting price rise (Kahn J. *et al*., 2002).

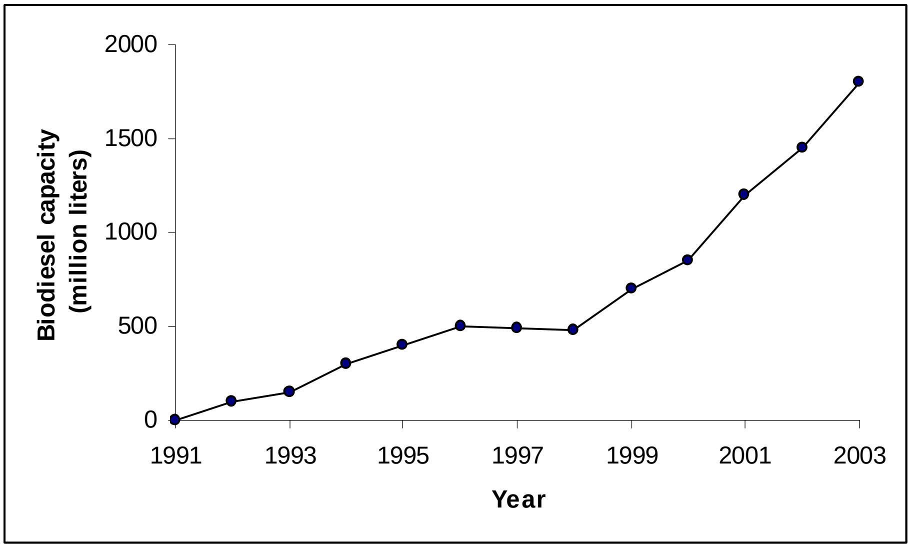

Figure 1.1 : World biodiesel capacity, 1991-2003

Source: International Energy Agency (IEA) (2004)

1.2 PROBLEM STATEMENT

The Malaysia oil palm industry recorded an impressive performance in 2006. Export earning of oil palm products rose to a record RM 31.8 billion, while palm oil stocks declined and prices firmed up sharply especially during the last quarter of the year. The industry also saw exciting developments shaping up in the local biofuel industry with the Honorable Prime Minister of Malaysia launching the Envo Diesel (palm olein blend with diesel) and the first integrated palm oil biodiesel plant using MPOB technology in March and August 2006 respectively.

Biodiesel is usually produced from food-grade vegetable oils that are more expensive than diesel fuel. Therefore, biodiesel produced from food-grade vegetable oil is currently not economically feasible. Waste cooking oils, restaurant grease and animal fats have found to be potential feedstock for biodiesel. This inexpensive feedstock represent one-third of the US total fats and oil production, but are currently devoted mostly to industrial uses and animal feed (Mustafa Canakci, 2005).

In this study, waste cooking oil (WCO) was selected as raw material for production of biodiesel because it is inexpensive and can save our environment from pollution. In Malaysia, the citizen disposing of used cooking oil by pouring it down the drain can clog pipes thus damaging wastewater systems. By using waste cooking oil as raw material, it can give a lot of benefit to our country. According to the Environmental Protection Agency (EPA), approximately 2.5 billion pounds (300 million gallons) of waste cooking oils are collected annually from restaurants and fast-food establishments in the U.S (Haumann, 1990).

However, there are problems with the usage of waste cooking oil which are the higher viscosity than diesel fuel, lower volatilities that causes the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics.

The negative influence of base catalyzed transesterification of triglycerides containing substantial amount of free fatty acid (Turck *et al.*, 2002). Free fatty acids react with the basic catalyst added for the reaction and give rise to soap, as a result of which, one part of the catalyst is neutralized and is therefore no longer available for transesterification.

In the transesterification of vegetable oil with alkaline catalysts, Romano (1982); Freedman *et al.* (1984), have emphasized that the vegetable oil and alcohol should not contain water and free fatty acids (FFA) since they slow the reaction. Even a small amount of water, such as 0.1%, in the transesterification reaction will decrease the amount of ester formed significantly (Romano, 1982; Canakci and Van Gerpen, 1999).

