THE UNIVERSITY OF BIRMINGHAM

BIODIESEL PRODUCTION FROM DIFFERENT METHODS

By

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ABSTRACT

Hydrolysis, esterification and transesterification reactions were conducted in different reactor configurations, with the overall objective of enhancing the fundamental knowledge of Free Fatty acids (FFA) and biodiesel production, while providing key processing parameters and kinetic models for process design.

Hydrolysis and esterification reactions were conducted in a non-catalytic continuous flow reactor, esterification reactions in a stirred batch reactor and transesterification reactions in a state-of-the-art Downflow Gas contactor Reactor (DGCR). The DGCR was operated in batch mode with a recycle loop. All samples were collected as a function of time and the concentrations of FFA and Fatty Acid Methyl/Ethyl Esters (FAME/FAEE) were determined, using gas chromatography for FFA and FAME/FAEE and titration for FFA. Tested processing variables for each reaction were varied according to the reaction objectives and reactor limits. Extensive kinetic models for continuous flow and batch reactions were performed and rate constants were established.

FFA are an important intermediate for several industrial applications. Non-catalytic continuous flow hydrolysis with the aid of subcritical water produced high quality FFA with a maximum yield of 92 % at 350 ^{o}C, 20 MPa and 50:50 water oil volume ratio. Temperature, time and water/oil initial ratio were found to be significant factors in the hydrolysis reactions. However, pressure had a minor influence.

Esterification reactions were undertaken as a second step processing after hydrolysis, in order to minimise the amount of alcohol and produce biodiesel in mild reaction conditions to that in supercritical transesterification. A maximum yield of

97 % was obtained at 320 ^{o}C, 10 MPa and 1:7 ratio of FFA:methanol. The yield of FAME was affected by temperature and, to some extent, the ratio of methanol to FFA.

Finally, transesterification reactions were undertaken using the DGCR with extraordinary results. A high mixing intensity in DGCR was developed which fulfilled the European standard EN14214 of purity (esters contents 96.5 %) for biodiesel in the very short time of 2.5 min and at a temperature of 40 ^{o}C and pressure of 0.11 MPag.

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NOMENCLATURE

i.d	Internal diameter of, m
o.d	Out diameter of pipe, m
D	Diameter of tube, m
H	Tank height, m
k	Reaction rate constant, (min^{-1}[mol/mol of oil]$^{-1}$)
L	Length, m
P	Pressure, MPa
Re	Reynolds number
R	Gas constant, 8.314 kJ/mol.K
t	Reaction time, min or s
T	Temperature, ^{o}C or K
V	Volume, m^3
v	Velocity, m/min or cm/min
HHVs	Higher heating values, MJ/kg
Ea	Activation Energy, kJ/mol
A_o	Arrhenius constant or Pre-exponential factor, (min^{-1}[mol/mol of oil]$^{-1}$)
$F_{w,}$	Flow-rate of water, m/min or cm/min
F_o	Flow-rate of oil, m/min or cm/min

Greek symbols

ρ	Density, kg/m^3 or g/cm^3
ρ_o	Density of sunflower oil, kg/m^3 or g/cm^3
ρ_w	Density of water, kg/m^3 or g/cm^3
ρ_m	Density of methanol, kg/m^3 or g/cm^3
μ	Viscosity, kg/m.s or g/cm.s
D_{AB}	Diffusivity coefficient, m^2/s or cm^2/s

Φ	Solvent association parameter
M_B	Molecular weight of the solvent B, g/mol
υ_A	Molar volume, for component A
ε	Relative permittivity, F/m
$\bar{\bar{\rho}}$	Average density, kg/m^3 or g/cm^3
$\bar{\mu}$	Average viscosity, kg/m.s or g/cm.s

Acronyms

DGCR	Downflow Gas Contactor Reactor
GC	Gas Chromatography
HPLC	High Pperformance Liquid Chromatography
BOC	British oxygen company
PFR	Plug Flow Reactor
FID	Flame Ionization Detector
CI	Compression Ignition
WMG	Wrick Manufacturing Group
RPM	Revaluation Per Mminutes
CORM	Crop Origin Row Materials
USDA	United States Department of Agriculture
FFA	Free Fatty Acids
TG	Triglyceride
DG	Diglycerides
MG	Monoglycerides
G	Glycerol
AL	Alcohol
FAME	Fatty Acids Methyl Esters
FEEE	Fatty Acids Ethyl Esters
E	Esters

CHAPTER 1

INTRODUCTION

1.1. Background

1.1.1. Hydrolysis of vegetable oils/animal fats

Fats/oils are considered to be the esters of glycerols and Free Fatty Acids (FFA). The industrial production of FFA from fats/oils is generally achieved by a fat splitting process, also referred to as a hydrolysis process. The hydrolysis of oils/fats is of commercial significance because of the extensive use of FFA in preparing soaps, synthetic detergents, plasticisers, coatings, greases and many miscellaneous organic derivatives (Reinish, 1956). FFA can also be used to produce biodiesel fuel via an esterification reaction.

The hydrolysis of oils/fats is an area where chemical engineering techniques have been extensively applied. A chemical reaction is induced to break down the fats/oils and release glycerol and FFA. Hydrolysis reactions are reversible and proceed in a step-wise fashion with the production of monoglycerides (MG) and diglycerides (DG) as intermediate compounds. As water and oils/fats are considered insoluble at ambient conditions, the hydrolysis takes place when solubility is improved with the help of temperature and pressure. Hydrolysis is efficient under conditions that favour homogeneity. i.e., where water has greatest solubility within the fatlike phase (Sonntag, 1982). The hydrolysis process is followed by separation of FFA from the by-product glycerol. This is usually done by gravity or centrifugation. The separated FFA can be used to identify the original fat or oil. Each fat or oil has a certain amount of individual FFA and, if for example, Linoleic acid (C18:2) (the short formula is expressed in Cx:y where x is the number of carbon atoms and y is the number of the double bounds) is required, the best oil to use is sunflower oil. A number of methods are available for the production of FFA and these will be discussed in section 2.1.4.

The original idea of hydrolysing fats at high temperature and pressure was established in a patent by Tilghmann (1854), as cited by (Burrow, 1953). Due to a narrow range of operating conditions and suitable materials as well as methods of construction, this process was not commercialised. The catalytic process known as the Twichell process however, was patented (pat. 601,603) in 1898 as one of the earliest processes for fat splitting and was soon applied on an industrial scale (Ackelsberg, 1958).

Many companies have adopted a cleaner and more efficient attitude towards their processes. Many researchers are returning to nature to develop newer technologies which would reduce the final product cost while maintaining the quality. One of the newest technologies in hydrolysis reactions, that has often been investigated by numerous researchers (Al-Zuhair et al., 2003, sreenath, 1999, Weatherley and Rooney, 2008) makes use of enzymes. Enzymatic hydrolysis offers an alternative method for the production of FFA under mild reaction conditions; however, there are many obvious problems with lipases hydrolysis. The cost of enzymes is very high, so industrial applications are still in their infancy (H-Kittikun et al., 2000). Moreover, the hydrolysis requires hot water in order to increase the solubility of oils/fats in water, but the enzymes cannot tolerate high temperatures. Ultrafiltration and membrane separation techniques are also essential to recover the enzymes from the final products.

Continuous flow hydrolysis under subcritical water conditions is a process which has recently been reported (Minami and Saka, 2006). This process offers the advantages of eliminating catalyst separation and purification techniques from the FFA product, and is therefore simpler. Subcritical water which is in a liquid state in a temperature range from 100 to 374 ^{o}C and below the critical points (Fujii et al., 2006) , grant shorter reaction times (several minutes) than enzymatic hydrolysis (several hours) and up to 90 % more FFA is yielded (Krammer and Vogel, 2000). The continuous flow process has the advantage of increased production, while maintaining the product quality, and in addition, reduces the maintenance requirement and it can easily be scaled up.

1.1.2. Biodiesel production

The term Biodiesel (from Greek, *bio*, life + diesel from *Rudolf Diesel*, known as fatty acid m(e)thyl ester), refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel fuel is an attractive alternative to petroleum diesel (petrodiesel). Biodiesel is easily produced and requires low energy inputs, depending on the method of production, as will be discussed later. It can be made from animal fats (e.g., tallow), although the main feedstock comes from vegetable oils, which can be obtained from a wide variety of plants (e.g., soybean, rapeseed/canola, coconut, palm, safflower and peanut). The choice of feedstock depends mainly on the geographical situation (Knothe, 2005b). The main drawback to biodiesel production is the availability of vegetable oil. In many countries, biodiesel is blended with petrodiesel in a certain ratio. The resulting blend is indicated by acronyms such as B20, which means 20 % biodiesel with petrodiesel. B20 can be used in almost all diesel engines and is suitable for most storage and distribution equipment (Demirbas, 2009).

Humanity's dependence on fossil fuels for transportation has become critical. Most of the world's energy needs are supplied through petrochemical, coal and natural gases, and all these resources will be exhausted in less than a century, as predicted by the World Energy Forum (Sharma and Singh, 2009). The environmental impact of fossil fuels, moreover, is well known, it contributes to global warming through greenhouse gases. It is also the major source of air pollution. Efforts are being made in many countries to search for suitable alternative diesel fuels, which are environmentally friendly and can be used in place of long-term supplies of conventional diesel fuel.

Biodiesel production is a technological area for many researchers, due to its relevance to today's problems. The number of papers published in the field of biodiesel production each year is exponentially increasing (see Figure 1-1), which indicates the growing attention in this area. However, the total amount of research is still much less than it is in other energy related fields, such as fuel cells, on which

12,229 papers were published in 2008 (Slinn, 2008). Biodiesel is gaining wider interest worldwide as a blending component or direct replacement for diesel fuel in vehicle engines (Demirbas, 2009). This may be because biodiesel seems to be more commercially viable than fuel cells and other alternative energy sources, such as wind and solar energy, which will require more research breakthroughs in order to make them widespread in the market place. Nevertheless, there are still challenges in biodiesel production and many things need to be investigated, such as new energy saving methods of production, the separation of the catalyst from biodiesel, the utilisation of by-products and new feedstocks.

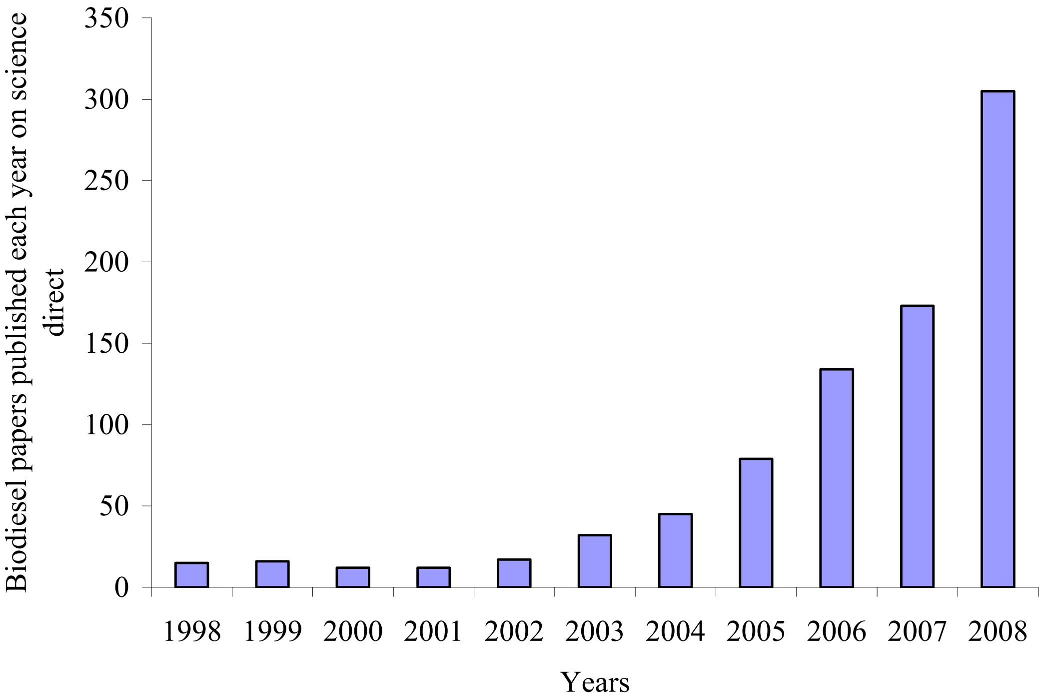

Figure 1-1. The number of biodiesel papers published over 10 years.

1.2. Thesis objectives

The objectives of biodiesel research are varied, ranging from overall surveys to specific areas. This is because the topic of biodiesel is a very current and interesting area of research for the reasons discussed above. Moreover, the new two-step method (hydrolysis and esterification) gives an intermediate product of free fatty acids, which are also fundamental products for many food and industrial applications.

The overall objectives of the present study are to:

A. further fundamental knowledge of the following:
    1- non-catalytic vegetable oil hydrolysis reactions conducted under subcritical water conditions,
    2- new economic processes for biodiesel production.

B. provide key processing parameters essential to the development and enhancement of environmentally friendly processes, which will produce value added products using locally available feedstocks.

The specific objectives are to

1- study the continuous flow production of free fatty acids in a shorter reaction time.

2- develop kinetic models and confirm the mechanism for hydrolysis and esterification reactions.

3- investigate the two-step method (hydrolysis and esterification) for biodiesel production in order to establish milder reaction conditions and a reduce in the amount of alcohol required.

4- produce high quality biodiesel in a state-of-the-art apparatus, the Downflow Gas Contactor Reactor (DGCR), under extremely mild reaction conditions and compare with those reported in the literature.

1.3. Layout of this thesis

This thesis consists of seven chapters. Chapter 1 gives the introduction to hydrolysis of vegetable oils/animal fats and to biodiesel production. Chapter 2 includes an extensive literature survey on the hydrolysis of vegetable oils/animal fats, an introduction to sub-and supercritical fluids, background on biodiesel production methods and the state-of-art apparatus, the DGCR. This chapter also covers the importance of FFA and biodiesel as commercial products and different methods of producing them. Chapters 3, 4, 5 & 6 are written in the style of research papers and can be approached separately. In Chapter 3, the production of FFA in a subcritical water continuous flow system is detailed and the process variables are optimised. Chapter 4 discusses the kinetics of sunflower oil hydrolysis. Chapter 5 deals with the esterification process of FFA with supercritical alcohol and optimisation of the process variables. Moreover, the kinetics of esterification reaction are established. The state-of-the-art DGCR utilised for biodiesel production is detailed in Chapter 6. Finally, in Chapter 7, the conclusions are outlined, along with recommendations for future work.

CHAPTER 2

LITERATURE SURVEY

2.1. Hydrolysis of vegetable oils/animal fats

2.1.1. Introduction

Fats[1] and oils are naturally occurring chemical substances. The industrial applications of fats and oils are considered as one of the largest fields where chemical engineering techniques have been applied. Fats and oils are obtained from both animals and vegetables sources. They provide the raw materials for manufacturing of both edible and non-edible products. The oils and fats industries produce many

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[1] The term fat derived from the old English word “faett” which means plump or obese.

valuable products, ranging from cooking fats and margarine to cosmetics, soap and detergents. The other advantages that encourage the use of vegetable oils are their relatively low viscosity variation with temperature. Their chemical compositions and specific properties allowed them to have multi-use. All fats and oils have certain features in common and will be discussed later in section 2.1.3.

Human use of fats and oils is documented to 3000 years ago as they could be easily separated from their sources (Weiss, 1983). The main use of non-edible fats and oils is for soap manufacturing. The soap production process has been carried out even before history was recorded. This process involves hydrolysis of fats with a hot solution of sodium hydroxide. This process is known as saponification (from the Latin sapon meaning soap) (Rooney, 1997). The hydrolysis of fats with a solution of sodium hydroxide is considered now as one of the most important methods for production of soap and other applications, such as in the food industries. The major source of fats originates from cooking meats and that of hydroxide from wood ashes. However, in 1779 and again in 1823, it was acknowledged that fats can be hydrolysed with water to yield glycerol and free fatty acids (FFA) (Burton, 1972). The use of vegetable oils and animal fats in the lubrication industries was established many years ago (Aluyor et al., 2009).

The modern world has high demand for higher quality products with cheaper prices. These demands have lead to the large scale production of FFA, which are the basic building blocks of all oils and fats. There are many processes available for the production of FFA which will be discussed later. Almost all of these processes for large scale production of FFA require high energy consumption.

2.1.2. Fats and oils

Fats and oils are defined as the oleaginous material. Fats and oils, are hydrophobic substances of vegetable, animal lard or marine animal, consist predominantly of glyceryl esters of fatty acids and are insoluble in water at ambient conditions (Sonntag, 1979c). There are roughly about quarter of a million known plant species, but only 4500 species have been examined for the production of oils (Sonntag, 1979b). Recently, O'Brien (1998) has reported that out of more than 100 types of plants known to have oil-bearing seeds, only a few have been commercialised. Roughly, only 22 vegetables have been reported by Sonntag (1979b) to be commercially developed for a large scale oils productions and 12 of them represent more than 95 % of the reported annual world vegetable oil production. The oil content of oil-bearing materials, i.e. the seed from the vegetable, can vary between 3 and 70 % of the total weight. For fats, there are only three main sources considered, i.e. hogs, cattle and sheep (O'Brien, 1998).

The most important products of fats and oils are for food, however, some of the fats and oils are used for non-food products. Some examples for the uses of vegetable oils as non-food products are shown in Figure 2-1. Moreover, Warwick Manufacturing Group (WMG) is investigating a number of natural sources for the production of materials such as polymers, fibres and fuels (WMG, 2007) to alleviate the pressure on Crop Origin Raw Materials (CORM) as feedstocks.

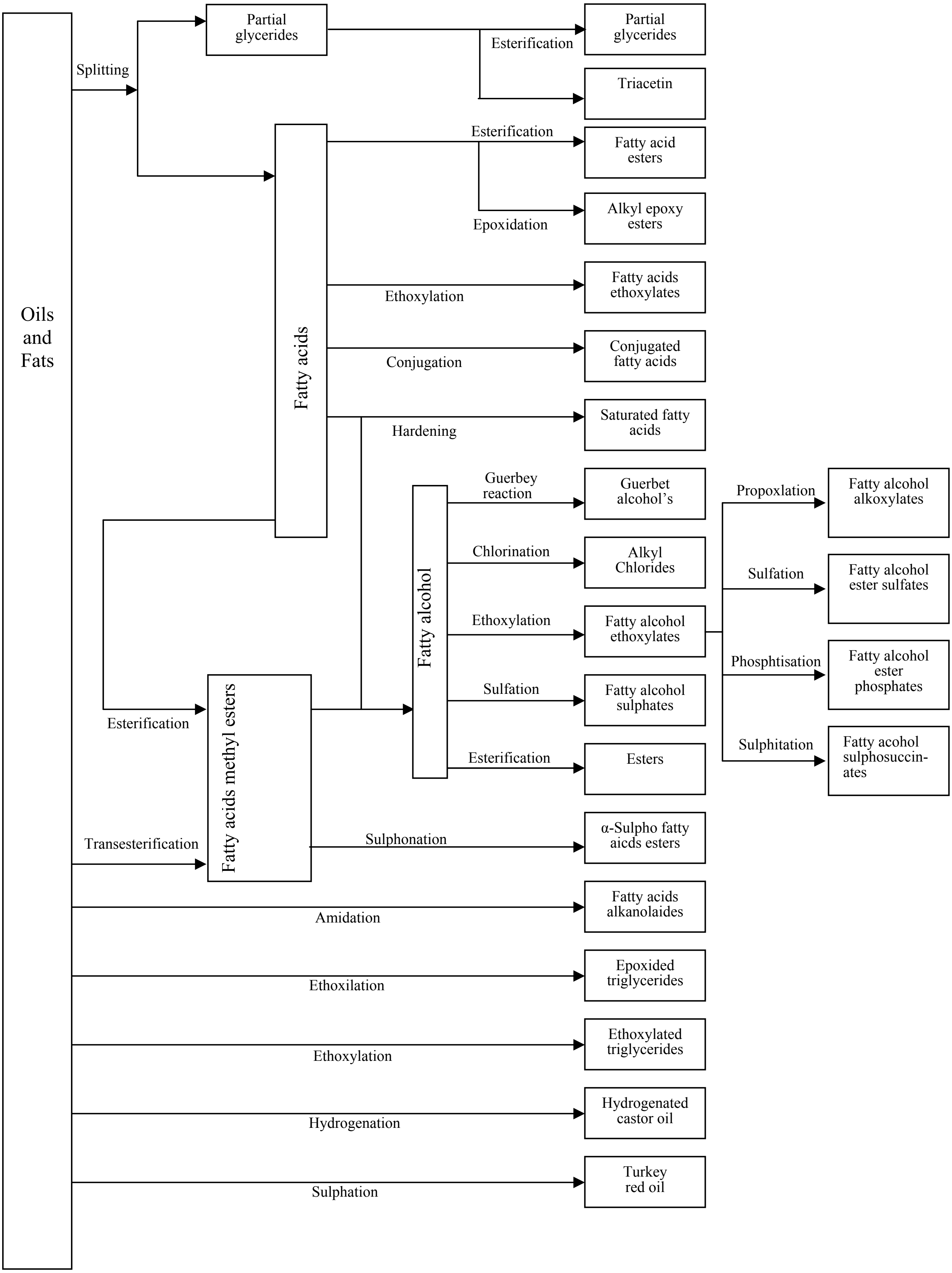


Figure 2-1. Oils and fats and their derivations cited in Gregorio (2005).

The world's vegetable oils/animal fats industries have been grown rapidly over the last few decades. The world oil seed production rate is presently around 300 million tonnes/annum, providing us with around of 70 million tonnes of vegetable oils such as rapeseed, soybean, peanut, olive and sunflower oil (Rooney, 1997). The world's fats and oils production have been growing rapidly over the past few decades, far beyond the need for human nutrition. The world's production and consumption of natural oils and fats have grown from 79.2 million tonnes in 1990 to 117 million tonnes in 2001 (Gregorio, 2005). This indicates that the oils and fats industries are crucially important to the world's economy. Figure 2-2 illustrates the production rate of seed oil within the Europe Union (E.U.). Rapeseed oil is the largest oil production industry and has been almost stable over the period from 1998 to 2003 (United States Department of Agriculture USDA (USDA, 2009)). However, a large percentage of rapeseed oil is used for the production of biodiesel. As cited by Hammond (1991), "the amount of fats and oils in feed and industrial products has ranged from 25-30 % of total use in recent years".

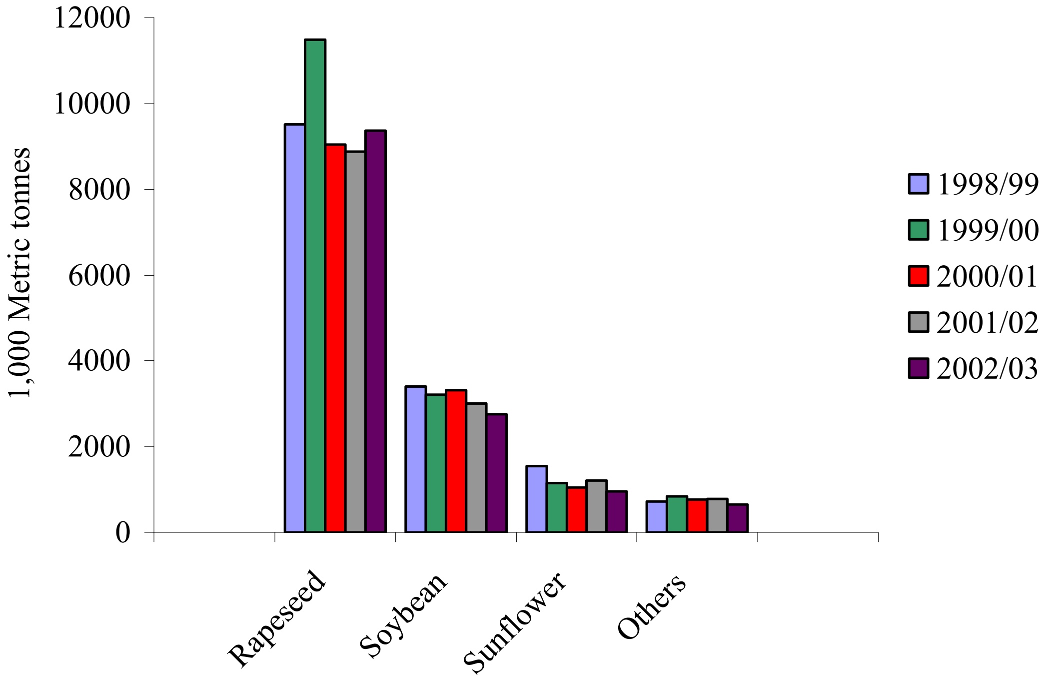
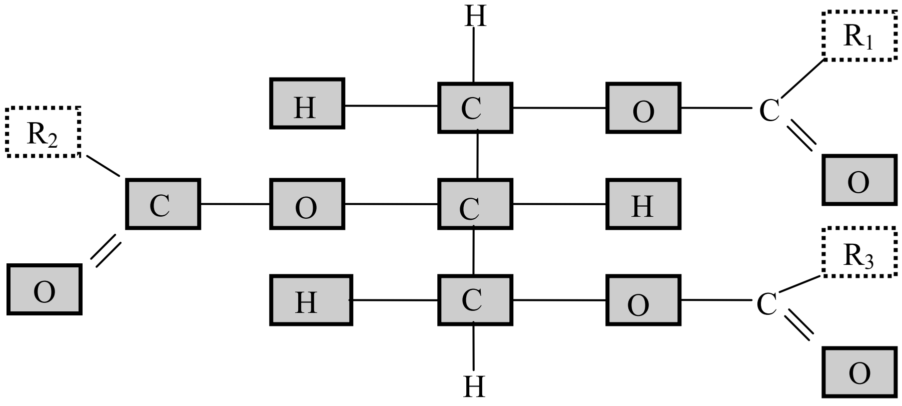


Figure 2-2. European Union: oilseeds production rate (from http://www.fas.usda.gov/oilseeds/circular/2003/03-04/table15.pdf.).

2.1.3. Properties of oils/fats

Fats and oils are chemical substances that are composed of triglycerides, diglycerides and monoglycerides. These molecules are composed of three, two and one chain of fatty acids, respectively, containing from 4 to 24 carbons atoms with up to three double bonds, attached to a glycerol backbone (O'Brien, 1998). Triglycerides are the most common component in edible oils and fats. Figure 2-3 shows the typical arrangement of triglycerides molecules.



Glycerol backbone

R_1, R_2, R_3 = Alkyl chain

Figure 2-3. Structure of triglycerides molecules (Rooney, 1997) .

Triglycerides are made up of carboxylic acids, which are known as alkyl chain and have been represented in Figure 2-3 by R_1, R_2 and R_3. Glycerides normally are esters based on the alcohol glycerol and form when the alcohol takes part in a condensation reaction with carboxylic acid. The scientific name for glycerol (glycerine) is propane-1,2,3-triol and has a molecular weight of 92.0 g/gmol. The molecules of glycerol contains three (-OH) functional groups.

Fats and oils have different physical properties, even though they are composed of similar fatty acids. These differences in physical properties arise from differences in the proportion of fatty acids and the structure of individual triglycerides (O'Brien, 1998). The physical properties of fats and oils are significant for a number of reasons. Many practical applications of fats and oils depend on their oiliness (ability to form lubricant films), surface activities and melting point. The viscosity of an oil is affected by oil saturation and temperature. Generally speaking, the viscosity of oil decreases slightly with increase of the degree of unsaturation. It can be seen from Table 2-1 that oils having higher kinematic viscosities contain higher molecular weight of saturating fatty acids e.g., castor oil has the highest specific gravity and viscosity compared to the other oils in the table. Its high viscosity comes from the high content of ricinoleic acid that readily forms intermolecular hydrogen bonds. Conversely, in comparison to castor oil, the viscosities of other common oils differ by an order of magnitude. The majority of oils act as Newtonian fluids, i.e. the relationship between shear stress and shear rate is linear (Wan, 1991). It is clear that the physical properties of fats and oils are dependant on the types and proportions of fatty acids in their content. Some of the main factors that affect the vegetable oil fatty acids composition are climate conditions, soil type, growing season, plant health, plant maturity and genetic variation of the plant (O'Brien, 1998).

Table 2-1. Kinematic viscosities and specific gravities of common fats and oils (Formo, 1979).

Oil	*Specific Gravity*	*Kinematic Viscosity (cSt)*		*Oil*	*Specific Gravity*	*Kinematic Viscosity (cSt)*	
		37.8 ^oC	*98.9 ^oC*			*37.8 ^oC*	*98.9 ^oC*
Almond	0.9188	43.2	8.74	Castor	0.9619	293.40	20.08
Olive	0.9158	46.68	9.09	Coconut	0.9226	29.79	6.06
Rapeseed	0.9114	50.64	10.32	Palm Kernel	0.919	30.92	6.50
Mustard	0.9237	45.13	9.46	Lard	0.9138	44.41	8.81
Cottonseed	0.9187	35.88	8.39	Neatsfoot	0.958	43.15	8.50
Soybean	0.9228	28.49	7.60	Sardine	0.9384	27.86	7.06
Linseed	0.9297	29.6	7.33	Cod liver	0.9138	32.79	7.8
Raw Perilla	0.9297	25.24	6.85	Refined whal	0.9227	31.46	7.48
Sunflower	0.9207	33.31	7.68				

2.1.3.1. Sunflower oil

Sunflower oil is obtained from the seed plant called *Helianhus annus* and the oil content from this seed varies between 22 and 36 % (Sonntag, 1979c). In 1569, sunflower oil was brought to Spain and it was spread all over Europe. Sunflower oil was processed in Russia in 1830, and the seed quality and average oil yield were enhanced from 29 % in 1940 to 46 % 1971 and today Russia is still the main producer (O'Brien, 1998).

Sunflower oil is obtained from the decorticated seed by hydraulic screw pressing or solvent extraction. Crude sunflower oil is amber in colour while the refined oil is pale yellow. Crude sunflower oil also contains some phosphatiedes and muncilaginious matter, which is lower than in corn oil or cotton seed (O'Brien, 1998). The FFA content of sunflower oil is about 0.5 % and is similar to the majority of other oils. However, as reported by O’Brien (1998) the composition of fatty acids varies from year to year and region to region. The average FFA compositions and typical properties of sunflower oil are illustrated in Table 2-2 (O'Brien, 1998, Sonntag, 1979b). The short formula is expressed in Cx:y where x is the number of carbon atoms and y is the number of the double bounds.

Table 2-2. Typical sunflower oil properties.

Property	***Value***
Refractive index at 25 °C	0.915 to 1.474
Specific gravity index at 25 °C	1.472 to 1.474
Iodine number	125.0 to 136.0
Saponification value	188 to 194
Unsaponification value	1.5 max.
Wax, %	0.2 to 3.0
Melting point, °C	16.0 to 20 .0
Cloud point, °C	-9.5
Free Fatty Acids composition,%	

Name	Short formula ($C_{x:y}$)	Composition (%)
Myristic	C14:0	0.1
Palmitic	C16:0	7.0
Palmitoleic	C16:1	0.1
Margaric	C17:0	0.1
Stearic	C18:0	4.5
Oleic	C18:1	18.7
Linoleic	C18:2	67.5
Linoleinic	C18:3	0.8
Arachidic	C20:0	0.8
Gadoleic	C20:1	0.1
Behenic	C22:0	0.7

2.1.4. Hydrolysis processes

As mentioned in section 2.1.2, the hydrolysis of oils is a very old technology, and has been in place since pre-historic times. Fats splitting (hydrolysis) has been conducted for over a century for manufacturing FFA for soap-making and the production of candles (Sonntag, 1982). Hydrolysis reactions sometimes occur ad hoc in post-harvest handling, oil extraction processes, crude oil storage and shipping and will produce FFA in the crude oil (Hammond, 1991). Hydrolysis reactions are important in the processing of oils/fats by the chemical industry (King et al., 1999). Hydrolysis process can be divided into groups; one of them carried out at atmospheric pressure, and the other one carried out at high temperature and pressure. The processes carried out at atmospheric pressure include:

- Acid splitting
- Twichell type splitting (will be discussed in section 2.1.4.1)
- Enzyme hydrolysis

In the acid splitting method, the FFA is produced through the reaction of acidification of soap with sulphuric acid. This method is limited only to a laboratory scale and is not recommended for a large scale production due to cost. Enzyme hydrolysis for FFA production has been investigated by numerous workers (Al-Zuhair et al., 2003, Patil et al., 1988, Tanigaki et al., 1995, Weatherley and Rooney, 2008). Enzymes are proteins and are produced from plants, animals and microbial sources. The enzymatic hydrolysis of fats/oils is catalysed by one type of enzyme called lipase (glycerol ester hydrolases EC 3.1.1.3) (Rooney, 1997). In the lipase catalyst process, increasing the reaction temperature increases the rate of lipase-catalyst reaction per unit amount of active enzyme, but further increases in temperature will lead to thermal deactivation of the lipase itself which therefore, decreases the amount of active enzyme (Al-Zuhair et al., 2003). The enzyme processes require a special reactor design that allows the separation of products and recovery of the enzymes (Tanigaki et al., 1995). As shown in Figure 2-4, even with the help of stirrer contact and sprayed electricity (high voltage of electrical fields, which can be considered a temperature effect due to localised heating), enzymatic hydrolysis still requires a period of time in hours to attain 60 % of oil hydrolysis. Moreover, enzymes hydrolysis can only be carried out for specific applications due to the high cost of the enzymes (Hammond, 1991). For mass production on the industrial scale, the process conducted at high pressure and temperature will be discussed in section 2.1.4.

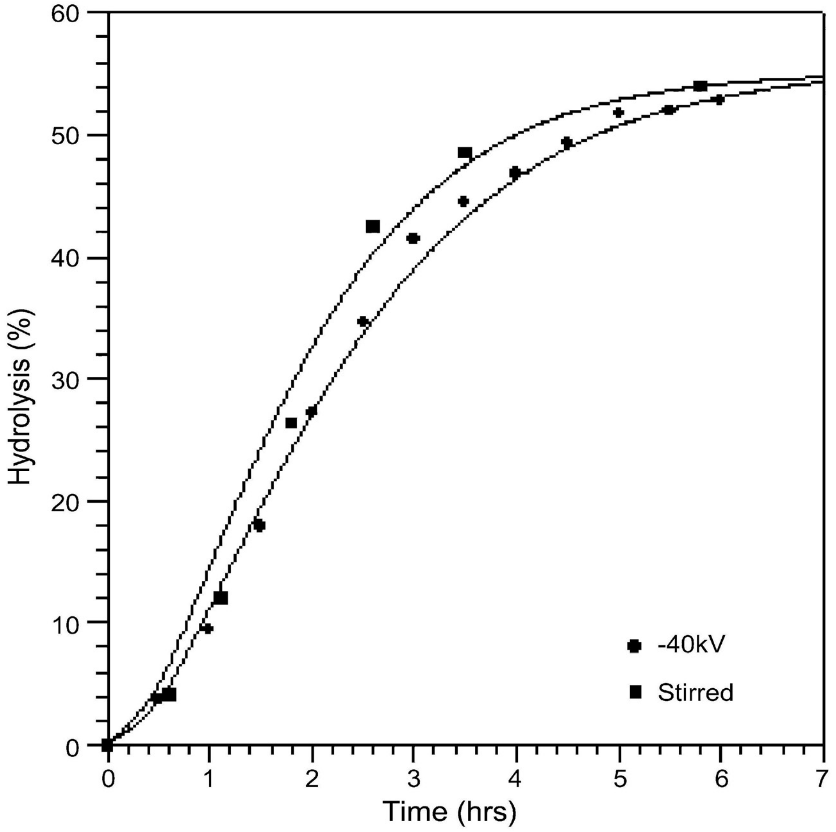


Figure 2-4. Batch enzymatic hydrolysis of sunflower oil; with aid of stirrer contact and electricity sprayed contact (Weatherley and Rooney, 2008).

2.1.5. Principles of fats/oils hydrolysis

(see chapter 3 for detailed discussion of FFA process variables)

Hydrolysis reactions of fats/oils form a heterogeneous system in two liquid phases. This consists of a dispersed aqueous phase of water and glycerol which are hydrophilic, and a continuous lipid phase of FFA and oil (glycerides) which are hydrophobic. In order to overcome this challenge, hydrolysis reactions have to be carried out at special reaction conditions and catalysts. Increasing the solubility of the hydrolysis reactants is crucial to increasing the rate of hydrolysis. Lascaray (1949), reported that hydrolysis reactions take place in the oil phase and did not take place at the interface between fats/oils and water. He also, documented that the reaction rate increases with temperature and with the amount of catalyst.

For hydrolysis of oils/fats using water, the process can be defined as a mass transfer controlled chemical reaction whereby water reacts with oils/fats to form FFA and glycerol (Lascaray, 1949) . The hydrolysis reaction as shown in Figure 2-5 has been proposed by many researchers (Lascaray, 1949, Mills and McClain, 1949, Patil et al., 1988, Pinto and Lancas, 2006) as three stepwise reversible reactions in which: (1) the triglyceride (TG) is hydrolysed to diglycerides (DG), (2) DG is hydrolysed to monoglycerides (MG) and (3) MG is hydrolysed to glycerol, and in each step a production of FFA results. FFA and glycerol are valuable intermediate raw materials having a variety of applications. The industrial important of FFA will be discussed in section 2.1.6.

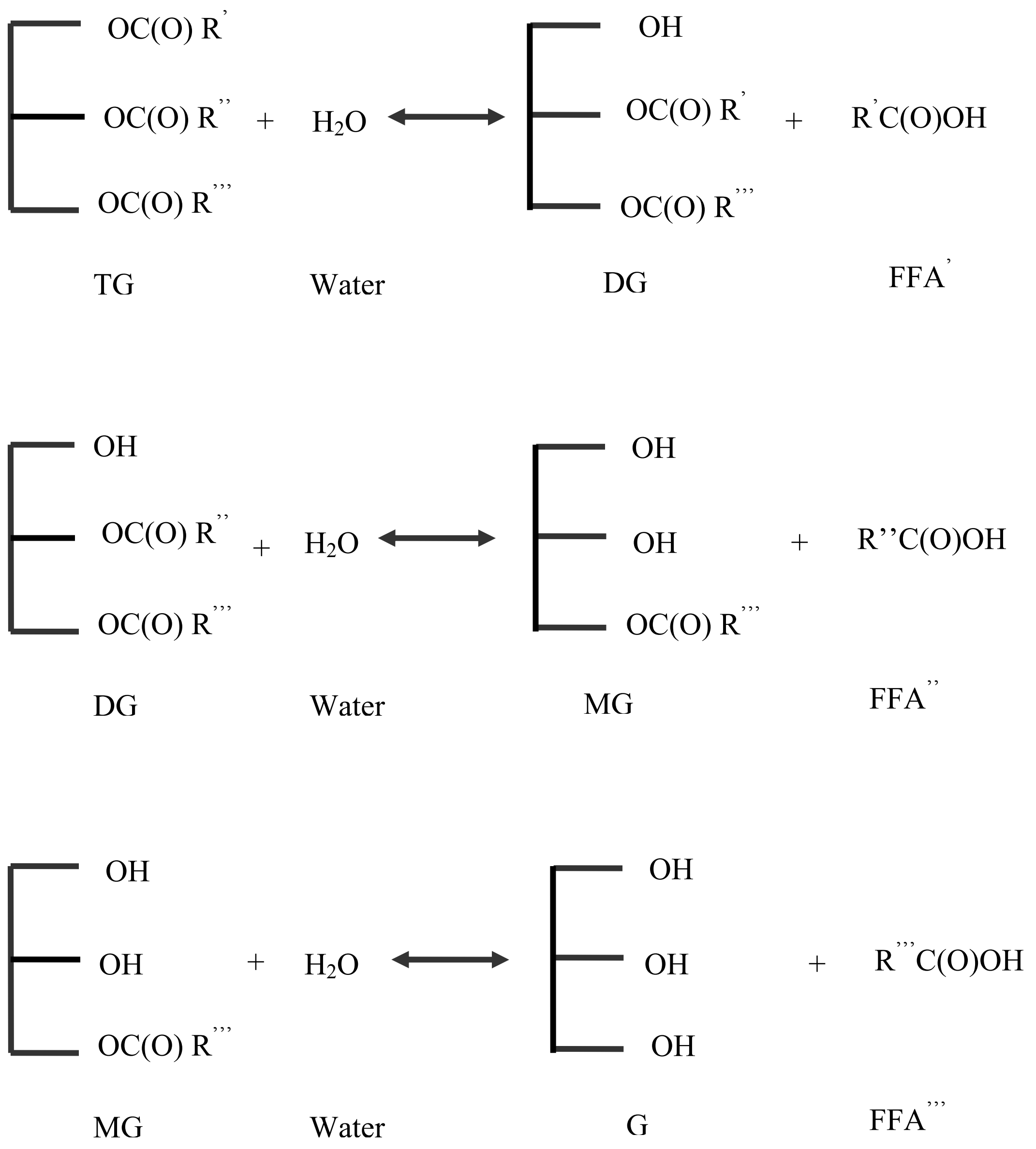


Figure 2-5. Hydrolysis reaction of vegetable oils/animal fats (Patil et al., 1988), where $R^{'}$, $R^{''}$ and $R^{'''}$ represent different side chains and TG, DG, MG, G, and FFA stands for riglycrides, diglycerides, monoglycerides, glycerol and free fatty acids.

2.1.5.1. Twichell type splitting

The Twichell process for oil hydrolysis was patented in 1898 (US pat. 601,603) as one of the earliest processes for fat splitting (Ackelsberg, 1958). In this method, fats in a large open tank are reacted with an organic catalyst known as a Twitchell reagent and sulphuric acid which acts as a surface–active agent for the hydrolysis process (Hartman, 1951). The process operates at atmospheric pressure and a maximum temperature limited by the boiling point of water. These conditions allow simple construction of the tank from acid resistant materials such as wood, lead and monel linings.

In the process fat:water volume ratios range from 1:4 to 1:1, 1-2% of sulphuric acid and 0.75-1.25% of organic catalyst. The process takes about 12 to 24 hours under vigorous agitation provided by steam (Ackelsberg, 1958). The tank is also covered to avoid discolouration of the products. Usually, the process is repeated two to four times depending upon the degree of hydrolysis required and in each step glycerol is formed. A portion of the aqueous phase removed from the tank and replaced with fresh water. A high degree of hydrolysis of up to 90-95 %, can be achieved using four step processes. The main disadvantages of the Twitchell process are the high consumption of steam and long reaction period which leads to high operational costs that make it unattractive in the present climate.

2.1.5.2. Batch autoclave process

The batch autoclave process is the oldest method for fat/oil hydrolysis and was patented in 1850's (Rooney, 1997). In this method, the drawback of the Twichell process is avoided by shortening the reaction period to between 1.5 and 6.0 hours but at the cost of higher temperature of 220 ^{o}C and pressure of 2 MPa. A degree of hydrolysis of about 88-90 % can be achieved (Ackelsberg, 1958). The process used special kinds of oils that can tolerate high temperature such as coconut, babassu and palm kernel. The process was not initially developed into large scale due to lack of materials that can tolerate high operation pressures at that time, but with the availability of new feedstocks in the following years, this process has been revitalised.

The degree of hydrolysis in the autoclave batch process can be accelerated by employing reagents such as zinc oxide, manganese and lime to act as catalysts. Lascaray (1949) reported that the degree of hydrolysis was directly proportional to the activity of the catalyst and that zinc oxide and manganese were the most effective reagent. The catalyst reacts with the fatty acids in the oils to form metal soaps that are insoluble in water, but soluble in fatty acids. In autoclave batch process, the degree of hydrolysis of fats is catalysed by hydrogen ions and not by hydroxide ions.

The autoclave reactor typically has a cylindrical shape that is 1.0 to 2.0 metres in diameter and 6.0 to 12.0 metres in height. It is usually made from 316 stainless steel and charged with oils, water (up to approximately half of the oil weight) and 2.0 to 4.0 wt.% of catalyst (Ackelsberg, 1958, Rooney, 1997). In the beginning of the reaction the air in the autoclave is evacuated with steam to prevent oxidation and darkening of the fatty acids. Mechanical agitation may or may not be used depending on the operation pressure. At a lower pressure of around atmospheric, mechanical agitation is required because of the lower solubility of oils in water. Usually, steam is injected continuously from the bottom of the autoclave and vented in a small amount to maintain continuous agitation and to raise the operating temperature and pressure to the desired values. This process rarely uses more that one stage of hydrolysis compared to the four stages of the Twichell process and the products are normally transferred to settling tanks to allow phase separation. Also, the water and glycerine are drawn off after a certain time and the oils are recharged to the reactor again with sweet water (fresh water) to give a higher split, if required. Mineral acid is added to the product of fatty acids in order to separate the soap formed during the process and the final products are washed with water.

2.1.5.3. Continuous process

The continuous counter-current process operates at high pressure (about 6 MPa) and temperature (about 260 ^{o}C). It is considered the most organised process for fat hydrolysis (Ackelsberg, 1958, Sonntag, 1979a). This process utilises high pressure and temperature together with a catalyst to increase the reaction rate. As reported by Lawrence (1954), the process required less catalyst by operating at high temperature (260 ^{o}C), which resulted in simplification of the process. The reactants are heated by two sources; from a heat exchanger between the two streams and by direct injection of high pressure steam at a temperature maintained between 249 and 260 ^{o}C. The reaction period varies between 1.5 to 2.5 hours resulting in 96-99% splitting of fats. The typical arrangement of this process can be seen in Figure 2-6.

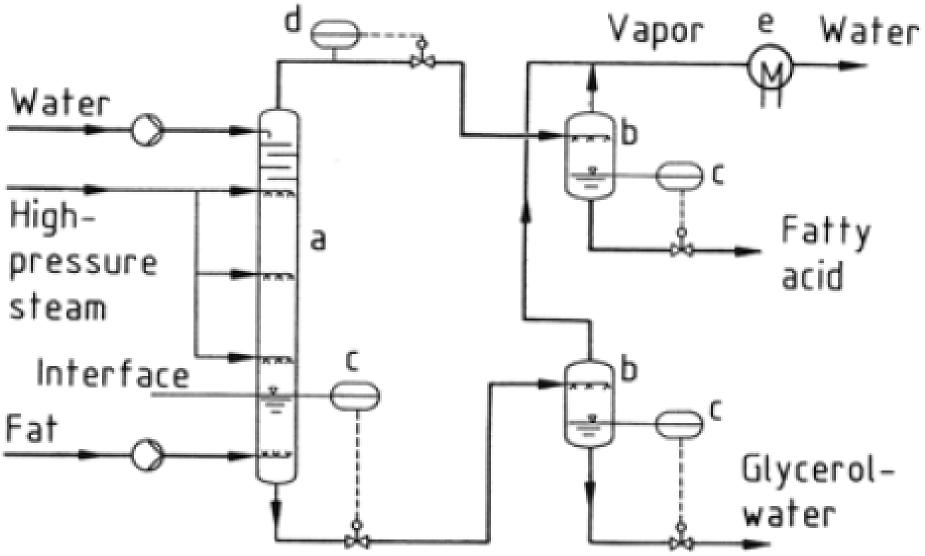


Figure 2-6. Continuous fat splitting process, a. splitting column, b. flash tank, c. level control, d.pressure control, e. condenser (Anneken, 2006).