1.3 OBJECTIVE

The aim of this study is to produce biodiesel from waste cooking oil assisted by ultrasonic to achieve the highest conversion of production biodiesel with short residence time at optimum temperature.

1.4 SCOPE OF RESEARCH WORK

To achieve the objective of this research, there are four scopes that have been identified:

i. To determine the optimum conditions for production of the biodiesel.
ii. To study effect of alkali catalyst concentration on production of biodiesel.
iii. To study effect of using ultrasonic on transesterification reaction time.

CHAPTER 2

LITERATURE REVIEW

2.1 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, biodegrade and biological source in difference to traditional petroleum-based diesel fuel; ‘‘diesel’’ refers to its use in diesel engines. Biodiesel can be used in efficient form or mixed with petroleum-based diesel as an alternative fuel (Jon Van Gerpen, 2005).

Dr. Rudolf Diesel (1895) developed the first diesel engine to run on vegetable oil. Dr. Diesel demonstrated his engine at the World Exhibition in Paris in 1900 using 100% peanut oil as fuel. In 1911 he stated ‘‘the diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries, which use it’’. In 1912, Dr. Diesel said, ‘‘the use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time’’(Shay EG., 1993).

The properties of biodiesel differ a bit from conventional diesel depending on the oil feedstock and alcohols used but are very close to diesel fuel (Mittelbach *et al.*, 1992; Peterson *et al.*, 1992). Biodiesel must meet American Society of Testing and

Materials (ASTM) specifications designated in ASTM D-6751. Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels is shown in Table 2.1. The purpose of this standard is to have biodiesel meet the performance requirements of engines without specifying the actual composition of the fuel. This will allow biodiesel to be made from any feedstock as long as the standard can be met. Many studies have shown that the properties of biodiesel are very close to diesel fuel (Mittelbach *et al.*, 1992; Peterson *et al.*, 1992, 1994). Therefore, biodiesel fuel can be used in diesel engines with little or no modification.

Table 2.1 : Standard specification for biodiesel fuel (ASTM D 6751-02)

Property	ASTM method	Limits	Units
Flash point (closed cup)	D 93	130.0 min	˚C
Water and sediment	D 2709	0.050 max	vol %
Kinematic viscosity, 40˚C	D 445	1.9-6.0	mm^2/s
Sulfated ash	D 874	0.020 max	mass %
Sulfur	D 5453	0.05 max	mass %
Copper strip corrosion	D 130	N0. 3 max	-
Cetane number	D 613	47 min	-
Cloud point	D 2500	Report	˚C
Carbon residue, 100% sample	D 4530	0.050 max	mass %
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020 max	mass %
Total glycerin	D 6584	0.240 max	mass %
Phosphorus content	D 4951	0.001 max	mass %
Distillation temperature, atmospheric equivalent temperature, 90% recovered	D 1160	360 max	˚C

Source: http://www.astm.org

Petrodiesel is the industry term for diesel produced from petroleum. Biodiesel has a viscosity similar to petrodiesel. It can be used as an additive in formulations of diesel to increase the lubricity of pure Ultra-Low Sulfur Diesel (ULSD) fuel. However care must be taken to ensure that the biodiesel used does not increase the sulfur content of the mixture above 15 ppm. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix. For example, fuel containing 20% biodiesel is labeled B20. Pure biodiesel is referred to as B100.

2.1.1 Characteristic of biodiesel

Biodiesel is a light to dark yellow liquid. It is practically immiscible with water, has a high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point around 150 °C (300 °F), making it rather non-flammable. Biodiesel has a density around 0.88 g/cm³, less than that of water. Biodiesel uncontaminated with starting material can be regarded as non-toxic. Selected properties of diesel compared to biodiesel fuels are given in Table 2.2.