2.1.6. Importance of producing FFA

FFA are produced by hydrolysis reactions of fats/oils in different processes as mentioned above. FFA are widely used for industrial applications as well as the characteristic flavouring of foods. The oldest application of FFA is in the production of candles from saturated FFA (C16:0-C18:0). Other applications of FFA include the production of biodiesel, soap, emulsifiers, polymers, paper chemicals, lubricants. When reacted with nitrogen they find applications in even more varieties of products, such as food-packaging materials, water repellent textiles, mold-releasing agents, printing ink, and liquid detergents (O'Brien, 1998, Scrimgeour, 2005). Research has also proven that FFA are essential for human health. Linoleic acid (C18:2) is responsible for the pathway to make arachidonic acid that appears in human cell membrane. Moreover, linoleic acid (C18:2), γ-linoleic acid (C16:3) and omega-3 fatty acids (from fish oil) are used as additives for oil based health care products (Hodson et al., 2008, Rooney, 1997, Sonntag, 1979c). The division of the main end-use sectors of FFA are given in Table 2-3 for Europe and worldwide.

Table 2-3. Main applications of FFA in 2003 (Anneken, 2006).

Applications	***Europe, %***	***World, %***
Detergents, personal care, soaps, cosmetics	40	49
Plastics	14	10
Rubber and tire industry	7	6
Lubricants and Greases	6	3
Paper chemicals	5	3
Protective coatings and resins	5	3
Others (food, feed, candles, textile, leather, adhesives, agrochemicals, construction ….)	23	26

2.1.6.1. Properties of FFA

There are about 1000 known FFA, but only about 20 to 50 FFA are of concern to industry and health. FFAs have a straight chain and an even number of carbon atoms ranging from C4 (butanolic acid) to C24 (lignoceric acid). The most common FFA range between C12 to C22. In general, FFA have a carboxyl group (COOH) attached to its chain. About 97 % of FFA found in commercial vegetable oilseeds have been estimated to consist of only eight FFA as shown in Table 2-4 (Gunstone, 1996). FFA are described by the number of carbon atoms in the chain, followed by colon and other number which indicates the number of double bounds. The comparative structure of fatty acids is shown Figure 2-7. The melting point of a FFA depends on the number of carbon atoms, the degree of saturation and structure of the hydrocarbon chain. For straight chain FFA, the melting point increases with increasing the chain length. These FFA are either saturated with no double bounds and chemically stable, solid phase at room temperature with adequate hydrogens or unsaturated with one or more double bonds and chemically unstable, liquid phase at room temperature with missing adequate hydrogens.

Table 2-4. Selected FFA and their melting points and annual production (Gunstone, 1996).

FFA common name	*Formula*	*Structure*	*Melting point (^oC)*	*Annual worldwide production (%)*
Lauric	$CH_3(CH_2)_{10}COOH$	C12:0	44.0	4
Myristic	$CH_3(CH_2)_{12}COOH$	C14:0	54.5	2
Palmtic	$CH_3(CH_2)_{14}COOH$	C16:0	63.0	11
Stearic	$CH_3(CH_2)_{16}COOH$	C18:0	70.0	34
Oleic	$C_{17}H_{33}COOH$	C18:1	16.0	34
Linoleic	$C_{17}H_{31}COOH$	C18:2	-5.0	5
α- Linoleic	$C_{17}H_{29}COOH$	C18:3	-11.0	3

The solubility of FFA in water and water in FFA has been investigated by many authors (Eggenberger et al., 1949, Hoerr et al., 1942). The solubilises are almost similar, but not identical to that of fats/oils in water and water in oils, i.e., TG.

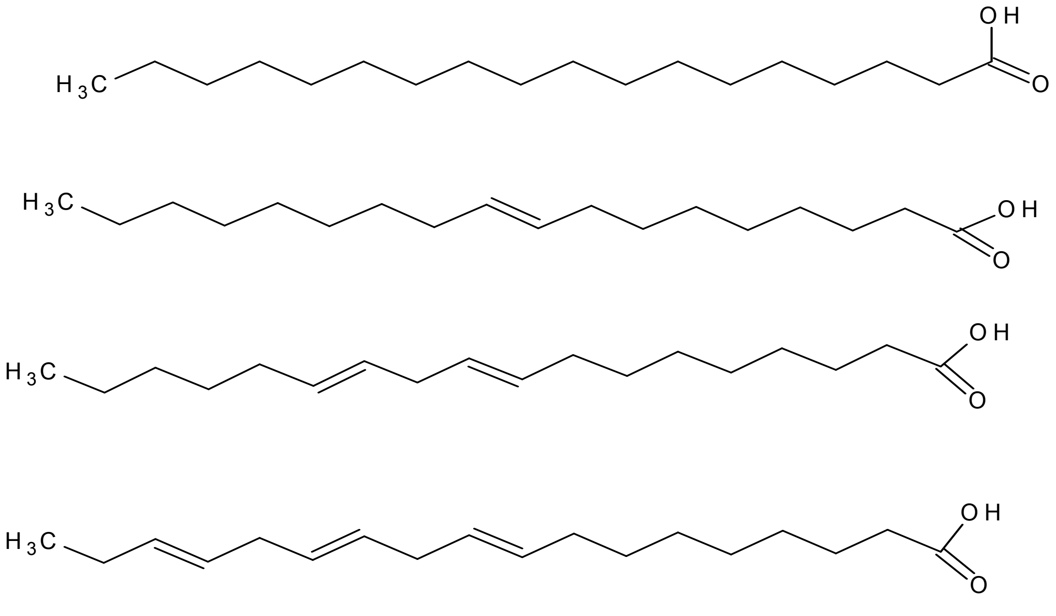


Figure 2-7. Structure of the C18 series of fatty acids (from top to bottom): C18:0 stearic acid, C18:1 oleic acid, C18:2 linoleic acid and C18:3 linolenic acid, respectively.

2.2. An introduction to sub-and supercritical state fluids

Any component or an element can be classified as supercritical when its pressure and temperature exceed its critical temperature (T_c) and critical pressure (P_c), respectively. Above this point, the supercritical region exists as indicated by the shaded area in the pressure-temperature phase diagram below (Figure 2-8). At the critical point, the densities of the liquid and vapour phases become identical. At the critical point, there is no longer a distinction between the liquid and vapour phases as the phase boundary disappears and the substance is now described as a fluid. The existence of this fluid was proven experimentally 170 years ago by Baron Charles Cagniard de la Tour (1822) (Clifford, 1999). For each particular substance there are particular values for P_c and T_c as shown in Table 2-5

Figure 2-9 and Figure 2-10 show the subcritical water and supercritical methanol regions, respectively.

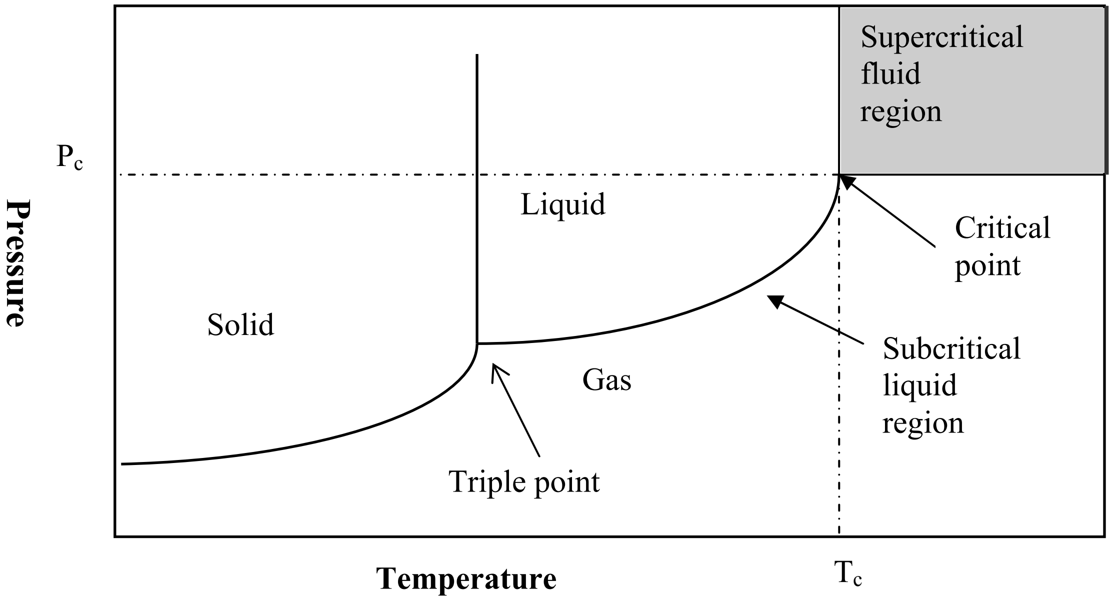


Figure 2-8. Generic pressure-temperature diagram for a pure substance.

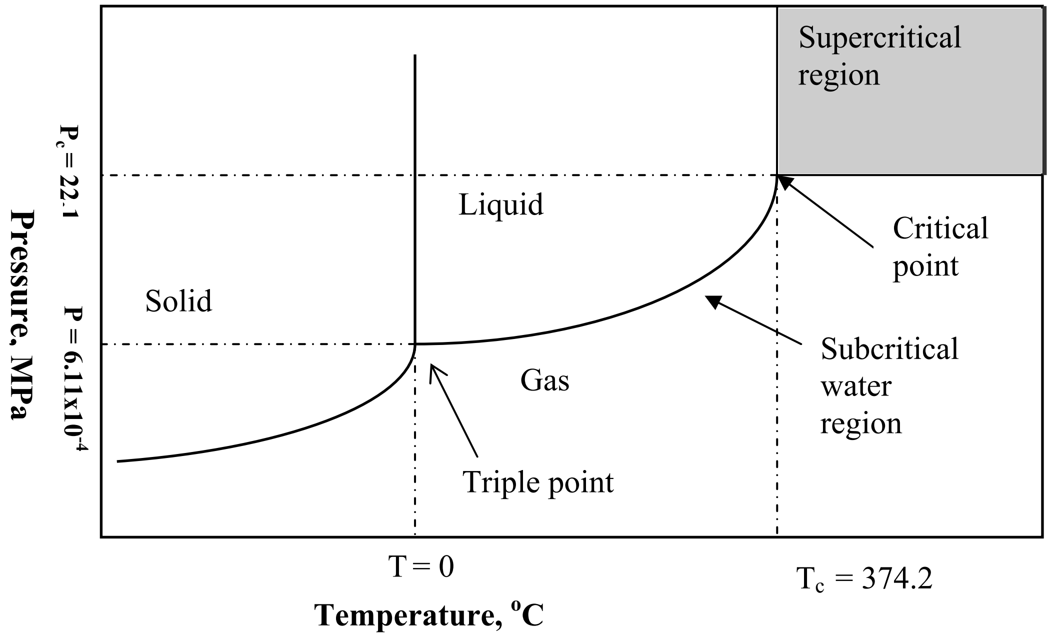


Figure 2-9. Subcritical water region.

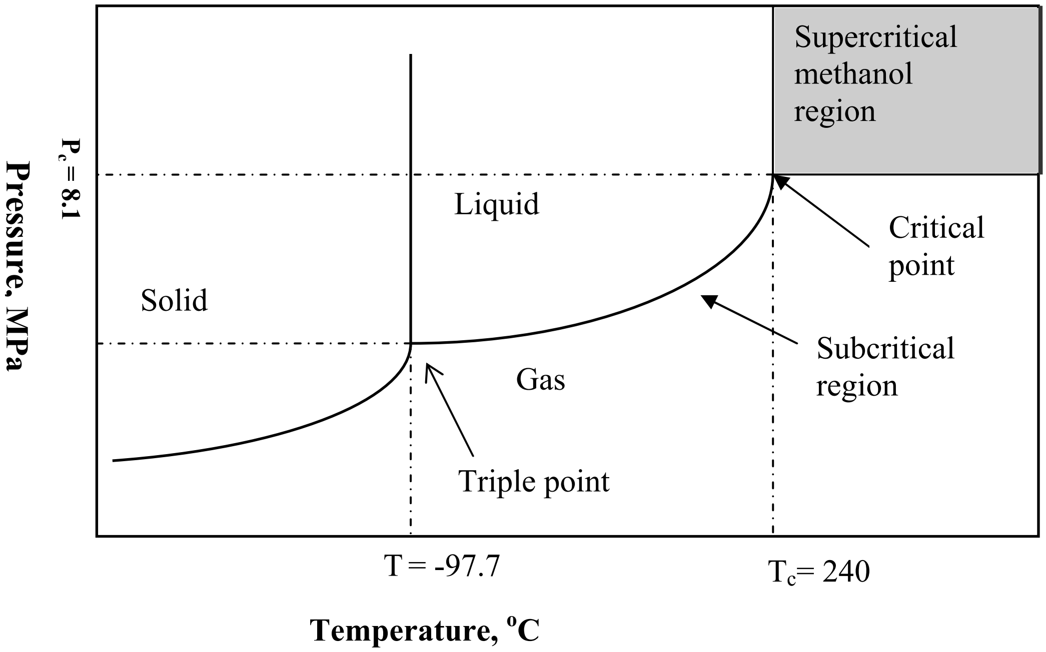


Figure 2-10. Supercritical methanol region.

Table 2-5. Critical pressure and temperature for common substances (Reid, 1987).

Substance	***Critical Temperature (°C)***	***Critical pressure (MPa)***
Water	374.2	22.10
Carbon dioxide	30.85	7.38
Methanol	239.85	8.10
Ethanol	240.85	6.10
Acetone	234.85	4.70
Toluene	318.85	4.10

Generally, supercritical fluids offer a number of advantages over organic solvents as they have low viscosity and high diffusivity which leads to significant increases in mass transfer (Rooney, 1997). Any advantage of using supercritical fluids has to be weighed against the cost and the safety requirements of a process. Therefore, supercritical fluids processes are subjected to certain areas, such as oil extraction of uranium from aqueous solutions, removal of heavy metals from soils and sludges and chemical reactions (Clifford, 1999).

2.2.1. Properties of supercritical fluids

In the last few years, supercritical fluids have been proven to be an environmentally friendly media for chemical and related processes. Several new processes and products have been developed by utilising the physical and chemical properties of supercritical fluids, for example, supercritical carbon dioxide and water, are viable replacement solvents for a variety of hazardous organic solvents (Hauthal, 2001). The physical properties of a substance at or above its T_c and P_c are much more complex than the apparently simple definition of a supercritical fluid as a dense fluid. Pure supercritical fluids remain in a single phase at any point above T_c and P_c. Supercritical fluids exhibit characteristics such as compressibility, homogeneity and a continuous change from gas-like to liquid-like properties. A liquid-like density in the supercritical region can be transformed into one of vapour-like density by slightly changing the temperature and pressure, without appearance of an interface (Clifford, 1999, Yesodharan, 2002). Usually, the intermediate conditions close to those of liquid and gas have a particular interest.

Supercritical fluids have lower viscosity and higher diffusion coefficient than that of ambient fluids. Moreover, they have sufficient density so that they exhibit liquid-like solvation powers and gas-like mass transfer rates. Minor adjustments of the pressure and temperature around the critical points can have remarkable effects on the physico-chemical properties of supercritical fluids. Furthermore, the properties of supercritical water such as density and dielectric constant can be continuously controlled between gas-like and liquid-like values by varying its pressure and temperature (Yesodharan, 2002). These properties make supercritical fluids attractive for chemical reactions and separation applications.

Carbon dioxide (CO_2) is the most commonly used supercritical fluid in industry. The decaffeination of green coffee beans has been established using supercritical CO_2 (Palmer and Ting, 1995). The main advantages of supercritical CO_2 are its mild critical conditions (31 ^{o}C, 7.38 MPa), non-toxicity, cheapness, non-flammability and ease of separation from the final product as it is a gas at ambient temperature and pressure (Suehiro et al., 1996). Since supercritical CO_2 has mild critical constants, the thermal degradation and decomposition of sensitive products and catalyst can be avoided. Normally supercritical CO_2 is used in extraction processes and purifications, synthetic chemical reactions including polymerizations and inorganic catalytic processes (Ramsey et al., 2009).

The difference between selected properties of liquid, superheated steam and supercritical water have been reported by Ding et al. (1996) as shown in Table 2-6. superheated steam has the lowest density, viscosity and relative permittivity, but it has the highest diffusion coefficient than both ambient and supercritical water. The density of superheated water is three orders and two orders of magnitude less than that of ambient water and supercritical water, respectively. Superheated water, therefore, has unique properties over ambient and supercritical waters. The properties of subcritical water will be discussed in detail in the next section (2.2.1.1).

Table 2-6. Physicochemical properties of ambient water, sub-and supercritical water (Ding et al., 1996) .

Properties	***Ambient water***	***Supercritical water***	***Superheated steam***

	25 °C, 0.1 MPa	*450 °C, 27.57 MPa*	*450 °C, 1.38 MPa*
Density (g/cm^3)	1.0	$1.2x10^{-1}$	$4.2x10^{-3}$
Viscosity (g/cm.s)	$8.9x10^{-3}$	$2.9x10^{-4}$	$2.5x10^{-7}$
Relative permittivity, ε, (F/m)	78.0	1.8	1.0
Diffusion coefficient (cm^2/s)	$7.7x10^{-6}$	$7.6x10^{-4}$	$1.7x10^{-3}$

2.2.1.1. Properties of subcritical water

Water which remains in a liquid state from 100 to 374 °C is regarded as subcritical water and is indicated in Figure 2-8 as the subcritical region. There is a wide range in temperature and pressure between ambient and supercritical water. Water in the sub and supercritical states (> 374 °C; 22.1 MPa) provides unique properties over water at ambient conditions. These properties have been exploited by numerous researchers (Ackelsberg, 1958, Alenezi et al., 2010, Clifford, 1999, Khuwijitjaru et al., 2004, Lascaray, 1952, Moquin and Temelli, 2008) as alternative solvents to eliminate the use of organic solvents in chemical synthesis and in the destruction of hazardous waste (at supercritical conditions). The dissociation constants (K_w)of water from 200 to 300 °C are three orders of magnitudes greater than that of ambient water, which may also contribute to the reactivity of subcritical water with certain organic compounds (Yang and Hildebrand, 2006).

The two distinct advantages of subcritical water are its low relative permittivity (as shown in Table 2-6) and large ionic product. The ionic product in the subcritical state are of the order of 10^{-11} K_W (Clifford, 1999). The relative permittivity of subcritical water (between 10 and 20 MPa; 270 to 350 °C) is comparable to that of acetone or methanol at ambient conditions, and can be adjusted from a value of 80.0 at ambient conditions to 5.0 at the critical point. Moreover, the surface tension of water also decreases dramatically with temperature under moderate pressures of the subcritical region. Both these properties therefore make it a suitable solvent for dissolving organic compounds (Weatherley and Rooney, 2008). Water at ambient condition on the other hand is too polar to dissolve organic compounds. Another major advantage of using subcritical water is the ability to achieve the same results as a process that employs either acidic or alkaline catalysts for the hydrolysis of vegetable oils (Alenezi et al., 2009, Minami and Saka, 2006, Pinto and Lancas, 2006).

2.3. A background to biodiesel production

2.3.1. Introduction to biodiesel

The purpose of this section is to give an overview of biodiesel history, alternative uses of biodiesel, advantages and disadvantages of biodiesel, methods for biodiesel productions, production cost of biodiesel and biodiesel policy.

Biodiesel is an attractive alternative to petrodiesel. The production of biodiesel can be carried out in a relatively easy way and requires low energy input. While it can be made from animal fat, the main fuel stock is vegetable oil, which can be obtained from a remarkably wide variety of plants (Knothe, 2005b). Biodiesel can be defined as a mixture of monoalkyl esters of long chain fatty acids methyl/ethyl esters (FAME/FAEE). This long chain compounds comprise alkyl fatty acid esters that can vary between C_{14} to C_{22}. Typical raw materials include canola, soybean, rapeseed, and palm oils as well as beef and sheep tallows and poultry oil (Demirbas, 2009). The selection of vegetable oils for biodiesel production in many countries is dependent upon the climate and soil conditions. For example, soya bean oil could be used in the U.S.A., rapeseed and sunflower oils in Europe and palm oil in Southeast Asia; mostly Malaysia and Indonesia (Srivastava and Prasad, 2000). Vegetable oils are extracted or pressed from oil seed to obtain crude oils. These oils usually contain FFA, water, sterols, phospholipids, odorants and other impurities. The presence of FFA and water has significant drawbacks on biodiesel process reactions with alcohols using alkaline or acid catalysts (Demirbas, 2003).

Fangrui and Hanna (1999) have reported many problems in using vegetable oils for long periods of time in a diesel engine as follows:

- Carbon deposition,
- Oil ring sticking,
- Lubricant problems,
- Coking and trumpet formation on the injectors to such an extent that fuel atomization does not function properly,
- Thickening and gelling of the lubricant oil leading to contamination by the vegetable oils.

Pure biodiesel is referred to as B100 or ‘‘neat” biodiesel fuel. A biodiesel can be blended with petrodiesel from fossil fuel according to its applications. Biodiesel blends are referred to as BXX, where the XX indicates the amount of biodiesel in the blend for example; a B80 blend is 80% biodiesel and 20% petrodiesel. B20 biodiesel can be used in nearly all diesel equipment and are compatible with most storage and distribution equipments. However, B100 (pure biodiesel) can be used in many diesel engines with slight modifications (Demirbas, 2009).

Some technical properties of biodiesel are shown in Table 2-7. The colour of biodiesel is a clear amber-yellow liquid with a viscosity like petrodiesel. However, for the density and kinematic viscosity there are standards such as ASTM and EN that will be discussed in section 6.3.4. In the EU countries, biodiesel is sold according to the technical regulations of EN14214 European Standard, which stipulates a 96.5% ester content (European-Standard, 2008).

Table 2-7. Technical properties of biodiesel (Demirbas, 2009).

Common name	Biodiesel (bio-diesel)
Common chemical name	Fatty acid (m)ethyl esters
Chemical formula range	C_{14}-C_{24} (m)ethyl esters or $C_{15-25}H_{28-48}O_2$
Kinematic viscosity range (mm^2/s, at 40 ^{o}C)	3.3-5.2
Density range (kg/m^3, at 15 ^{o}C)	860-894
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

2.3.1.1. History of biodiesel

Biodiesel was developed by Rudolph Diesel, the inventor of compression ignition (CI) engine in 1900 (Knothe, 2005a). Peanut oil was used as the fuel to run the diesel engine. Also, in 1900, a French company which operated a diesel engine with peanut oil without any modification. It worked well and only a few insiders knew about this remarkable circumstance. Crude oil at that time was available and was refined to operate the majority of diesel engines (Sharma and Singh, 2009). Diesel engines first appeared in ships in 1900's and in automobiles in 1924. In this period, the low cost and easy accessibility of petroleum made it the main energy source and petroleum diesel was the primary fuel for diesel engines. In the 1930's and 1940's, vegetable oils were used as a diesel fuel usually for emergency situations only (Fangrui and Hanna, 1999, Knothe, 2005a). However, with the international petroleum crises in the 1970s and 1990s, an increasing concern about the depletion of the world's non-renewable of fossil fuel resources and environmental awareness has granted new interest in the search for renewable fuel sources. Also, there are other reasons for considering biofuels for both developing and industrialised countries such as energy security and the economic potential provided that fossil fuel prices increase (Cadenas and Cabezudo, 1998).

2.3.1.2. Alternative uses of biodiesel

Biodiesel which consists of the esters of vegetable oils and animal fats can be used for many other applications besides fuel (Knothe, 2005c). The methyl esters which are considered as an intermediate in the production of fatty alcohol are used by surfactant and cleaning suppliers. Moreover, vegetable oil esters are utilised because they possess solvent properties. Pereira and Mudge (2004) reported that pure vegetable oil biodiesels (rapeseed and soybean) were highly effective in the clean-up of oiled sands such as those found on beaches contaminated with crude oil. Methyl esters of rapeseed oil have been used as plasticizers in the production of plastic (Wehlmann, 1999).