Table 2.2 : Specification of diesel and biodiesel fuel

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value (MJ/m^3)	36.6×10^3	32.6×10^3
Kinematic viscosity @ 40˚C (mm^2/s)	1.3-4.1	1.9-6.0
Specific gravity @ 15.5 ˚C	0.85	0.88
Density @ 15˚C (kg/m^3)	848	878
Water (ppm by wt)	161	0.05 % max
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (by diff.) (wt %)	0	11
Sulfur (wt %)	0.05 max	0.0-0.0024
Boiling point (˚C)	188-343	182-338
Flash point (˚C)	60-80	100-170
Cloud point (˚C)	-15 to 5	-3 to 12
Pour point (˚C)	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Stoichiometric air / fuel ratio (wt / wt)	15	13.8

Source: Tyson, KS biodiesel handling and use guidelines National Renewable Energy Laboratory NREL/TP-580-30004 September 2001.

2.2 RAW MATERIAL

Biodiesel can be produced from variety of vegetable oils and animal fats (Demirbas, 2005; Ma and Hanna, 1999; Pinto *et al*., 2005). Several sources for producing biodiesel have been studied such as rape seed, coal seed, palm oil, sunflower oil, waste cooking oil, soybean oil, etc. Due to the high cost of the fresh vegetable oil, waste cooking oil gives interesting properties because it can be converted to biodiesel and it is available with relatively cheap price (Nisworo, 2005; Zhang *et al*., 2003).

The synthesized biodiesel samples were tested for physico- chemical properties in Table 2.3 as per ASTM D-6751 and Indian IS-15607 specification. From Table 2.3, biodiesel prepared from different oils meet most of the specifications, all biodiesel samples failed in oxidation stability test, with the exception of palm biodiesel.

Table 2.3 : Physico-chemical properties of biodiesel

Property (units)	ASTM 6751 test method	ASTM 6751 limits	IS 15607 test method	IS 15607 limits	Jatropha ME	Pongamia (Karanjia) ME	Sunflower ME	Soybean ME	Palm ME
Flash point (ºC)	D-93	Min. 130	IS 1448 P:21	Min. 120	163	141	180	160	135
Viscosity at 40ºC (cSt)	D-445	1.9-6.0	IS 1448 P:25	2.5-6.0	4.40	4.16	4.10	4.00	4.50
Sulphated ash (% mass)	D-874	Max. 0.02	IS 1448 P:4	Max. 0.02	0.002	0.002	0.001	0.001	0.002
Sulphur (% mass)	D-5453	Max. 0.05	ASTM D 5453	Max. 0.005	0.004	0.003	0.003	0.002	0.003
Cloud point (ºC)	D-2500	N.A	IS 1448 P:10	N.A	4	4	4	4	16
Copper corrosion	D-130	Max. 3	IS 1448 P:15	Max. 1	1	1	1	1	1
Cetane number	D-613	Min. 47	IS 1448 P:9	Min. 51	57.1	55.1	55.6	58.1	54.6
Water and sediment (vol %)	D-2709	Max. 0.05	D-2709	Max. 0.05	0.05	0.03	0.04	0.023	0.01
CCR 100% (% mass)	D-4530	Max. 0.05	D-4530	Max. 0.05	<0.01	<0.01	0.01	<0.01	<0.01
Neutralization value (mg KOH/gm)	D-664	Max. 0.80	IS 1448 P:1/Sec. 1	Max. 0.50	0.48	0.10	0.20	0.15	0.24
Free glycerin (% mass)	D-6584	Max. 0.02	D-6584	Max. 0.02	0.01	0.01	0.02	0.01	0.01
Total glycerin (% mass)	D-6584	Max. 0.24	D-6584	Max. 0.25	0.02	0.01	0.02	0.01	0.01
Phosphorus (% mass)	D-4951	Max. 0.001	D-4951	Max. 0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Distillation temperature	D-1160	90% at 360ºC	Not under spec.	-	90 %	90 %	90 %	90 %	90 %
Oxidation stability, hrs	N.A	N.A	EN 14112	Min. 6 h	3.23	2.35	1.73	3.80	13.37

2.2.1 Animal fats

Some recovered animal fats are one of the raw material for biodiesel production (Ana and Enoch, 2003; Han *et al.*, 2003). The examples of animal fats are tallow, lard, yellow grease, chicken fat, and the by-products of the production of Omega-3 fatty acids from fish oil. Preliminary laboratory tests at Oak Park suggest that a good quality biodiesel could be produced from tallow, but that much more work was needed to establish process requirements and methyl ester properties.

The main sources of animal fats are primarily meat animal processing facilities. Another source of animal fats is the collection and processing of animal mortalities by rendering companies. Table 2.4 gives the compositions of crude tallow. In beef tallow the saturated fatty acid component accounts for almost 50% of the total fatty acids. The higher stearic and palmitic acid contents give beef tallow the unique properties of high melting point and high viscosity (Fangrui and Milford, 1998).

Table 2.4 : Properties and composition of crude beef tallow

Characteristics	
Iodine number	35-48
Saponification number	193-202
Titer, C	40-46
Wiley melting point, C	47-50
Fatty acid composition	
Myristic	2-8
Palmitic	24-37
Stearic	14-29
Oleic	40-50
Linoleic	1-5
Glyceride composition, mole %	
Total GS_3	15-28
Total GS_2U	46-52
Total GSU_2	20-37
Total GU_3	0-2

Source: Sonntag (1979)

The disadvantages to the use of animal fats are the high viscosity (about 11–17 times higher than diesel fuel), lower volatilities that causes the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics. These problems are associated with large triglyceride molecule and its higher molecular mass (Meher *et al.*, 2004).

2.2.2 Vegetable oil

In the 1930s and 1940s, vegetable oils were used as diesel substitutes from time to time, but usually only in emergency situations. Vegetable oil can be categorized into two types which are virgin vegetable oil and waste cooking oil (WCO). Examples of virgin vegetable oil are rapeseed, soybean oils, mustard, flax, sunflower, canola, palm oil, hemp, jatropha, algae, etc. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Sonntag, 1979). Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The fatty acids found in vegetable oils are summarized in Table 2.5.

Table 2.5 : Chemical properties of vegetable oil

Vegetable oil	Fatty acid composition, % by weight								
	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Crambe	2.07	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.40	0.00	22.30	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00

Source: Goering *et al.* (1982)

The advantages of using vegetable oils as fuels are not over-burden the environment with emissions. Vegetable oil's production requires lesser energy input in production and vegetable oil combustion has cleaner emission spectra. The current prices of vegetable oils in world are nearly competitive with petroleum fuel price (Avinash Kumar, 2006).

Approximately 2.5 billion pounds of waste restaurant fats are collected annually from restaurants and fast-food establishments in the US (Haumann, 1990). Waste vegetable oils and fats are commonly low in cost and are currently collected from large food processing and service facilities. The problem with processing waste cooking oils is that they usually contain large amounts of free fatty acids (FFA) that cannot be converted to biodiesel using an alkaline catalyst due to formation of fatty acid salts (soap). The soaps can prevent separation of the biodiesel from the glycerin fraction. The alternative method is to use acid catalysts, which are able to esterify free fatty acids (Aksoy *et al.*, 1988; Freedman and Pryde, 1982; Liu, 1994).

2.3 THE PRODUCTION OF BIODIESEL

There are four primary ways to make biodiesel, direct use and blending, micro-emulsions, thermal cracking (pyrolysis) and transesterification. The most commonly used method is transesterification of vegetable oils and animal fats.

2.3.1 Direct use and blending

Vegetable oil can straight use or blending with petrodiesel in engine (Anon, 1982). Direct use of vegetable oils and or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines (Fangrui and Milford, 1998).

2.3.2 Micro-emulsion

To solve the problem of the high viscosity of vegetable oils, micro-emulsions with solvents such as methanol, ethanol and 1-butanol have been studied. Micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Schwab *et al.*, 1987). Micro-emulsion can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (Pryde, 1984).

2.3.3 Pyrolysis

Pyrolysis is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst; involves heating in the absence of air or oxygen (Sonntag, 1979). Pyrolysis involves cleavage of chemical bonds to yield small molecules (Weisz *et al.*, 1979). Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum (Sonntag, 1979).

The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Since World War I, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. A large scale of thermal cracking of tung oil calcium soaps was reported (Chang and Wan, 1947). Tung oil was first saponified with lime and then thermally cracked to yield a crude oil, which was refined to produce diesel fuel and small amounts of gasoline and kerosene. 68 kgs of the soap from the saponification of tung oil produced 50 L of crude oil.