2.3.1.3. Advantages and disadvantages of biodiesel

There are many advantages and disadvantages for the production of biodiesel and these have been reported by many researchers (Bozbas, 2008, Cadenas and Cabezudo, 1998, Canakci et al., 2006, Demirbas, 2007b, , 2009, Knothe, 2005b, Sharma et al., 2008, Tan et al., 2004).

Biodiesel has several advantages compared to petroleum and coal derived diesel:

- It has a lower emission of sulphur dioxide (SO_2), the major pollutant that causes extensive damage to forests, building and health. This is because biodiesel is derived from plants which contain only trace quantities of sulphur.
- It is non-toxic.
- The higher heating values (HHVs) of biodiesel (39–41 MJ/kg) are only slightly lower than that of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg) or petroleum (42 MJ/kg), but are higher than coal (32–37 MJ/kg).
- It has significantly lower emissions of green house gases, such as carbon dioxide when burnt. Reductions in net CO_2 emissions are estimated between 77 and 104 g/MJ of diesel displaced by biodiesel. Also, the emission of CO_2 forms part of the carbon cycle as shown in Figure 2-11
- Commercial biodiesel fuel exhibits a significant reduction in the emission of particulate matter (PM). This is between 75 and 83% lower than petrodiesel fuel.

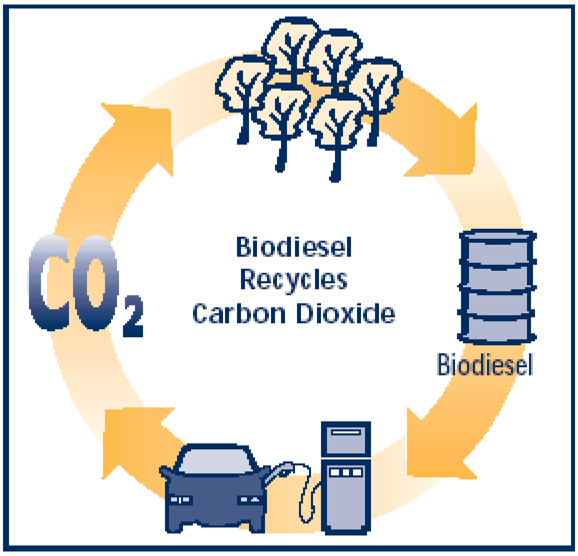


Figure 2-11. Emission of CO_2 from burning biodiesel (from www.biodiesel.com).

- Biodiesel can be used in several indusial applications other than engine fuel (see section 2.3.1.2).
- It has a higher flash point of 150 ^{o}C as compared to 64 ^{o}C for petrodiesel, thus will lead to safer handling and storage.
- It prolongs engine lifetime and reduces the need of maintenance, since the biodiesel has 66 % better lubrication than fossil fuel. A blend of petrodiesel and biodiesel with a biodiesel percentage below 1.0 % can provide up to 30 % increase in lubricity.
- It is naturally biodegradable, so the waste of biodiesel has lower environmental problem than that of petrodiesel. It can degrade four times faster than petrodiesel.

Although biodiesel has these many advantages over petrodiesel and coal, it has certain disadvantages, the main ones are:

- Biodiesel fuel produces 5% lower power compared to petrodiesel. Also, the torque is lower by 1.3 Nm at 1500 rpm. Peak torque is less for the biodiesel but occurs at lower engine speed and generally the torque curves are flatter.

- It has higher viscosity and lower volatility than petrodiesel.
- The price of biodiesel is about 1.5 to 3 times higher than that of petrodiesel. The higher price can be manipulated by using a cheaper feedstock, such as waste cooking oils and non-edible oils.
- It has slightly higher NO_x emission than petrodiesel, due to oxygen content in the biodiesel which is about 11-12 wt. %.
- Biodiesel has an inverse relationship of oxidation stability with its low temperature properties, for example, cloud point and pour point.

2.3.2. Alternative methods for biodiesel production

In the 1900s, with the development of the diesel engine, vegetable oils were used directly as a fuel, but there are many problems related to this action. As mentioned above (see section 2.3.1), the viscosities of vegetable oils are 10−20 times higher than that in modern diesel fuel. Many methods have been investigated to develop the properties of renewable oils for use as a fuel in diesel engines. These methods include dilution, microemulsions, pyrolysis (thermal cracking), transesterification (alcoholysis) and two-step non-catalytic methods (hydrolysis and esterification). The purpose of these methods is to reduce the viscosity of vegetable oils. The most preferred choice is transesterification; a reaction that replaces the glycerol structure in oils (triglycerides) with a short-chain alcohol to produce fatty acid esters (biodiesel) and glycerol as by-product (Pinnarat and Savage, 2008). The transesterification and two-step non-catalytic methods will be discussed in detail in the following sections 2.3.2.1 and 2.3.2.2, respectively.

Pyrolysis (thermal cracking) method can be defined as conversion of one substance into another by heat with or without the aid of a catalyst (Sonntag, 1979c). It involves heating of the oils in the absence of air or oxygen. The removal of oxygen during thermal cracking process produces some low value materials and more gasoline than biodiesel (Fangrui and Hanna, 1999). Moreover, pyrolytic chemistry is difficult to describe because there are variety of reaction paths that can occur yielding a variety of products. The pyrolysis of fats has been considered for more than a century, particularly in those areas of the world that lack petroleum resources (Sonntag, 1979c). The pyrolysed materials are varied from vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids (Demirbas, 2009).

The dilution method is a method where solvents are used with vegetable oils in order to reduce their viscosity. The viscosity of the oils can be lowered by blending with methanol or petrodiesel. However, the majority of previous studies have suggested that blending vegetable oils with petrodiesel was not applicable for long term direct injection into a diesel engine (Demirbas, 2009, Dunn, 2005). The main engine problems with the dilution method are injector coking and carbon deposition (Fangrui and Hanna, 1999).

In the microemulsion or co-solvent blend method, the formation of *hybrid* diesel fuels by mixing with a low molecular weight alcohol or a short chain alcohol, such as ethanol or methanol, is another approach for reducing the viscosity of vegetable oils. These alcohols have a limited solubility in non-polar vegetable oils and as a result, amphiphilic compounds are added to increase the solubility, dilute the oil and reduce the viscosity (Dunn, 2005, Schwab et al., 1987). 2-octanol was found as an effective amphiphile in the micellar solubilisation of methanol in triolein and soybean oil. (Fangrui and Hanna, 1999, Ziejewski et al., 1984). However, Ziejewski et al,.(1984) stated that the major problem with microemulsions was the incomplete combustion at low load engine operation.

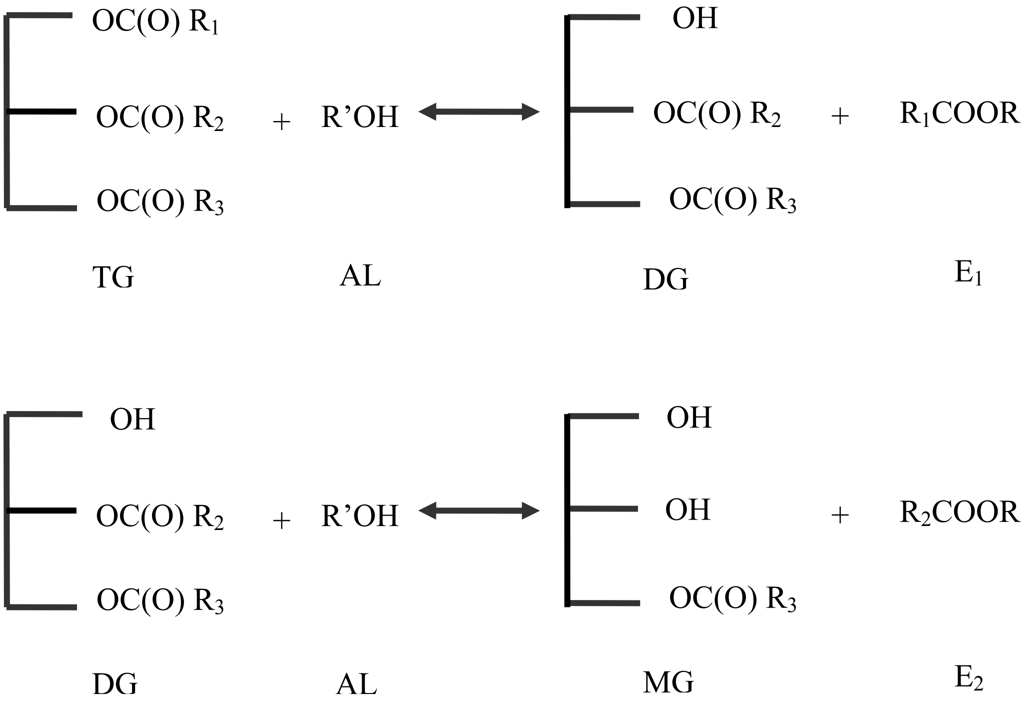
Biodiesel can be produced by either catalysed or non-catalysed transesterification or two-step non-catalytic reactions. Both methods require chemical reactions and a certain amount of alcohol to convert the raw materials to biodiesel. The raw materials for transesterification and two-step non-catalytic methods are vegetable oils/animal fats and vegetable oils/animal fats with water, respectively, in addition to alcohols. In the following sections the full details of the catalytic and non-catalytic transesification methods and two-step non-catalytic methods are discussed.

2.3.2.1. Transesterification methods

(see chapter 6 for detailed discussion of biodiesel process variables)

For the last several years, the transesterification of vegetable oils to produce esters, and in particularly methyl esters, has drawn special attention. In Europe, environmental concerns and agriculture considerations have resulted in the construction of several fuel FAME plants, in 1998 the largest was in Italy and it had a capacity of 250,000 tons per day (Boocock et al., 1998). The transesterification (alcoholysis) reactions are carried out with catalytic or non-catalytic processes using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms (Demirbas, 2009). Sharma at.el., (2008) have described the transesterification process as the most employed process at present for biodiesel production. The process reduces the viscosity of vegetable oils and improves other characteristics such as engine performance. The alcohols used in the transesterification reactions are methanol,

ethanol, propanol, butanol and amyl alcohol, with methanol and ethanol being the most frequently used (Demirbas, 2003). The differences between the two types of alcohols (solvents) and the effect of the amount of alcohol in the transesterification reactions are illustrated in section 6.3.2.4. Since transesterification reactions are reversible, an excess amount of alcohol is always recommended to shift the reactions forward to the product side. The transesterification reactions are similar in behaviour as the hydrolysis reactions stated in section 2.1.5. However, in transesterification reactions alcohol is used instead of water (Srivastava and Prasad, 2000). The transesterification reaction consists of a sequence of three consecutive reversible reactions where alcohol (AL) and triglycerides (TG) are converted to diglycerides (DG), and then DG are converted to monoglycerides (MG), and finally conversion of MG to glycerol (G) and esters (E). In each step an ester is liberated and so three E molecules are produced from one molecule of TG. Typical transesterification reactions are shown in Figure 2-12.



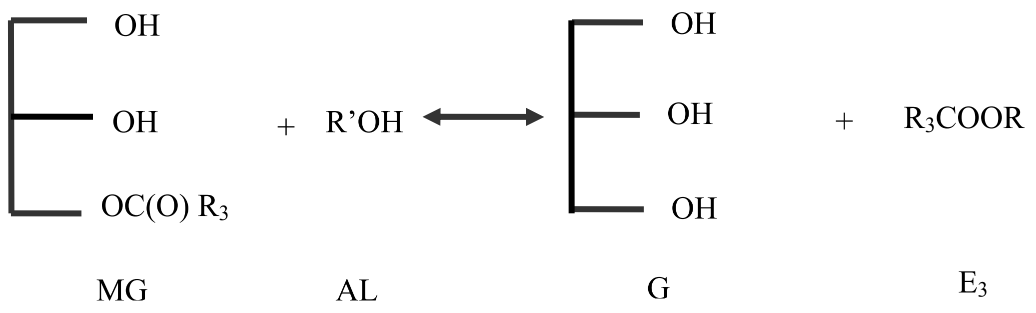


Figure 2-12. Typical transesterification reactions of vegetable oils/animal fats.

There are two main approaches the transesterification reaction; either catalytic transesterification (see chapter 6) or non-catalytic transesterification at supercritical conditions. Transesterification reactions of oils/fats which are non-polar molecules with alcohols, which are polar molecules, are usually heterogeneous (two liquid phases). The reactions at conventional ambient conditions of pressure and temperature are incomplete because of the immiscibility of the nonpolar and polar components. With the help of supercritical conditions, the mixture becomes a single homogeneous phase, which will accelerate the reaction rate because there is no interphase mass transfer to limit the reaction rate (Pinnarat and Savage, 2008). Higher temperatures can offer faster reaction rates, however this necessitates the use of pressurised vessels. In conventional transesterification reactions of vegetable oils/animal fats, the presence of FFA and residual water causes problems. These are responsible for soap formation, consumption of the catalyst and a reduction in catalyst effectiveness which eventually results in a low yield of biodiesel (Komers et al., 2001). Moreover, the separation of catalyst from the final product is not an easy task, and consequently, creates an extra cost to the process (Demirbas, 2003). The catalyst can not be recovered from the waste.

Table 2-8 summarises the most favourable reaction conditions of the supercritical method with different feedstocks. A 96 % yield of biodiesel can be achieved within 26.7 min reaction time. Although, supercritical method possesses some advantages, there are also disadvantages. Almost all authors utilised a high molar ratio of alcohol, which creates difficulties in consumption and in separation of the excess alcohol from the biodiesel for its recovery and reuse. Other drawbacks are the severe reaction conditions which require high energy consumptions and the high capital cost of equipment (Pinnarat and Savage, 2008).

Table 2-8. Reaction conditions with yields for supercritical non-catalytic transesterification reactions.

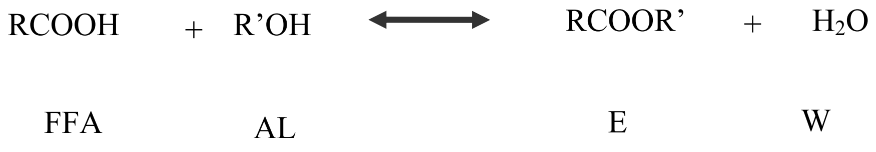
Type of oil	*Temperature (^0C); Pressure (MPa)*	*Reaction time (min)*	*Alcohol:oil molar ratio*	*Yield (%)*	*References*
Sunflower oil	252; 24.0	26.7	41:1	96	(Demirbas, 2007a)
Sunflower oil	350; 20.0	40.0	40:1	96	(Madras et al., 2004)
Soybean oil	310.0; 35.0	25.0	40:1	77	(He et al., 2007b)
Soybean oil	280.0; 25.0	30.0	42:1	90	(He et al., 2007a)
Rapeseed oil	380.0; 20.0	15.0	42:1	85	(Minami and Saka, 2006)
Soybean oil	235.0; 6.2	600.0	27:1	85	(Diasakou et al., 1998)

2.3.2.2. Two-step non-catalytic methods

(*See chapter 5 for detailed discussion of alkyl esterification process variables)*

An alternative to the single step supercritical non-catalytic biodiesel process is the two-step process without a catalyst. As the name suggests, this process involves two-steps of chemical reactions. The first-step is the hydrolysis of the fats/oils induced by subcritical water which converts the triglycerides to FFA and glycerol. The second-step is the alkyl esterification of the FFA in supercritical alcohol to produce the alkyl ester (biodiesel). These hydrolysis reactions have been fully discussed in section 2.1.5.

In between the two-steps, the reaction mixture from the hydrolysis reactions contains of two layers: the upper layer is FFA and the lower layer is an aqueous solution of glycerol, which are separated by gravity. The alkyl esterification can make the reaction reach completion more easily. In this reaction, Free Fatty acids (FFA) reacts with Alcohol (AL) to generate Esters (E) and water (W) as by-product as shown in Figure 2-13.



$$\underset{\text{FFA}}{\text{RCOOH}} + \underset{\text{AL}}{\text{R'OH}} \longleftrightarrow \underset{\text{E}}{\text{RCOOR'}} + \underset{\text{W}}{H_2O}$$

Figure 2-13. Alkyl esterification reaction of FFA and alcohol.

This two-step process was suggested by Kusdiana and Saka (2004). It offers the same advantages as the direct transesterification in supercritical alcohol but has added advantages that it can be carried out at lower operating conditions, which can reduce the cost of production. Moreover, the alkyl esterification of FFA, has a faster reaction rate than the transesterification of triglycerides under the same operation conditions (Warabi et al., 2004). The biodiesel produced by this method has no intermediate products, for example MG, DG, and by-product, G, from the ester formation step since these compounds have been removed after hydrolysis reactions stage.

Pinnarat and Savage (2008) stated that from the scientific point of view, there were many items that remain unknown about the non-catalytic synthesis of biodiesel. The reaction kinetics and mechanism have not yet been sufficiently understood. The phase behaviour of supercritical non-catalytic methods is also an important issue. Moreover, the kinetics of free fatty acid esterification and biodiesel process variables have not been yet fully solved (Sendzikiene et al., 2004, Slinn, 2008).

2.3.3. Production and production cost

In the European Union (E.U), biodiesel is considered the most important biofuel, which comprises 80 % of the total biofuel production in Europe (Demirbas, 2007b). The production of biodiesel in the E.U. uses around 1.4 million hectares of arable land. There are approximately 40 biodiesel plants in the E.U. and the number of plants and their production capacities are growing quickly (Bozbas, 2008). Figure 2-14 shows the biodiesel production of the E.U. (1993–2005). There is a large increase in biodiesel production from 2002 to 2005. Within the E.U, Germany leads the production of biodiesel by about 35 % followed by France and Italy (see Table 2-9). In Germany, biodiesel production capacity rose to 1,060 kilo-tonns in 2004 and sales reached 1,000 kilo-tonns in 1800 filling stations. Until 2004, Germany used pure biodiesel predominantly after which it started mixing biodiesel with petrodiesel

(Bozbas, 2008). The E.U. produced nearly 89 % of all biodiesel production worldwide in 2005, and Germany produced more than half of the total world production.

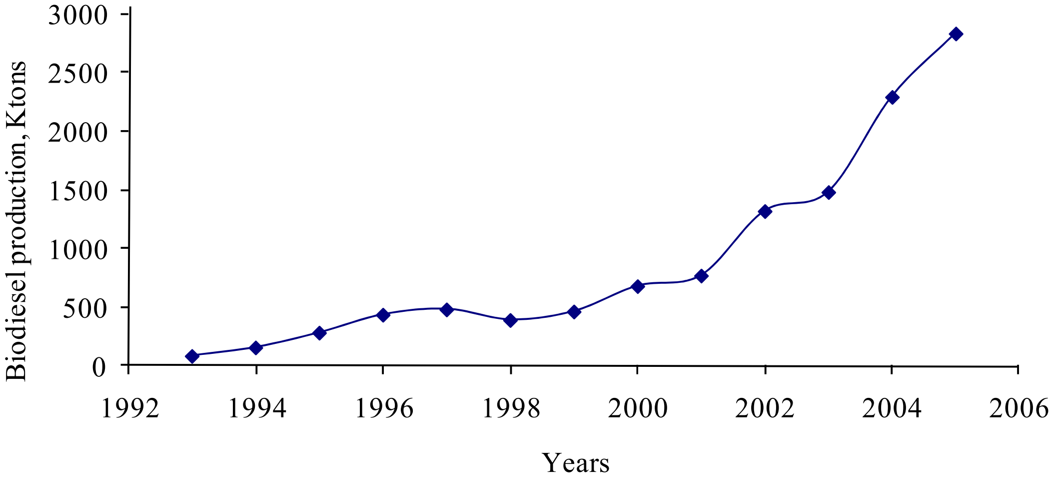


Figure 2-14. Biodiesel production in the E.U (Demirbas, 2009).

Table 2-9. E U biodiesel production capacity in 2008 (EBB, 2010).

Country	*Ktons*
Germany	2,819
France	1,815
Italy	595
Belgium	277
Poland	275
Portugal	268
Denmark/Sweden	231
Austria	213
Spain	207
UK	192

Slovakia	146
Greece	107
Hungary	105
Czech Rep.	104
The Netherlands	101
Finland	85
Lithuania	66
Romania	65
Latvia	30
Ireland	24
Bulgaria	11
Cyprus	9
Slovenia	9

The price of biodiesel is more than double the price of petrodiesel. The cost of feedstocks, labour, methanol and catalyst contribute about 80 % of total production cost, however, the cost of feedstocks is considered as the major economic factor with respect to the input costs of biodiesel production. In most oilseed-producing countries, biodiesel is commercialised. In these countries, such as Germany, the price of biodiesel in the filling stations is cheaper than conventional petrodiesel, because biodiesel is exempted from tax (Amigun et al., 2008, Bozbas, 2008, Demirbas, 2007b). There are many factors effecting the cost of biodiesel fuels for example, the base stock, geographic area, variability in crop production from season to season and the price of crude petroleum (Demirbas, 2009).

2.3.4. Biodiesel policy

If biodiesel is potentially used for energy supply, it would be beneficial for the environment and the local population. Demirbas (2003), concluded that with the increase in the price of petroleum and uncertainties of its long term availabilities, there is special interest in vegetable oils for diesel engines as a renewable resource. In February 2006, the E.U. has set the target of achieving 5.75 % of transportation fuel demand from biofuel by 2010. In light of this, various policy initiatives have been adopted such as the regulation for using biodiesel mandatory in Germany, Italy, France, Austria and Sweden (Demirbas, 2007b). A fuel taxation approach is the most reasonable method to make biodiesel competitive against petrodiesel fuel. If tax concessions are considered, biodiesel would be economically viable with that of petrodiesel. As a result, the accomplishment of biodiesel target depends on government support. Currently, the UK government reduces the tax of biodiesel by 20p/litre over that of petro-diesel. In 2007, the UK government removed the tax for biodiesel producers that had a production rate under 2500 litres/year (Slinn, 2008). This offer promoted biodiesel production for personal consumption and for small and medium producers. However, this action forced a rise in price of the vegetable oils which forced some of the small and medium producers out of business. The large oil collector companies that have the power over the raw material (vegetable oil) are succeeding in this new industry.

2.4. Downflow Gas contactor Reactor (DGCR)

2.4.1. Introduction to DGCR

In many industrial applications, there are a number of processes where contacting between phases and within the same phase (with reference to gases, liquids and solids) is essential for high-value-added products. Some of these applications include the upgrading and conversion of petroleum feed stocks and intermediates and the manufacture of pharmaceuticals, in particular certain chemicals, and processes in the production of polymers.

A series of experiments with biodiesel using a DGCR were carried out at WRK Design and Services. WRK is a chemical engineering consultancy established in 2002, expertise in contract research & development, pilot plant studies and technology transfer.

The name of the DGCR was developed from the Cocurrent Downflow Contactor Reactor (CDCR). The DGCR is operated in batch mode with recycle loop. The DGCR is a novel mass transfer and reaction device and one of the most powerful available; the system which may or may not contain a solid. The idea of the DGCR was originally revealed by Boyes and Ellis (Boyes and Ellis, 1976), with the objective of designing a contactor with a high absorption and high reaction rate. It has been reported that the DGCR was used in the past for several chemical reaction industrial processes, such as slurry and fixed bed catalytic hydrogenation of soybean and rapeseed oils, and also in mass transfer studies of gas adsorption (Boyes et al., 1992, Boyes et al., 1995, Chughtai, 1993, Lu, 1988). More recently, DCCR has been shown to be very efficient in the treatment of wastewater, which contains persistent pollutants (Ochuma et al., 2007a, Ochuma et al., 2007c). Moreover, it is still used in improving the hydrogenation of vegetable oils (triglyceride) of soybean oil (Fishwick et al., 2007, Winterbottom et al., 1999, Winterbottom et al., 2000). Boyes et al. (1992) and other authors (Fishwick et al., 2007, Kulkarni et al., 2005) have reported that the mass transfer performance and selectivity of the DGCR, compared to a Continuous Stirring Tank Reactor (CSTR) and trickle bed reactors, have been shown to be superior. In general, the high velocity of the reactant mixture causing a submerged jet that subsequently attains the reactant mixture to disperse in the top of the column. Then, the level of dispersion is expending down of the column to reach a disengagement point where the dispersion occurs freely.

The DGCR consists of a single column made of glass or stainless steel (Boyes et al., 1995). A diagram of the DGCR can be seen in Figure 2-15. The dimensions and configuration of the column depend on the operating conditions, for example, pressure, temperature and flow rate. The concept of the DGCR was derived from the theory of contacting liquids continuum and a dispersed phase. The DGCR can be applied to many industrial applications which use contacting liquids or a gas/liquids continuum and dispersion phase. A powerful shearing of the diffuse phase is introduced, with a minimum expenditure of energy over that required for motive power. A DGCR is a small container in volume; however, there is an enormous interfacial area generated of dispersed gas in liquid or liquid in liquid. All this can be obtained by exploiting a controlled hydrodynamic regime. The system does not require mechanical stirring and a pump is the only mechanical device employed to create a high velocity fluid flow. Moreover, there are no baffles fixed on the walls of the DGCR to cause the pressure to drop.

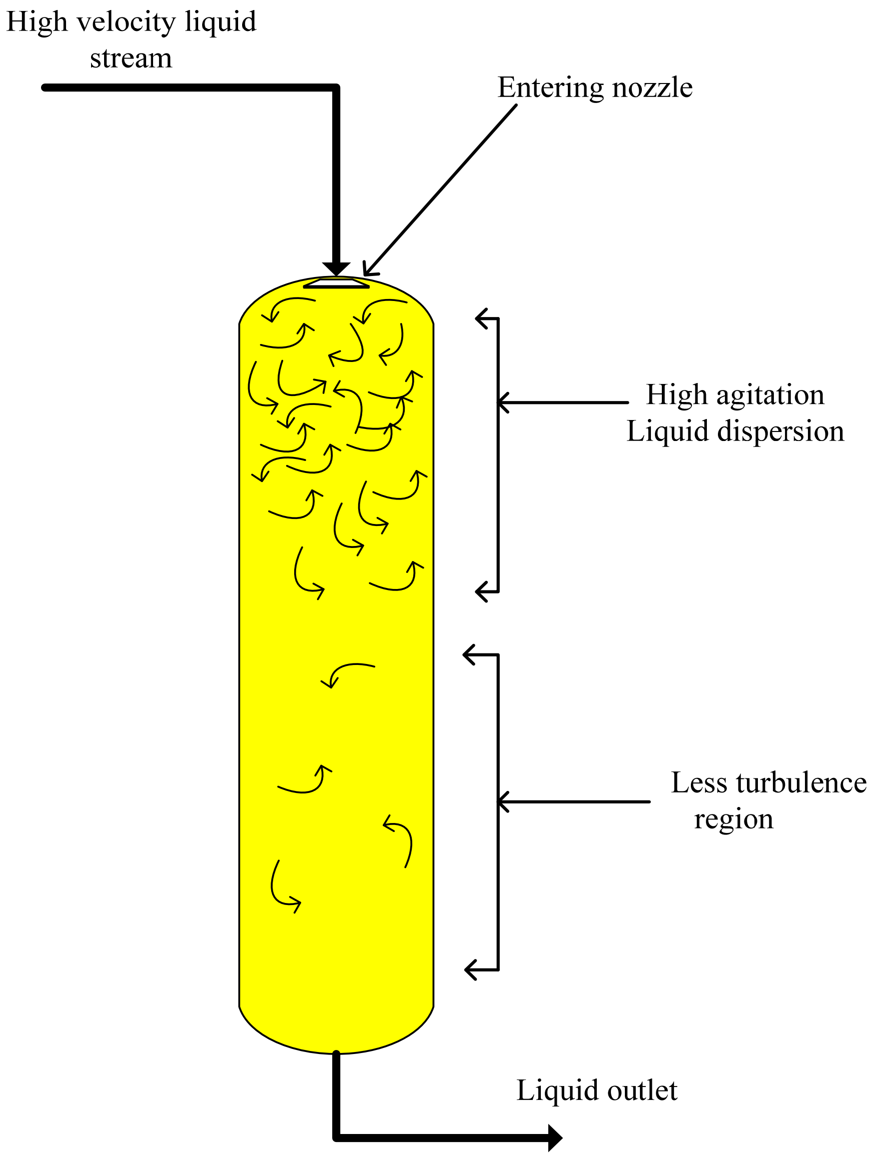


Figure 2-15. Diagram of the DGCR column.

Swirl flow or a tangential inlet to the DCDR column was developed by Boyes (1989) in order to further enhance mass transfer in the column. In swirl flow, part of the liquid or liquid-gas stream is fed into the column via a tangential inlet to produce a greater degree of turbulence in the middle of the column, leading to an increase in the mass transfer at this point. The addition of swirl flow has been shown to enhance mass transfer by 4 to 5 times (Boyes et al., 1992).

2.4.2. Theory of DGCR

Knowledge of the transport parameters and fluid dynamics is a vital issue for the development of appropriate reactor models and scale-up rules. The state-of-the-art of the phenomena occurring in the DGCR transport parameters and fluid dynamics has been reviewed by many authors (Boyes, 1989, Boyes et al., 1992, Boyes et al., 1995, Fishwick et al., 2007, Ochuma et al., 2007b, Winterbottom et al., 1999).

The DGCR is composed of a centrally mounted straight column with an orifice in its inlet top part. The continuous liquid phases enter the column at the top through a defined orifice into a fully flooded column. The kinetic energy (pump mechanical component) of the liquid jet entering the column produces forceful turbulence and a fluid motion, which afterwards attains rapid surface renewal and high efficiency mass transfer between the phases of the liquids. This results from the high velocity of the liquids' jet stream which generates powerful shear and energy, causing a vigorous agitation in the liquids' stream dispersion in the upper part of the column. The inlet geometry is necessary in order to obtain the appropriate high velocity (Khan, 1995). In this case, the turbulence between the reactants in the mixture of liquids introduces the dispersion. The dispersion liquid then slowly moves down the fully flooded column and the level of the dispersion can be controlled by manipulating the operating conditions of the system, such as the column inlet flow rate and the dimensions of the orifice. The centrifugal pump also contributes in the shear of the reactant liquids.

2.4.3. The interfacial area

Contactor reactors are easy to use, but their design relies upon the process requirements and the operating conditions to be used. However, among these reactors the liquid jet recycle reactor is the most often recommended technique because it allows direct liquid-liquid contact (Hanna and Noble, 1985, Zhong et al., 1998). Reactions which occur at the interfacial area between two liquids are of essential and fundamental significance. The interface between any two liquids is an exceptional environment, affected by electrical, structural, and dynamic properties which are only now beginning to be studied in great detail (Benjamin, 1997). Moreover, many important phenomena in chemistry and biology involve processes which occur at the interface between two liquids (Benjamin, 1997). The mechanisms and kinetic control of many reactions at liquid-liquid interfaces have not been established. The interfacial area is the available area which describes the interfacial transfer of mass, momentum and energy, and is a crucial parameter in a two-fluid model formulation (Hibiki et al., 2006). As mentioned by Hibiki (2006), although many trials have been made to measure the interfacial concentration, the available findings are limited to applicability and accuracy.

2.4.4. Advantages and disadvantages of DGCR

The DGCR possesses a number of distinctive advantages over conventional multiphase contactors (CSTR, packed column and trickle bed reactor). Many authors (Boyes et al., 1992, Boyes et al., 1995, Khan, 1995, Lu et al., 1994, Winterbottom et al., 2000) have listed the main advantages which include:

- No moving parts (stirring) in the column and therefore lower maintenance cost.
- Very high mass transfer efficiency.
- Simplicity of design and construction of the whole system.
- Very low pressures drop since no baffles are used and no flooding results.
- Easy up-scaling without much loss in mass transfer efficiency.
- Lower power consumption.
- Smaller operating volume, promising lower capital and operating costs.
- No sealing problems, due to the absence of any moving parts (stirrer).
- Can be used with precious metal catalysts, such as platinum and ruthenium without heavy losses.
- Suitable for slurry chemical reactions because of its tolerance toward particalte materials though the aid of a centrifugal pump.
- Portability from one place to other.

Although DGCR possesses these many advantages over other reactors, it has certain disadvantages, the main ones being listed below;

- The system is sensitive to the flow rate because of the strong influence of the hydrodynamic regimes (inlet liquid jet).
- The system investigated in the present study requires a long time more that two hours to reach 50 ^{o}C, because the heating media was oil and the reservoir was made glass. This gives poor heat transfer from the heating media oil to the reactant in the reservoir (see Figure 6-3). This limitation can be overcome by fixing a heating coil in the reservoir.
- It is hard to control the temperature inside the column (reactor).

The DGCR was used in this work to manufacture biodiesel though the reactions of sunflower oil with alcohols (methanol/ethanol) in the presence of catalyst (NaOH). The details of the design and experimental set-up are detailed in (section 6.2).

CHAPTER 3

CONTINUOUS FLOW HYDROLYSIS OF SUNFLOWER OIL WITH SUBCRITICAL WATER FOR BIODIESEL PRODUCTION[2]

3.1. Overview of vegetable oils/animal fats hydrolysis

3.1.1. Introduction

Biodiesel can be produced through transesterification of triglycerides with methanol. Most transesterification methods use alkali catalysts which lead to the production of undesirable saponified products as the FFA react with the catalyst.

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[2] This research has been published in Energy Source Part A-Recovery Utilization and Environmental Effects, 32 :(5): 1-8, 2010.

These require sophisticated purification steps and result in a lower yield of the desirable Fatty Acid Methyl Esters (FAME; biodiesel). Some researchers (Granados et al., 2007, Izci and Bodur, 2007) have proposed an acid-catalysed method coupled with an alkali catalyst process to overcome these disadvantages, but it is advantageous to develop an entirely catalyst free process to eliminate down stream separation of the catalyst and improve process economics. Kusdiana and Saka (2004), have developed a catalyst-free two step process for high-quality biodiesel production from oils and fats. The process firstly uses subcritical water to hydrolyse triglycerides to FFA followed by a methyl esterification step to FAME using supercritical methanol without any catalyst. In addition to the use in the production of biodiesel, FFA and glycerol are important raw materials for soap production, synthetic detergents, greases and cosmetics (lawrence, 1954).

Water in the sub or supercritical state (see Figure 3-1) provides unique properties over water at room temperature 25 ^{o}C and at ambient pressure 0.1 MPa. The two distinct advantages of subcritical water are its relatively low dielectric constant and large ion products (see section 2.2.1.1). The dielectric constant of subcritical water (10 to 20 MPa, 270 to 350 ^{o}C) is comparable to that of acetone or methanol at ambient conditions and can be adjusted from a value of 80 to 5 F/m at its critical point, which makes it a good solvent for organic compounds (Holliday et al., 1997). Many studies have been undertaken to explore the use of water near its critical condition (374 ºC, 22.1 MPa) to eliminate organic solvents in synthesis reactions (Ackelsberg, 1958, Lascaray, 1952, Patil et al., 1988, Pinto and Lancas, 2006). In the hydrolysis of triglycerides subcritical water has been shown to act as both a solvent and a reagent (Patil et al., 1988, Pinto and Lancas, 2006).

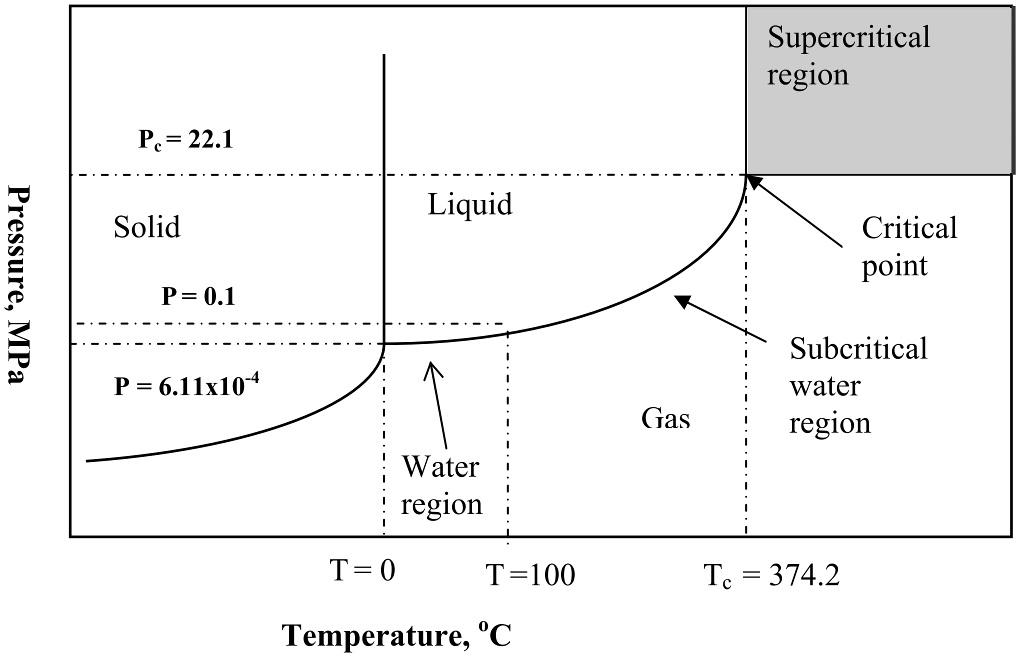

Figure 3-1. Ambient water, sub- and supercritical water regions diagram

The hydrolysis reactions shown in Figure 3-2 occurs as three stepwise reactions: (1) triglyceride (TG) is hydrolyzed to diglycerides (DG), (2) DG is hydrolyzed to monoglycerides (MG), (3) MG is hydrolyzed to glycerol (G), and in each step there is a production of a FFA. These reactions are a homogenous first order reversible reaction in the oily phase (Ackelsberg, 1958). It has been shown that FFA itself can act as an acid catalyst in the hydrolysis reaction of oil in subcritical water and can achieve up to 90 wt.% FFA without employing a catalyst (Minami and Saka, 2006). This non-catalytic reaction prevents the need to remove the catalyst from the final product which is technically difficult and decreases the production cost of biodiesel (Demirbas, 2003).

$$\begin{array}{llcll}
C_3H_8\,(OOCR)_3 & +\ H_2O & \longleftrightarrow & C_3H_8\,(OH).(OOCR)_2 & +\ RCOOH \\
\text{TG} & \text{water} & & \text{DG} & \text{FFA} \\
C_3H_8\,(OH).(OOCR)_2 & +\ H_2O & \longleftrightarrow & C_3H_8\,(OH)_2.\,(OOCR) & +\ RCOOH \\
\text{DG} & \text{water} & & \text{MG} & \text{FFA} \\
C_3H_8\,(OH)_2.(OOCR) & +\ H_2O & \longleftrightarrow & C_3H_5(OH)_3 & +\ RCOOH \\
\text{MG} & \text{water} & & \text{G} & \text{FFA}
\end{array}$$

Figure 3-2. Hydrolysis reactions of vegetable oils/animal fats.

Biodiesel can be prepared from numerous sources of vegetable oils, animal fats and waste greases. Researchers have reported the use of linseed oil, castor oil rapeseed (Varma and Madras, 2007) and sunflower oil (Granados et al., 2007) as oil sources; however, the data available for sunflower oil is focused on catalytic transesterification (as is the majority of the work for other oils) and data for catalyst-free subcritical water processing are unreported. This chapter investigates continuous flow hydrolysis of sunflower oil using subcritical water as a route to FFA for biodiesel production. A non-catalytic continuous flow process was investigated between 10 to 20 MPa, 270 to 350 °C for two volume percent mixtures of water and oil (50:50 and 80:20). The factors affecting the yield and rate of reaction were studied.

3.2. Materials and methods

The aims of this section are to give the reader a list of all materials consumed during the course of this study and to explain the details of the methods used to produce those results outlined in the proceeding section. Also, this section intends to show the progression of the experimental methods which is required to gain the understanding of the natural oil hydrolysis process.

3.2.1. Materials used `

3.2.1.1. Gases

The gases used throughout the present study were supplied by the British Oxygen Company (BOC) UK, as follows:

- Helium, Purity 99.99%.
- Hydrogen, Purity 99.95%.

3.2.1.2. Reagents

The chemical materials used are listed below in Table 3-1. Distilled and deionised water was used to prevent scaling on the walls of the tubular reactor and ancillary piping from salt deposition at the reaction conditions. All the chemicals used in the experiments were of reagent grade or higher and were used as received, without any purification. Deionised water was used to prepare all the chemical solutions.

Table 3-1. A list of chemical materials used.

Material	***Cas number***	***Grade***	***Supplier***
Ethanol (99.9 %)	64-17-5	A.R	Fisher
Sodium hydroxide	1310-73-2	A.R	Fisher
Chloroform (99.9 %)	67-66-3	A.R	Fisher
Phenolphthalein	77-09-8	A.R	Hopkin & Williams Ltd (UK)
Sunflower oil	8001-21-6	A.R	leading supermarket chain (U.K)
Hexamethyldisilazane	999-97-3	A.R	Sigma-Aldrich
Palmitic acid (99 %)	57-10-3	G.C.	Sigma-Aldrich
Stearic acid	57-11-4	G.C.	Sigma-Aldrich
Oleic acid (99 %)	112-80-1	G.C.	Sigma-Aldrich
Linoleic acid (99 %)	60-33-3	G.C.	Sigma-Aldrich
Heptadecanoic acid (98 %)	506-12-7	G.C.	Sigma-Aldrich

The sunflower oil was obtained from a leading supermarket chain in U. K. and supplied in gallon batches. Although no specific composition was explained for each batch of sunflower oil, a general composition for the sunflower oil analysed by GC was 77% triglycerides; 20% diglycerides; 2.5% monoglycerides; 0.3 to 0.5% FFA. The fatty acid distribution with their molecular weight, melting point and formula of the sunflower oil can be seen in Table 3-2 (Berrios et al., 2007). The short name is expressed in Cx:y where x is the number of carbon atoms and y is the number of the double bounds.

Table 3-2. Fatty acid composition of sunflower oil.

Name	***Short name***	***% W/W***	***Formula***	***M. wt. (g/mol)***	***M.P. (^oC)***
Palmitic acid	C16:0	6	$CH_3(CH_2)_{14}COOH$	256.43	62.9
Stearic acid	C18:0	3	$CH_3(CH_2)_{16}COOH$	284.48	70.1
Oleic acid	C18:1	17	$C_{17}H_{33}COOH$	282.47	14.0
Linoleic acid	C18:2	72	$C_{17}H_{31}COOH$	280.46	-5.0

3.2.2. Apparatus and methods

3.2.2.1. Experimental equipment

The hydrolysis of sunflower oil was carried out in PFR which had a total reactor volume of 6 x10^{-5} m^3. The items of equipment used are listed below:

- Two HPLC pumps: type 350, Gilson
- Dynamic mixer: type 811C, Gilson
- Muffle furnace: size 3, Gallenkamp, maximum 1100 ^oC
- A reactor: stainless steel tubing of 4.56 x10^{-3} m i.d and 4.0 m length, resulting in a volume of about 6 x10^{-5} m^3
- Coiling unit: Grant instrument Cambridge, type LTD 20G
- Butterfly valves: stainless steel Swagelok
- Needle valve : stainless steel Hoke
- Pressure gauges with transmitter: Druck, maximum 70 MPa
- Thermocouple: 12 way selection unit, K-type
- Glass feed column: Pyrex with volume of 250 ml

- Stainless steel pipe connections: 6x10^{-3} m o.d. and 1.5x10^{-3}m. with thickness of 1 x10^{-3} m and 0.25 x10^{-3} m, thus giving i.d. of 4 x10^{-3} and 1 x10^{-3}m, respectively.
- Plastic hoses: flexible plastic hoses with 3 x10^{-3} m o.d.
- Gas Chromatography: GC (6890A) with film ionisation detector (FID)
- Burette: volume of 25 x10^{-5} m^3 made from Pyrex , B-grade
- Heating element: Lab-Line Plaza, made from Lab-Line Instrument.
- Balances: Adventure-Ohus AR-2140 (accuracy 0.0001 g) and Metter-Toledo (accuracy 0.01 g).
- Rheometer: viscosity meter (TA-1000).
- Density meter: Anton Paar (DMA-35N)). Range: 0 to 1999 Kg/m^3, temperature: 0 to 40 °C.
- pH meter: Mettler Toledo (GMBH-8603). Range: -2 to 19.99, temperature: -30 to 130 °C. Accuracy: ± 0.01

3.2.2.2. Experimental methods

Figure 3-3 shows the laboratory–scale setup of the equipment used for the hydrolysis of sunflower oil under continuous flow conditions. In this system, sunflower oil and distillate water were separately fed by two HPLC pumps from the reservoir columns as seen in Figure 3-4. The solution then passed through an up-stream static mixer in order to mix the oil and water prior to the entering the tubular reactor coil. The dosage pumps were adjusted by push button switches to give the desired volumetric water:oil ratios. As the reaction conditions were not in the supercritical water region, the reactor was made from stainless steel 316 tubing. The tubular coil reactor was housed in an electrical furnace as shown in Figure 3-5. The pressure in the reactor was controlled by a back pressure regulator valve. In this way, the temperature and the pressure inside the reactor coil were continuously maintained at desired operational conditions. The reaction time *t (min)*, was calculated by dividing the volume of the reactor V (cm^3) by the total volumetric flow rate of the oil and water at the experimental conditions using Equation 3-1 (Minami and Saka, 2006):

$$t = \frac{V}{F_w(\frac{\rho_w}{\rho_w'}) + F_o(\frac{\rho_o}{\rho_o'})}$$

Equation 3-1

where F_w, is the set flow-rate of water (cm^3/min). ρ_w and ρ_w' are the densities (g/cm^3) of the water at the normal ambient and reaction conditions, respectively. F_o is the set flow-rate of oil (cm^3/min) and ρ_o and ρ_o' are the densities (g/cm^3) of the sunflower oil at ambient and reaction conditions, respectively and are assumed to be equal at the reaction conditions (Minami and Saka, 2006). F_w and F_o where measured at ambient conditions. Water was initially pumped through the reactor until the desired temperature was attained; which was typically no longer than an hour. Once the reactor reached a steady temperature, the oil pump was switched on to give the required dose.

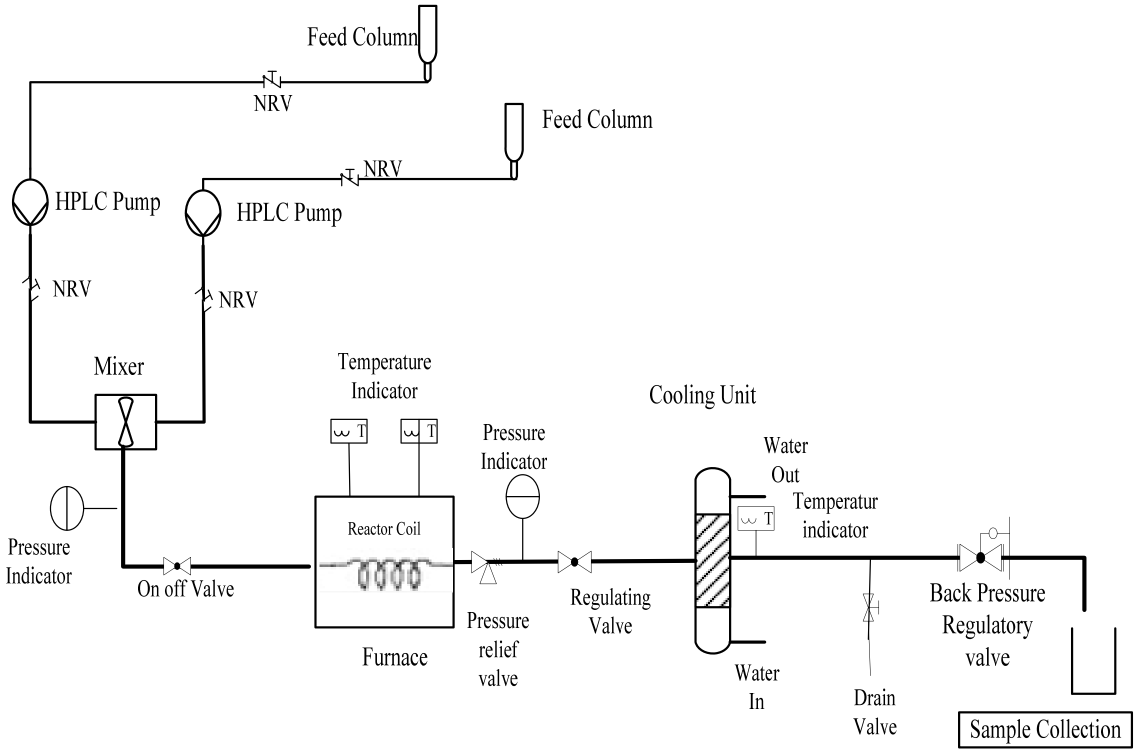

Figure 3-3. Subcritical water continuous flow hydrolysis rig.

Figure 3-4. Image showing the two HPLC pumps, a static mixer and feeding columns.

Figure 3-5. Image of tubular coil reactor housed in the electrical furnace.

The Reynolds number as shown in Equation 3-2 was calculated to be between 10 and 500, and so a plug flow system can be assumed; however, the purpose of this work is not to establish a reactor equation but to deliver an optimal yield of FFA and a kinetic expression for the hydrolysis of sunflower oil.

$$R_e = \bar{\bar{\rho}} v D / \bar{\mu} \qquad \textbf{Equation 3-2}$$

where $\bar{\bar{\rho}}$, $\bar{\mu}$ average density and viscosity, respectively. Upon leaving the reactor, the products were cooled in the cooling unit to ambient temperature. The samples were then collected at regular time intervals. These different sampling protocols were implemented in order to maximise kinetic data. The hydrolysis products as shown in Figure 3-6 were gravity-separated into two portions, the upper portion being mainly FFA, unreacted TG and intermediate compounds (DG and MG), and the lower portion, only glycerol (glycerine with water) without FFA product. In this study, only the composition of the upper oil layer was analysed by two methods (described below) to determine the total yield of FFA.

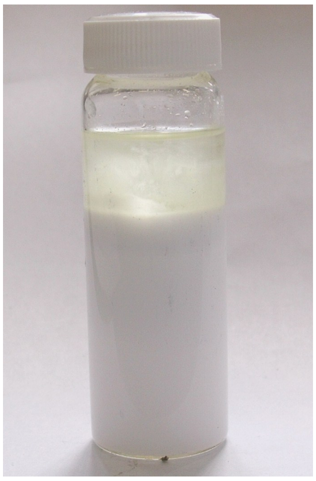

Figure 3-6. Sample of hydrolyzed sunflower oil: upper layer (FFA, TG,DG and MG) and lower layer (G and water).

3.2.2.2.1 FFA by Gas Chromatography

The concentration of FFA in the product was determined by a gas chromatography (G.C) (HP 6850A, Agilent Technologies, USA) equipped with a capillary column DB-5 (length 30 m x diameter 0.25 x10^{-3} m x film thickness 0.1µm; J&W Scientific, USA) and a flame ionization detector (FID) (340 ºC). Helium was used as the carrier gas at a constant flow (2 cm^3/min) with a split injector (340 ºC, 1:50). The oven temperature programme was 100 ºC for 3 min, 10 ºC/min to 150 ºC, 5 ºC/min to 250 ºC, 10 ºC/min to 350 ºC, with a 15-minute hold. The samples were derivatised to increase the volatility of the FFA components. These were prepared by adding 1 ml chloroform as a solvent, 10-30 mg of heptadecanoic acid as the internal standard (a C17:0 carbon chain FFA which does not naturally occur in nature) and 1 ml hexamethyldisilazane to ~100 mg of the sample. All these weights of sample and internal standard were individually recorded from a four decimal place balance

(Adventure–Ohaus AR-2140). The solution mixture was then heated in a heating block for 50 min at 70 ºC. After reacting the solution was allowed to cool to room temperature before injection of the silylated samples onto the GC column. The peak areas of all FFA components were recorded. A FFA component was identified from reference standards and its mass was calculated from a predetermined peak area response factor of the heptadecanoic acid internal standard. The total yield of FFA was determined by the addition of all FFA peaks. A typical gas chromatograph peaks used to calculate FFA content is shown in Figure 3-7. This calculated weight of FFA was then divided by the actual sample weight, to provide percentage FFA content for the samples (see Equation 3-3). This approach is consistent with Wan et al., (2007) who reported that the main FFA classes can be monitored closely with the FID method using area percentages. Injection errors were minimised by comparing the peak area of the internal standard to a predetermined set value of 99% of FFA and subsequently applying any necessary corrections to maintain quality control and assurance. This method of calculating FFA contents eliminates the error incurred by any variation in injection volumes because the peaks of FFA were always in the ratio to the peak of internal standard which was added to the sample.

$$FFA\,\% = \frac{Area\ \ of\ \ FFA\ peaks}{Area\ \ of\ \ internal\ \ standard\ \ peak}\,x\,\frac{Weight\ \ \ of\ \ \ internal\ \ \ standard}{Weight\ \ of\ \ sample}\,x100 \qquad \textbf{Equation 3-3}$$

In this study, the product yield of FFA is defining as the weight percent of FFA in the final product after removal the glycerol layer in the product mixture (Equation 3-4) as the molecular weight of oil is approximately three times the molecular weight of FFA (see Appendix 9.4) (Kusdiana and Saka, 2004, Minami and Saka, 2006).

$$Yeild\ of\ FFA\,\% = \frac{\text{Weight of FFA}}{\text{Weight of } product} x100$$ **Equation 3-4**

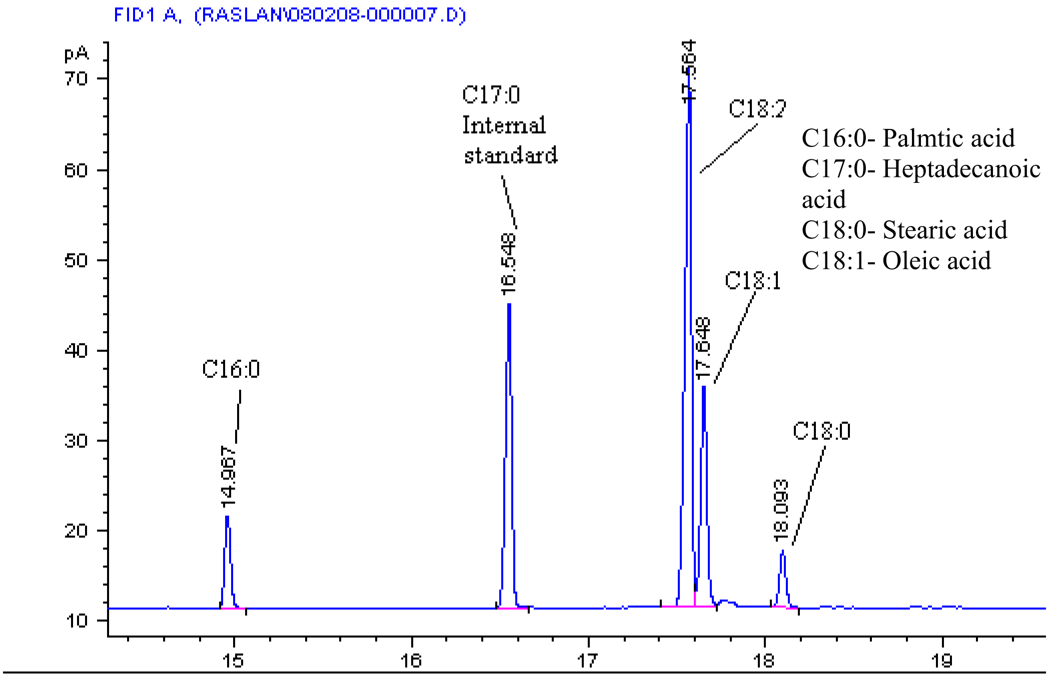

Figure 3-7. Typical chromatograph used to calculate FFA content.

3.2.2.2.2 FFA by titration

The percentage of hydrolysis is defined as the percentage weight of FFA in the sample. In order to calculate the extent of hydrolysis, an official titration method approved by the American Oil Chemist Society (Ca 5a-40) was used to determine the percentage of FFA in the collected samples (AOCS, 1998). This method can be applied to all crude and refined vegetable oils. The procedure is described as follows: 1 to 2 g of the sample was weighed, recorded and charged into a 200 ml conical flask on a two decimal balance (Mettler Toledo). 50 to 100 ml ethyl alcohol (99.9 %) was added to the sample and manually shaken until the oil had dissolved completely. In addition, 2.0 ml of phenolphthalein indicator solution was added. The phenolphthalein indicator solution was prepared by adding 1.0 g of phenolphthalein powder to 95 ml methanol and 5.0 ml of distilled water. The oil mixture was then titrated against a 0.25 N sodium hydroxide solution until a permanent pink colour persisted for at least 30 s. In order to account for error, random batches of the sodium hydroxide solution were calibrated against 99 wt. % of FFA. The weight percentage of FFA was calculated on an oleic acid basis using Equation 3-5. All samples were titrated in triplicate with a variance of < 0.5%.

$$Free\ \ fatty\ \ acids\ \ as\ \ oleic\ ,\% = \frac{ml\ \ of\ alkali\ \times N(conc\ .\ of\ \ NaOH\ ) \times 28.2}{wt\ .\ of\ \ sample} \qquad \textbf{Equation 3-5}$$

where;

$ml\, of\ \ alkali$ = volume of sodium hydroxide solution required during titration, ml.

$N(conc.\, of\ \ NaOH)$ = concentration of sodium hydroxide g/L.

$wt.\, of\ \ sample$ = weight of the sample taken, g.

In order to calculate the percentage of the FFA, the units should be weight of the FFA divided by the weight of the sample times 100. This can be done by converting the 0.25 N of the NaOH from g/ L to g/ml though divided by 1000. Now, in order to considerer the final results as a percentage, the equation should multiply by 100. So, the value of 28.2 arises from the molecular weight of oleic acid in the oil (see Table 3-2) divided by 10.0. This equation was considered sufficiently accurate to determine the degree of hydrolysis.

The agreement between GC and titration methods for analysing FFA will be discussed in section 3.3.2.

3.2.2.3. Properties of hydrolysed oil

The most common properties of the produced FFA, i.e. viscosity, density and acid value, were measured. In order to do this, the samples drawn from the reactor had two phases, as discussed previously in section 3.2.2.2. The upper layers containing mostly FFA and unreacted mono-, di- and triglycerides were removed by a dropper and measured.

3.2.2.3.1 Viscosity measurements

The rheological analysis of the FFA and sunflower oil was carried out using an AR-1000 Advanced Rheometer with controlled stress/controlled shear rate from TA Instruments (Crawley, West Sussex, UK). A sample (around 2.0 ml) of the oil or FFA was placed on the temperature controlled sample platform and analysed at 25 °C with an acrylic cone of 2° inclination (63 μm truncation) and 6×10^{-2} m diameter. A solvent trap was also used. A steady state flow-curve was gathered in a linear fashion, with a shear rate ramp from 1 to 100 s^{-1} (and 20 sample points). The viscosity was calculated as the slope of the line through data points of shear stress plotted against shear rate which was linear.

3.2.2.3.2 Density measurements

The density measurements were conducted by a Paar DMA 35 N portable inline digital reading densitometer (Atone Paar, Eastern petroleum supplies LTD.). The density meter uses a mechanical oscillator technique and a thermister to measure the temperature and density of the liquid contained within the cell. A sample of approximately 2.5 ml was injected into the apparatus. Care was taken to prevent the introduction of small air bubbles into the cell.

3.2.2.3.3 Acid value measurements

The FFA content is sometimes expressed in the literature by acid value instead of FFA content. The acid value, according to American Oil Chemical Society Cd 3d-63, Ca 5a-40 (AOCS, 1998), is defined as ‘the number of milligrams of potassium hydroxide necessary to neutralise 1.0 g of free acids sample.’ For the acid value calculation as stated by (AOCS, 1998) is expressed in terms of free fatty acid as percent of oleic, lauric, or Palmtic, multiply by 1.99, 2.81, or 2.19, respectively.

3.2.2.3.4 pH measurements

The pH of FFA was measured by using an inline digital reading pH meter (SevenMulti Modular Meter, Metttler Toledo, USA). The pH meter was calibrated with buffer solutions of pH 4, 7 and 10.

3.3. Results and discussion

3.3.1. Introduction

This section discusses the results of experiments performed to study the production of FFA in the continuous flow tubular reactor. The reactions studied were the hydrolysis of sunflower oil with distillated water. The hydrolysis reactions are commonly carried out in batch configuration system, however, the continuous flow system was proven to work in a very efficient way. The main objective of this work was to investigate the effect of various process variables, i.e. pressure (10 to 20 MPa), temperature (270 – 350 ^{o}C), reaction time (0 – 30 minutes) and the initial volume ratio of water to sunflower oil (50:50 and 80:20), in order to establish the optimal conditions for obtaining the highest yield of FFA.

3.3.2. Comparison between GC and titration methods for FFA analysis

The major fatty acids distribution in the sunflower oil were identified by GC to be palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2) which contributed to 97% of the total FFA content (Sonntag, 1979b). The comparison of concentration distribution of fatty acids measured by the silylation/GC and titration methods is shown in Figure 3-8 . Both methods compare well and give a strong correlation ($R^2 = 0.98$), though the GC tends to give higher values in particular in the 30 to 80% range. Both techniques are acceptable for determining FFA content following the subcritical water hydrolysis and certify the results with an appropriate assurance. However, silylation/GC method enables the determination of the concentration of each component in FFA, while titration method only measures the total FFA.

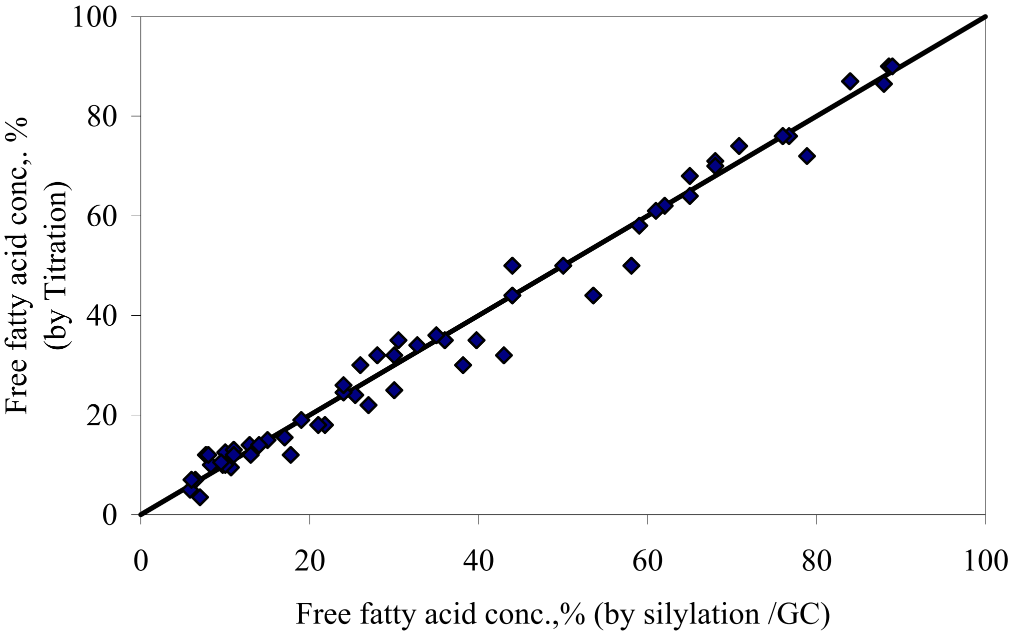

Figure 3-8. Comparison of total FFA concentration obtained by titration and GC.

Analysis of the four main fatty acids that were obtained at 300 ^{o}C, 15 MPa and 50:50 water/oil ratio are shown in Figure 3-9. There is an increase in total FFA yield as the reaction has progressed. The result shows that C18:2 is the most dominant FFA after hydrolysis reactions, followed by C18:1, C16:0 and C18:0, respectively. This result is in accordance with the percentage of FFA in the sunflower oil before hydrolysis took place as shown in Table 2-2. The percentage of each FFA is relatively constant during hydrolysis reactions and the proportion towards a particular FFA component does not vary with reaction time. The pupation for each FFA is shown in Table 3-3.

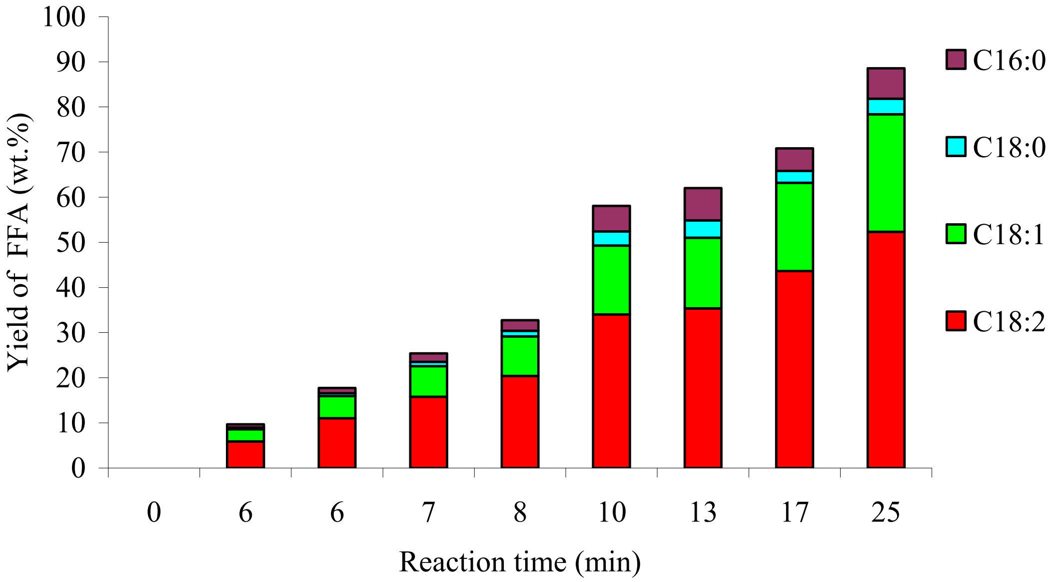

Figure 3-9. Yields of four main FFA at 15 MPa, 300 °C, and water/oil ratio 50:50 v:v%.

Table 3-3. Proportion of each FFA after hydrolysis reaction.

FFA	*Formula*	*Proportion (%)*
Palmtic acid	C16:0	7.2
Stearic acid	C18:0	3.8
Oleic acid	C18:1	27
Linoleic acid	C18:2	62

3.3.3. Effect of different process variables on the yield of FFA

In this study, four process variables were investigated to study their influence on the FFA yield; the effect of reaction pressure, the effect of reaction temperature, the effect of reaction time and the initial volume ratio of water to sunflower oil all on the FFA yield. The influence of these processes variables will be discussed in the following sections.

3.3.3.1. Effect of pressure on FFA yield

The effect of reaction pressure on the total yield of FFA can be seen in Figure 3-10. In order to determine the effect of pressure, the hydrolysis reactions were conducted between 10 and 20 MPa while keeping the temperature constant at 300 °C and a water:oil ratio of 50:50 vol%.

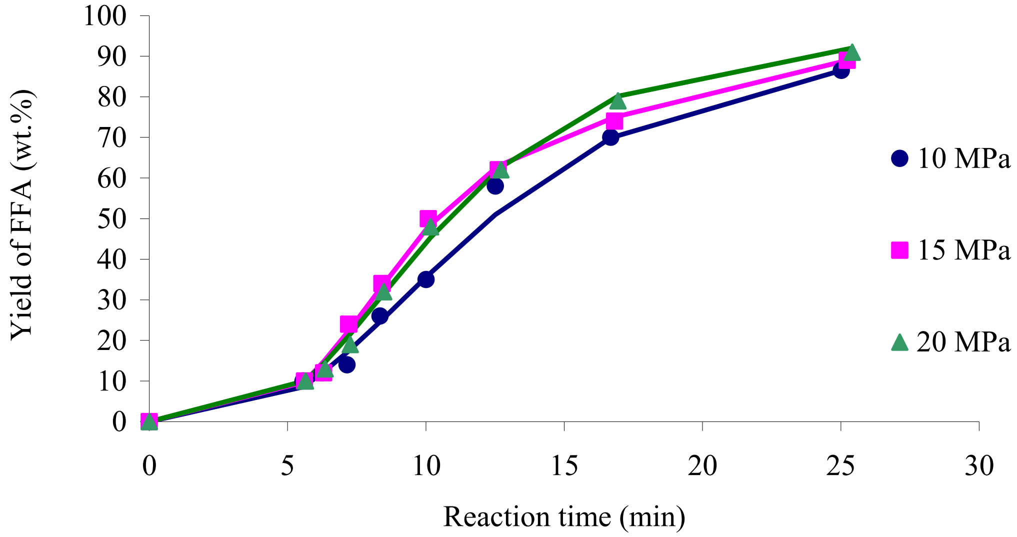

Figure 3-10. Effect of pressure in the total FFA yield at 300° C and water:oil ratio 50:50 v:v% (data points are experimental results and the lines show the best fit to the data).

It can be seen that the influence of pressure on the yield of FFA is not significant. At 10 MPa, the yield of FFA was 70 % after 17 min, while at 15 MPa the yield increased slightly to 75%. As the pressure rose to 20 MPa the yield of FFA increased to 80% at the same reaction time. At the 17 min point, there are therefore differences in yields of FFA with reaction pressures. However, before that time the yield of FFA was close for 15 and 20 MPa. At 10 MPa, the yield was always lower, except at 20 min where the yield was 86%. Generally, after the reaction pressure exceeds 15 MPa, there is less effect of pressure on the hydrolysis reaction and does not cause an obvious improvement in FFA yield. In the continuous flow hydrolysis of sunflower oil with subcritical water, the optimal reactions pressure was 15 MPa. This result indicates that the degree of hydrolysis is largely independent of pressure and therefore water density at these working conditions as shown in Figure 3-11.

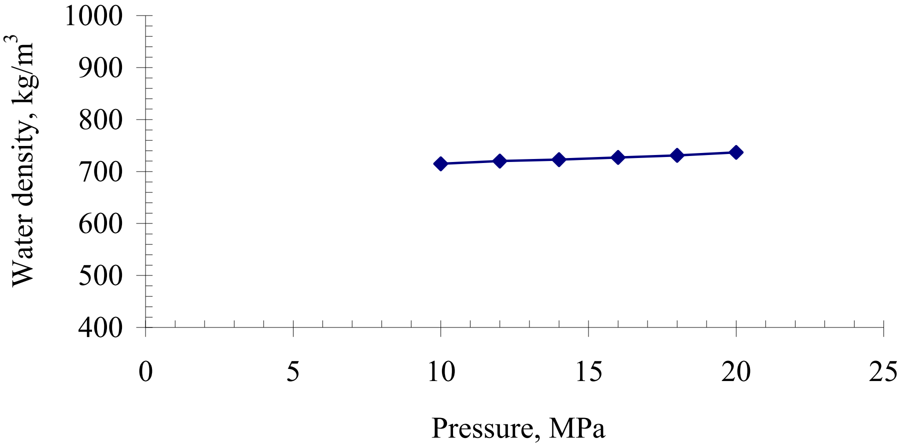

Figure 3-11. The relationship between water density and pressure at 300 ^{o}C (NIST, 2009).

3.3.3.2. Effect of temperature on FFA yield

The effect of temperature on the yield of FFA was investigated at 270, 300, 330 and 350 ^{o}C at 20 MPa using 50:50 water to oil volume ratio. The effect of reactions temperature is shown in Figure 3-12.

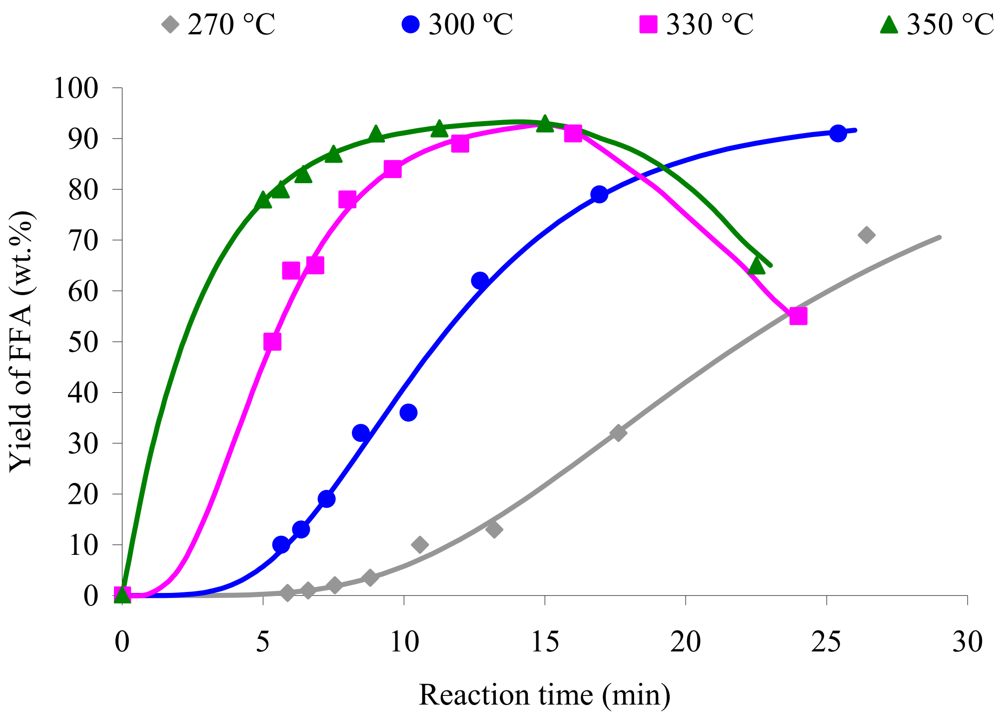

Figure 3-12. Effect of temperature in the total of fatty acids yield at 20 MPa and water:oil ratio 50:0 v:v% (data points are experimental results and the lines show the best fit to the data).

The yield of FFA at 270 °C very slowly increases in the early stages of the reactions. As water and oil are insoluble at temperatures below 250 °C, reactions in these conditions are controlled by transport properties. Increasing the temperature increases the oil solubility in water and the kinetic of the reactions (Pinto and Lancas, 2006) as is evident here. Ackelsberg reports (1958) that an increase of 10 °C in the temperature increases the rate of hydrolysis by a factor of 1.2 to 1.5. At 270 ^{o}C, the maximum yield of FFA was 75% at around 26 min reaction time, while at 300 °C the hydrolysis reaction reaches equilibrium at around 90 wt.% of FFA after 25 min. King et al. (1999) reported that a 22 % yield of FFA from soybean oil was achieved in 30 min at 270 ^{o}C for a flow reactor system. At 330 and 350 ^{o}C, the yield of FFA reached about 90 % after 16 and 8 min reaction time, respectively, without catalyst addition since the FFA acts as an acid catalyst in the hydrolysis reactions (Minami and Saka,

2006) and an increase in the ionic product of water. However, at 330 and 350 ºC the yield of FFA decreased after reaching the maximum yield of 90 %. This is either due to polymerisation of the FFA with the unreacted MG, DG and TG or decompositions and pyrolysis reactions (Holliday et al., 1997). Moreover, highly unsaturated fatty acids can polymerise when the temperature rises above 218 ^{o}C (Linfield et al., 1984).

Generally, higher temperatures lead to higher FFA yields and other researchers (Weatherley and Rooney, 2008) have reported enhanced rates of reaction and FFA yields using a high voltage electrical field, which can be considered a temperature effect due to localised heating. The rate of enzymatic hydrolysis of sunflower oil increased with the magnitude of the applied electrical field. These results verify that temperature has a significant influence on the reaction rate of the non-catalytic hydrolysis of vegetable oil.

3.3.3.3. Effect of water oil ratio on FFA yield

The effect of water:oil ratio (50:50 and 80:20) on the FFA yield at 15 MPa and 300 °C is shown in Figure 3-13. In a similar manner to the increase in temperature, a decrease in the water/oil ratio results in a higher FFA yield and in a shorter reaction time. At a reaction time of 11 min, a yield of 55 % FFA was obtained for a water/oil ratio of 50:50 v:v%, compared to 35 % FFA in the dilute system when the water:oil ratio was 80:20 v:v%. The amount of FFA available prior to subcritical water treatment would have been less and therefore its catalytic contribution would be less. This indicates that the ratio of water:oil is an essential parameter in the degree of hydrolysis. If the reaction time is sufficient the dilute system eventually gives higher

FFA yield due to increased collisions. As more FFA is produced there is a shift in the equilibrium to the right side and the reaction time decreases.

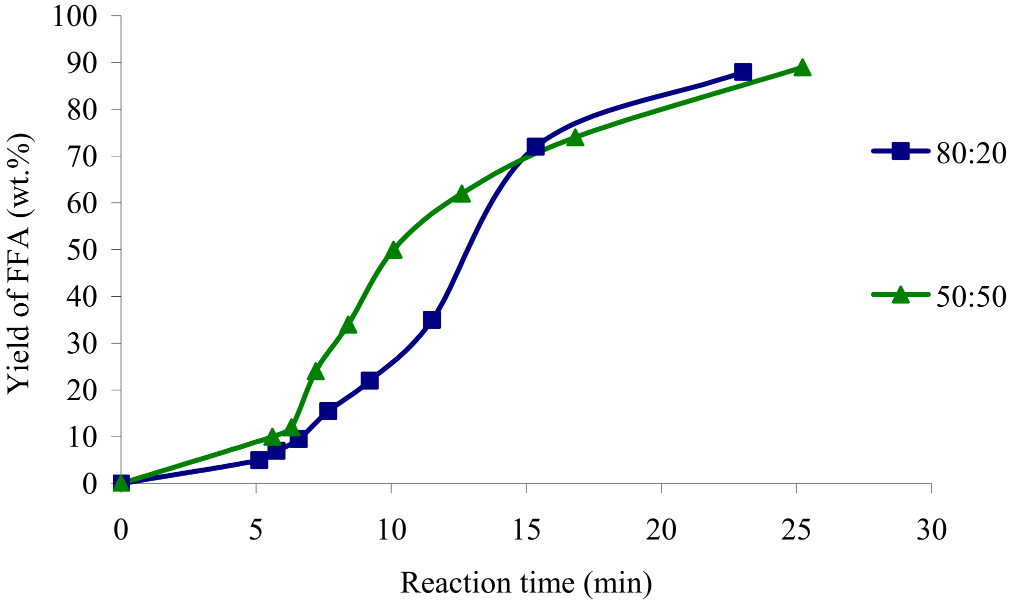

Figure 3-13. Effect of water:oil volume ratios on FFA yield at 15 MPa and 300 °C (data points are experimental results and the lines show the best fit to the data).

This result is in agreement with Lascaray (1949) who reported that higher water ratio gave lower FFA yield in the beginning of the hydrolysis reaction but gave higher yield as the reaction proceeded. Moreover, Sturzenegger and Hermann (1951) also reported that FFA yield curve was not affected by water:oil ratio in the first stage of the reaction but higher water ratio gave higher final FFA yield. The rates of hydrolysis have also been reported to be higher at lower initial water:oil ratios (Desai et al., 1984).

3.3.3.4. Change of FFA yield with pH

The change of pH with FFA yield can be seen in Figure 3-14. In this figure the product FFA we measured for the pH. An opposite relationship exists because the production of FFA causes the hydrolysed solution to become more acid and lowers the pH. When the pH is higher than 4.0 the yield of FFA was as low as 10 % and indicates that the reactions rates will be very low. However, there is a dramatic increase in FFA yield once the pH is greater than 3.5. Therefore, the hydrolysis reactions are mainly carried out in this range of pH. Figure 3-14 indicates that at the minimum pH of 3.2, the yield of FFA is 92 %. As the yield increases the concentration of FFA increases and the pH becomes down.

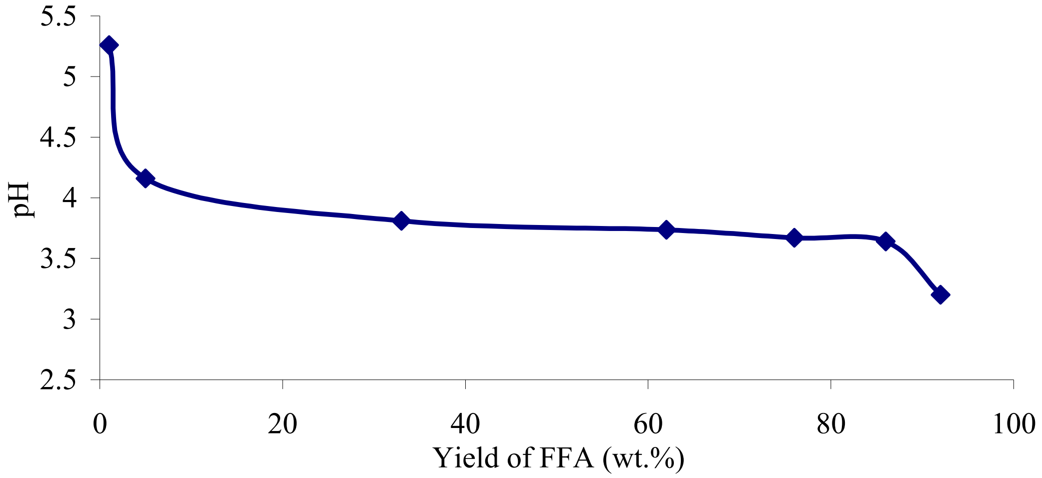

Figure 3-14. Change of pH on the FFA yield (data points are experimental results and the lines show the best fit to the data).

3.3.3.5. Change of FFA yield with water density

The relationship between the water density (affected by pressure and temperature) and the yield of FFA is shown in Figure 3-15. The water density at various operating conditions (270- 350 ^{o}C and 20 MPa) was obtained from National Institute of Standards and Technology (NIST, 2009). A high yield of FFA is obtained at low water density (below 0.65 g/ml) corresponding to high temperature. The yield deceases rapidly when the density of water is increases from 0.66 to 0.78 g/ml. The density of water therefore has a same affect on FFA yield to that of pH (see section 3.3.3.4).

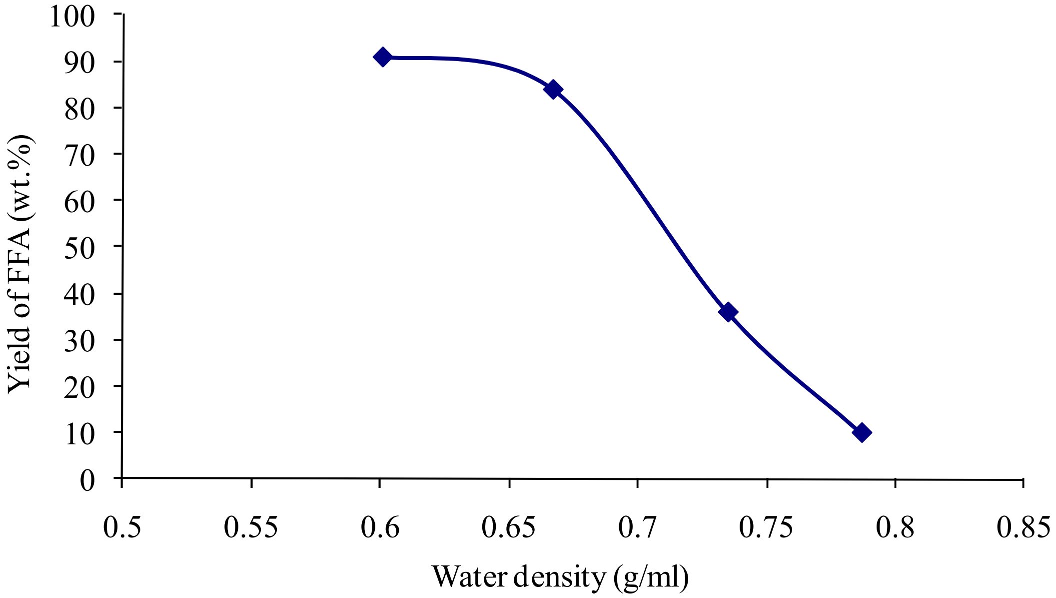

Figure 3-15. Change of water density on the FFA yield of sunflower oil with water ratio 50:50 and 20 MPa (data points are experimental results and the lines show the best fit to the data).

3.3.4. Properties of the produced FFA

The physical properties of sunflower oil and hydrolysed product (92 % FFA) are illustrated in Table 3-4. There is no significant change in the density or viscosity. Since both sunflower oil and FFA are considered as Newtonian fluids, i.e. the relationship between shear stress and shear rate is linear, their viscosities do not differ by the order of magnitude (Wan, 1991). Therefore, the oils and hydrolysed product have almost the same physical properties (density and viscosity). The acid value is considered as another expression for the percentage of FFA (AOCS, 1998) and the value is corresponds well to a sample containing 92 % FFA.

Table 3-4. Physical properties of sunflower oil and (92 %) FFA.

Name of component	***Temperature (^oC)***	***Density (kg/m^3)***	***Viscosity (Pa.s)***	***Acid value***
Sunflower oil	25.0	917.0	5.19×10^{-2}	1.0
Hydrolysed product (92 % FFA)	25.0	911.0	4.20×10^{-2}	183.0

3.4. Conclusion

The continuous flow hydrolysis reaction of sunflower vegetable oil with subcritical water is a promising method for production of a high yield FFA. The continuous process will offer the advantage of a large-scale production with minimum labour requirements, whilst maintaining product quality. Hydrolysis reactions with a high yield of up to 90 % within 7 to 15 min at 350º C, 20 MPa and water:oil ratio of 50:50 v:v% can be achieved without the addition of catalysts. It has been found that the rate of hydrolysis is strongly affected by temperature, reaction time and the water:oil ratio; however, the reaction pressure has a minor effect on the degree of hydrolysis. In order to achieve a high yield of FFA, there is a need to extend the reaction time but care should be taken to avoid the thermal degradation of the products. Furthermore, FFA yield is high at low pH and low water density. The results obtained in this work provide valuable data for the optimisation of vegetable oils hydrolysis with subcritical water in a continuous flow reactor. The extension of this technique to FAME production is investigated in chapter 5.

CHAPTER 4

HYDROLYSIS KINETICS OF SUNFLOWER OIL UNDER SUBCRITICAL WATER CONDITIONS [3]

4.1. Introduction

The oils and fats industry produces many beneficial products, ranging from cooking fats and margarine to cosmetics and soap detergents. These industries can now be considered environmentally friendly due to the development of green

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[3] This research has been published in Chemical Engineering Research & Design 87:(6):867-873, 2009.

processes, driven by the need to prevent pollution, to be publicly acceptable and to eliminate hazardous by-products. Processes that utilise biomass (such as vegetable oil, animal fats and spent yeast) for energy resources are also considered to be green and have associated economic and social advantages. Many researchers have developed green processes which use sub and supercritical fluids (such as water and carbon dioxide) to prevent the problems associated with volatile organic solvents. Avoiding the use of organic solvents is a major advantage in any process, simply because these solvents need to be separated, recycled, incinerated, or submitted to other utility processes. Another major advantage of using subcritical water is the ability to achieve the same results as a process, which employs either acidic or alkaline catalysts.

Hydrolysis reactions are important in the processing of oil and fats by the chemical industry. These reactions can be conducted thermally as a liquid-liquid reaction or gas-liquid reaction using superheated steam. They can also be conducted at ambient conditions by employing biolytic enzymes (Patil et al., 1988). The process for hydrolysing oil using water can be defined as a mass transfer controlled chemical reaction whereby water reacts with oil (triglyceride) to form free fatty acids (FFA) and glycerol (Lascaray, 1949). Some researchers have found advantages in using pressures exceeding 20 MPa and temperatures above 250 ºC to eliminate the use of either acidic or alkaline catalysts (King et al., 1999, Kusdiana and Saka, 2004, Minami and Saka, 2006). This is advantageous, because FFA react with alkaline catalysts to produce undesired saponified products. In this case, the final products need sophisticated purification processes to remove the saponified products and the catalyst, which results in a reduction in the yield of the final product.

Patil (1988) have presented oil hydrolysis as a three step reaction and proposed a model, which describes the thermal hydrolysis of different vegetable oils (peanut, tallow and coconut). Quantitative information on the reaction kinetics of non-catalytic vegetable oil hydrolysis is limited (Fujii et al., 2006, Minami and Saka, 2006); moreover, the kinetic data reported are not fully established as only one rate constant was considered for all the forward reactions. This work presents a kinetic study for the continuous flow thermal hydrolysis of sunflower oil in subcritical water at 20 MPa, between 270 and 350 ºC. This reaction is autocatalysed by the FFA and removes the need to add an additional catalyst. The process kinetics are discussed, together with the FFA yield and rate of reaction.

4.2. Materials and methods

Materials and methods for this section is the same as in section 3.2.

4.3. Results and discussion

4.3.1. Introduction

The sunflower oil consisted of about 77 % by wt. triglycerides (TG); 20 % diglycerides (DG); 2.5 % monoglycrides (MG); and only 0.3 - 0.5 % FFA, as analysed by gas chromatography (GC). Berrios et al., (2007) have analysed the FFA component of sunflower oil which was found to contain 72 % by wt. linoleic acid, 17 % oleic acid, 4 % stearic, the remainder being palmitic acid. The average molecular weight ($\overline{M\,Wt}$) of each constituent TG, DG, MG and FFA was calculated to be 874.1, 613.4, 352.7 and 278.7 g gmol^{-1}, respectively using Equation 4-1:

$$\overline{MWt} = \left(\sum \frac{x_i}{M\ Wt_i} \right)^{-1}$$ **Equation 4-1**

where x_i is the weight fraction of each fatty acid present and $M\ Wt_i$ is the molecular weight of each constituent based on 1.0 g of each TG, DG, MG and FFA. Since the average molecular weight of the TG was 874.1 g $gmol^{-1}$ and the weight of TG is 77 g, this gave the number of moles of TG equal to 0.088 moles. In similar calculations for DG, MG and FFA, this resulted in 0.0326, 0.007 and 0.0018 moles, respectively. In summation, the components gave a value of 0.13 moles. The mole fraction of each species was then calculated to be 0.68, 0.25, 0.055 and 0.014 for TG, DG, MG and FFA, respectively. This resulted in a 1 - 46.754 respective molar ratio of oil to water in the mixture that was fed into the reactor.

A number of hydrolysis experiments with sunflower oil in subcritical water were carried out in the tubular reactor at between 270 and 350 ^{o}C. In all experiments, the pressure was kept constant at 20 MPa and a water/oil feed ratio of 50:50 (v:v) was used as selected by pervious workers (Minami and Saka, 2006).The concentration of water is sufficient to affect the hydrolysis of the oil to > 90 wt.% FA and also acts as a solvent. Table 4-1 shows the standard deviation for three sets of experiments at 350 ^{o}C, which was no greater than 3.63 %.

Table 4-1. The standard deviation for three set of experiments at 20 MPa, 350 °C and water:oil ratio 50:50 v:v.

Residence time (min)	***Yield of fatty acids (wt. %)***	***Standard deviation***
0	0	0
5	75.7	3.63
5.6	79.2	0.62
6.4	83.8	0.61
7.5	86.3	0.67
9	89.7	1.62
11.25	91.7	1.7
15	92.8	1.3

The hydrolysis reaction has been shown by Mills and McClain (1949) to occur as three stepwise reactions (Equation 4-2 to 4-4):

$$C_3H_5\,(OOCR)_3 + H_2O \underset{k_1^{'}}{\overset{k_1}{\rightleftarrows}} C_3H_5\,(OH).(OOCR)_2 + RCOOH$$

Equation 4-2

TG water DG FFA

$$C_3H_5\,(OH).(OOCR)_2 + H_2O \underset{k_2^{'}}{\overset{k_2}{\rightleftarrows}} C_3H_5\,(OH)_2.\,(OOCR) + RCOOH$$

Equation 4-3

DG water MG FFA

$$C_3H_5\,(OH)_2.(OOCR) + H_2O \underset{k_3^{'}}{\overset{k_3}{\rightleftarrows}} C_3H_5(OH)_3 + RCOOH$$

Equation 4-4

MG water G FFA

This reaction is a pseudo-homogenous first order reversible reaction (with excess of one reactant, mainly water) in the oily phase (Ackelsberg, 1958). In the first step (TG) is hydrolysed to (DG), in the second step DG is hydrolysed to (MG) and in the third step MG is hydrolysed to glycerol (G); with each step, FFA is generated. The collected FFA product is equivalent to the sum of three times the moles of G reacted, two times the moles of MG reacted and one times the mole of DG, or equivalent to the total moles of water consumed. FFA can act as an acid catalyst in the hydrolysis reaction in subcritical water and yield up to 90 % wt. conversion without the use of any catalyst (Minami and Saka, 2006). This autocatalytic reaction has facilitated the task of catalyst removal from the final product; this is technically difficult and increases the costs of the final product (Demirbas, 2003).

4.3.2. Kinetics model

A new approach to implementing a kinetics model for the reversible oil hydrolysis reaction has been developed in this study. In this model, TG, DG, MG, G, W and FFA indicate the concentrations of $C_3H_8(OOCR)_3$, $C_3H_8(OH)(OOCR)_2$, $C_3H_8(OH)_2.(OOCR)$, $C_3H_5(OH)_3$, H_2O and RCOOH, respectively. The kinetic differential equations governing the hydrolysis of sunflower oil reactions (Equation 4-2 to 4-4) are indicated by Equations 4-5 to 4-10.

$$\frac{d[TG]}{dt} = -k_1([TG].[W]) + k_1^{'}([DG].[FFA])$$

Equation 4-5

$$\frac{d[DG]}{dt} = k_1([TG].[W]) - k_1^{'}([DG].[FFA]) - k_2([DG].[W]) + k_2^{'}([MG].[FFA])$$

Equation 4-6

$$\frac{d[MG]}{dt} = -k_3([MG].[W]) + k_3^{'}([G].[FFA]) + k_2([DG].[W]) - k_2^{'}([MG].[FFA])$$

Equation 4-7

$$\frac{d[G]}{dt} = k_3([MG].[W]) - k_3^{'}([G].[FFA])$$

Equation 4-8

$$\frac{d[W]}{dt} = -k_3([MG].[W]) + k_3^{'}([G].[FFA]) - k_2([DG].[W]) + k_2^{'}([MG].[FFA]) - k_1([TG].[W]) + k_1^{'}([DG].[FFA])$$

Equation 4-9

$$\frac{d[FFA]}{dt} = k_3([MG].[W]) - k_3^{'}([G].[FFA]) + k_2([DG].[W]) - k_2^{'}([MG].[FFA]) + k_1([TG].[W]) - k_1^{'}([DG].[FFA])$$

Equation 4-10

These six non-linear differential equations were solved using a fourth-order Runge–Kutta method (Kreyszig, 1999) programmed in Excel (Microsoft Office 2003). The initial values of k_1, $k_1^{'}$, k_2, $k_2^{'}$, k_3, and $k_3^{'}$ were estimated for the best possible representation of the experimental data. Figure 4-1 shows the algorithm to estimate these parameters. The step size was chosen to reduce the unnecessary computation without affecting the accuracy of the results. The values of all rate constants are positive and have been optimised using the built-in solver function in Excel with the rejection of negative values in the default settings. The sum of the squares of percentage error between experimentally measured (exp.) and numerically calculated (cal.) FFA values were minimised using the objective function (OF) given by Equation 4-11:

$$OF = Minimise \sum_{j=1}^{N} \left(\frac{[FFA]_j^{exp} - [FFA]_j^{cal}}{[FFA]_j^{exp}} \times 100 \right)^2$$ **Equation 4-11**

where N is the number of experimental data points and $[FFA]_j$ is the FFA concentration at a given temperature in the top layer. Using this approach, the experimental data were used to obtain all the rate constants for the complete kinetic reactions under investigation. The minimised average errors between experimental and calculated data were found to be 3.7 for 270 °C, 4.0 % for 300 °C, 2.3 % for 330 °C and 4.7 % for 350 °C. For all the temperatures the maximum variance between the experimental and predicted values was not greater than 5.8 %.

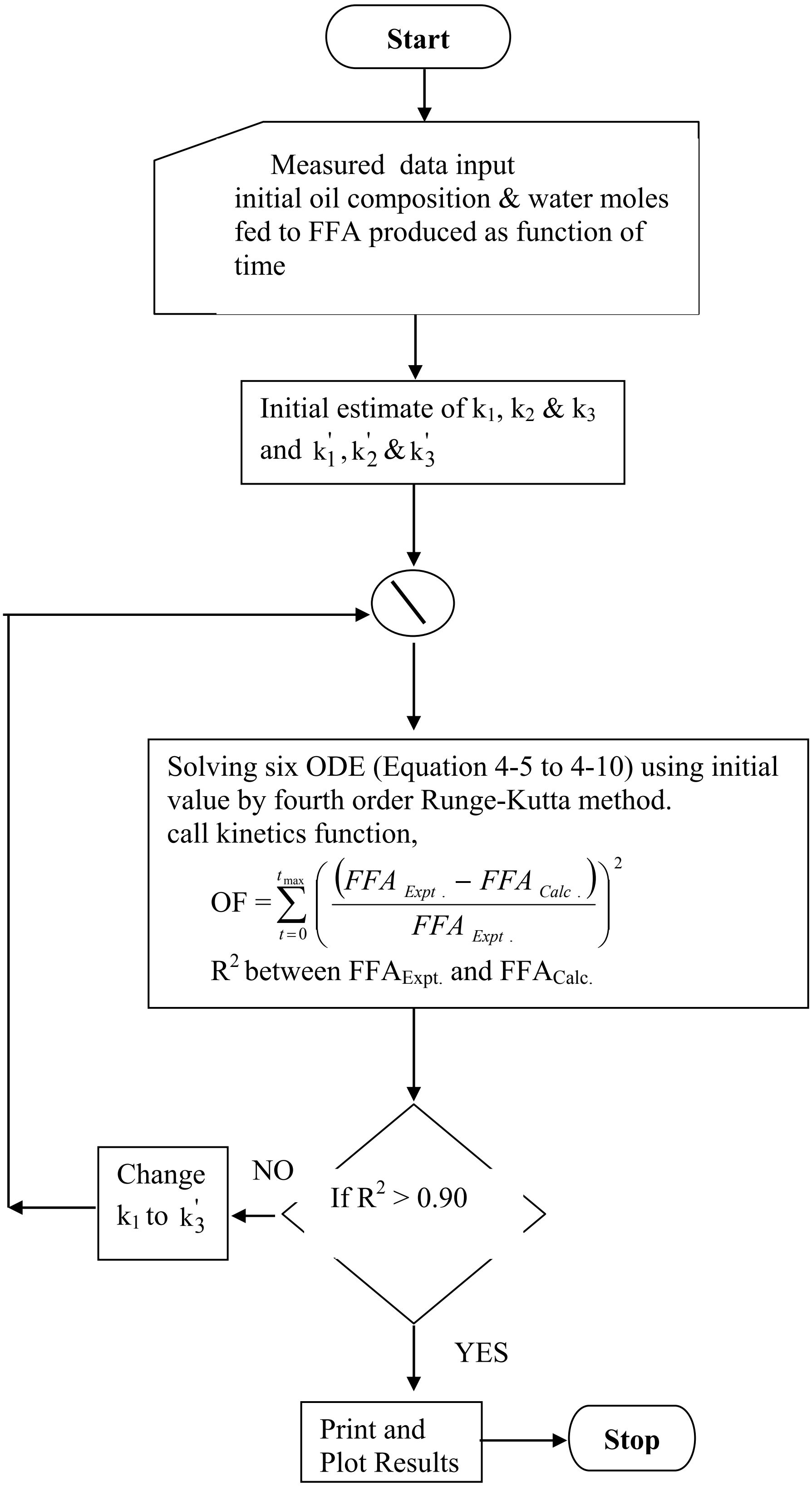

Figure 4-1. Flowchart of parameter estimation programme for chemical kinetics of hydrolysis of vegetable oils in subcritical conditions.

Figure 4-2 shows the moles of FFA as a function of time (min) after sunflower oil hydrolysis at 20 MPa and temperatures between (270, 300, 330 and 350 ^{o}C).The experimental data are shown as symbols and the fitted kinetic Equation 4-5 to 4-9 are shown as continuous solid lines. The maximum variance between the experimental data and the kinetic model is lower that 5.8 %. The oil hydrolysis reaction exhibits an induction period, in which the reaction rate is initially slow and then increases up to its normal level (Moquin and Temelli, 2008).

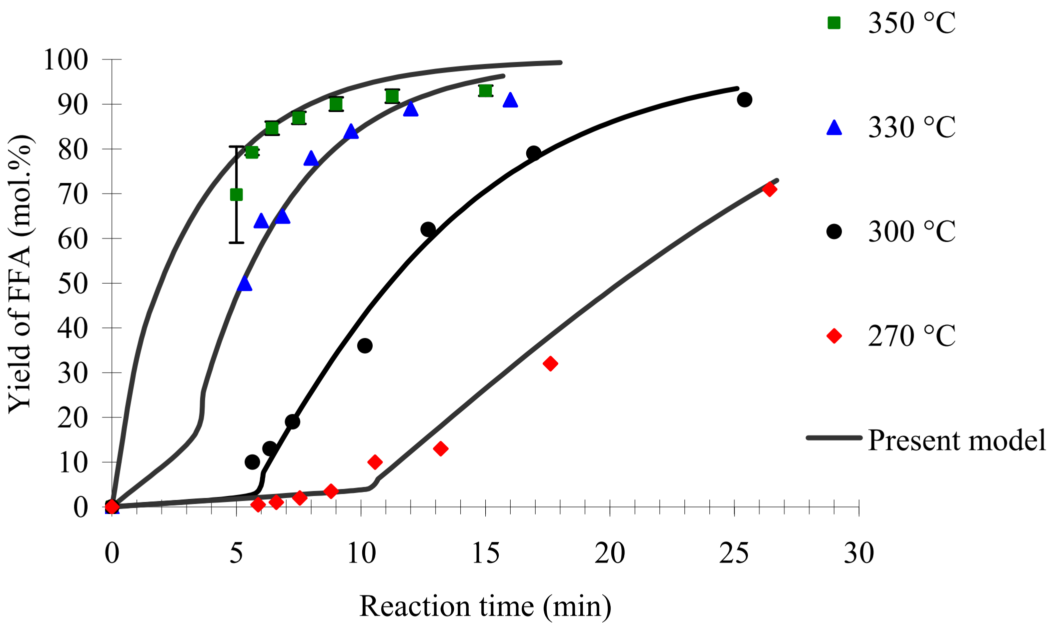

Figure 4-2. Hydrolysis of sunflower oil to FFA in subcritical water.

At lower temperatures there is a long induction period due to the lower solubility of water in oil; however, as the temperature increased the solubility increases leading to a reduction in the induction period. The induction period has been reported to end when there is about 10 wt.% FFA in the mixture (Lascaray, 1952, Minami and Saka, 2006). An induction period is evident for all the temperatures, except at 350 ^{o}C; however, the first sample was taken after 5 min and so this may not be conclusive. For the reaction at 270 ^{o}C, the induction period is found to be 9.5

minutes and at 300 and 330 °C, it is around 5.4 and 2.5 minutes, respectively as optimised by the program.

The mole fraction of TG versus the time predicted by the kinetic model for the four different temperatures is shown in Figure 4-3.

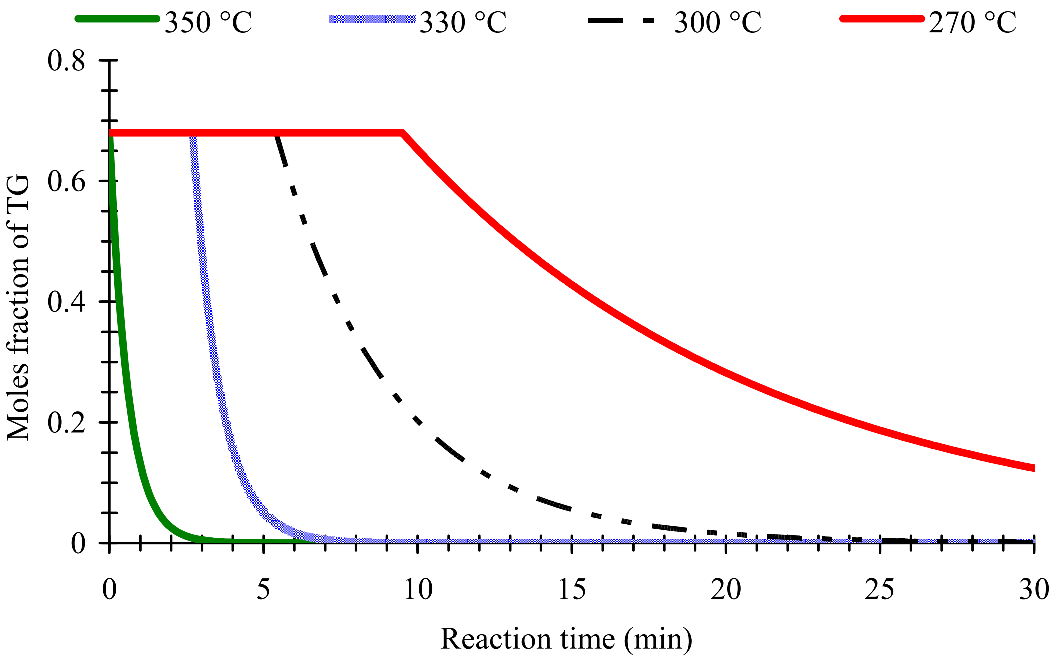

Figure 4-3. Change in mole fraction of triglycerides (TG) versus time.

As can be seen, the mole fraction of TG decreases with time and can be attributed to the conversion of TG to other components such as DG, MG, and G. An induction period is again noted for the lower temperatures.

The mole fraction of DG versus reaction time is shown in Figure 4-4. The mole fraction of DG is initially seen to increase for approximately two minutes, because DG is formed from TG in the first reaction, and subsequently in the second reaction DG is consumed to form MG. These reactions occur faster at higher temperatures, which are reflected in the sharper peak over a shorter reaction time.

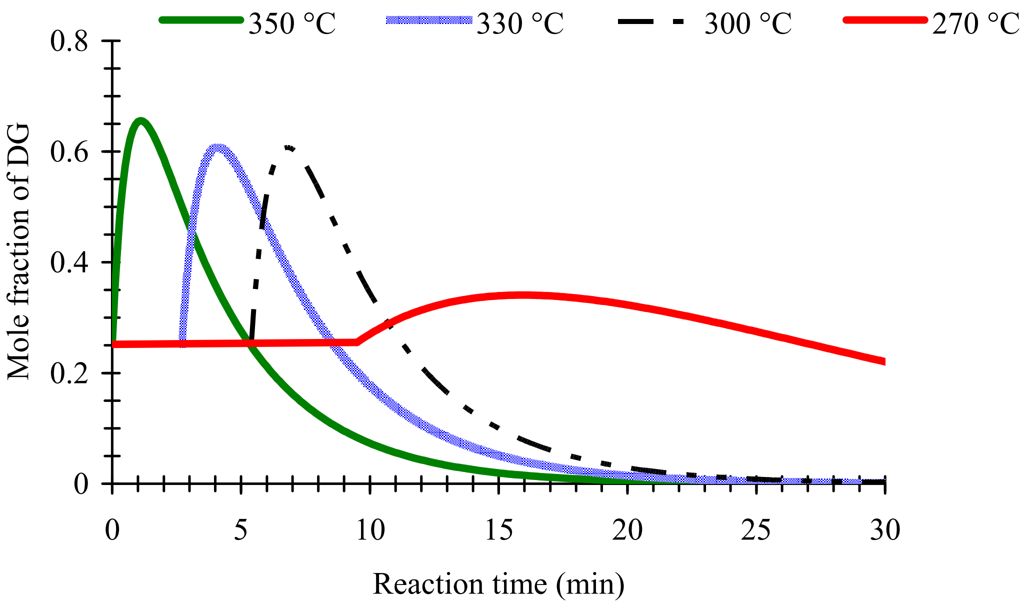

Figure 4-4. Change in mole fraction of diglycerides (DG) versus time.

The mole fraction of MG versus reaction time is shown in Figure 4-5. In a similar manner to that shown in Figure 4-4, the mole fraction of MG increases in the first period, because MG is formed from the DG produced in the second reaction, which is consumed in the third reaction as MG is consumed to form G. In each reaction step there is a production of FFA. The figure also shows a sharp decrease at the beginning for temperatures greater that 300 ^{o}C and is an artefact of the model.

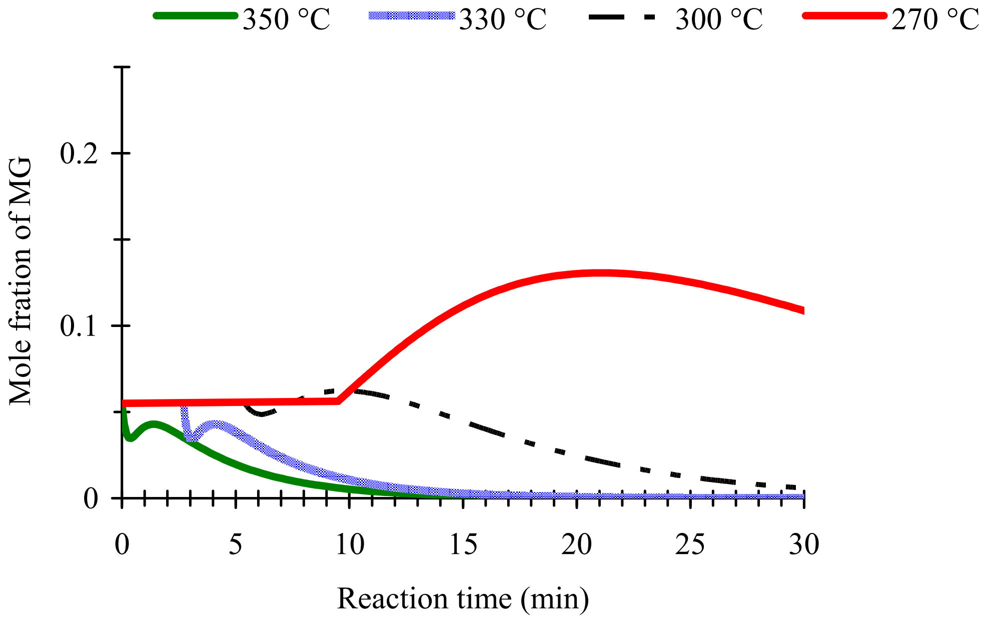

Figure 4-5. Change in mole fraction of monoglycerides (MG) versus time.

The mole fraction of G versus reaction time can be seen in Figure 4-6; the mole fraction of G increases with reaction time because it is the end product of the all reactions and follows a similar shape to the FFA yield shown in Figure 4-2.

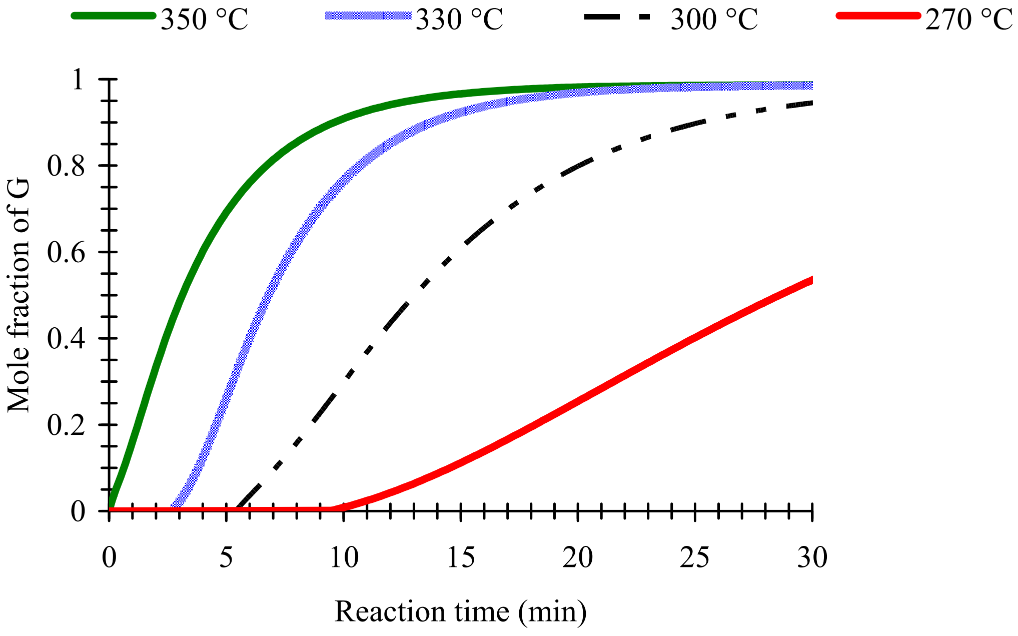

Figure 4-6. Change in mole fraction of glycerol (G) versus time.

The shape of the graphs for all the products (DG, MG, G, and FFA) follows a logical trend. The mole fraction values for TG, DG, MG and G throughout these reactions are based on the material balance obtained from the stoichiometry given earlier in this section.

The values of the rate constants $k_{1,}$ k_2 and k_3 for the hydrolysis reaction are presented in Table 4-2. These rate constants are found to increase as a function of temperature. Moreover, the values of the reversible reaction rates $k_1^{'}$, $k_2^{'}$ and $k_3^{'}$ were calculated to be close to zero and were therefore fixed accordingly at this value; this supports the inference that the reactions are irreversible. The rate constants were comparable with those of Moquin and Temelli (2008), who studied the same reaction but at different conditions (250 °C, 10 MPa, 1:3 oil:water ratio). They reported values of 9.8×10^{-3}, 1.6×10^{-1} and 8.15×10^{-2} g/min.mol for $k_{1,}$ k_2 and k_3, respectively.

Table 4-2. The kinetic parameters for the ternary system for continuous flow hydrolysis of sunflower oil at 20 MPa and water:oil ratio 50:50 v:v.

Item	*T*	k_1	k_2	k_3
	270	1.8×10^{-3}	2.1×10^{-3}	5×10^{-3}
	300	5.7×10^{-3}	3.6×10^{-3}	2.5×10^{-2}
	330	2.4×10^{-2}	5.6×10^{-3}	2.7×10^{-2}
	350	2.36×10^{-2}	5.9×10^{-3}	8.9×10^{-2}
E_{a1}		108		
E_{a2}			38	
E_{a3}				90
R^2		0.96	0.97	0.91
A_o		5.2×10^6	1.1×10^1	2.8×10^6

T, temperature (°C); k_1, k_2, and k_3 rate constants (min$-^1$[mol/mol of oil]$^{-1}$); E_{a1}, E_{a2} and E_{a3} energies of activation (kJ/mol); A, pre-exponential factor (min$-^1$[mol/mol of oil]$^{-1}$) .

Figure 4-7 shows the Arrhenius plot for the continuous flow hydrolysis of sunflower oil. A similar influence of temperature on the reaction rate can be observed for the four different reaction temperatures. The computed activation energy values from Equation 4-12, E_{a1}, E_{a2} and E_{a3} for the above reaction are also listed in Table 4-2. It is evident that the E_{a1} value for first reaction from TG to DG is higher than the E_{a2}

and E_{a3} value. This is because the hydrolysis needs higher energy to start the reaction and break up the first chain of TG to form DG as can be seen in Figure 2-5. Since reactions of organic compounds involve the making and breaking of bonds, the strength of bonds, becomes an important consideration (Santos et al., 2008, Schmickler, 2000). A high E_{a3} is required in the third reaction, but is less in energy than at the start of the reaction in order to break up the last chain of MG to form G. The activation energy required in the second step of the hydrolysis reaction from DG to MG is observed to be almost half of the E_{a1} indicating the forward driving force for the progression of reaction.

Arrhenius' Law $k = A \exp(-Ea / RT)$ **Equation 4-12**

Where:

Ea = Activation Energy in kJ/mol
R = Gas Constant = 8.314 J/mol.K
T = Absolute Temperature, K
A = Arrhenius constant or Pre-exponential factor, ($\text{min}^{-1}[\text{mol/mol of oil}]^{-1}$)

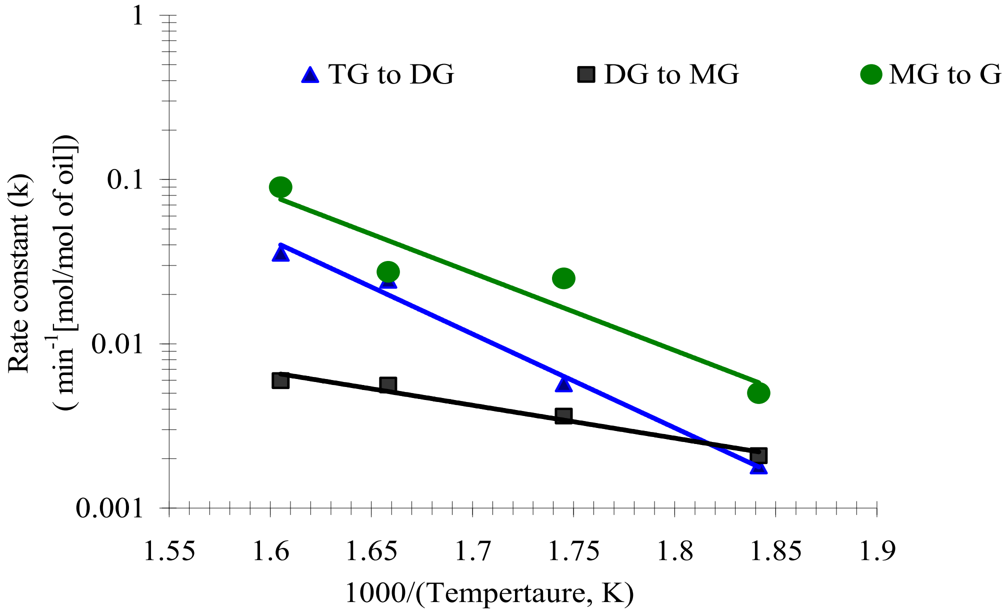

Figure 4-7. Arrhenius plots for sunflower oil hydrolysis.

4.4. Conclusion

Continuous flow autocatalytic hydrolysis reactions of sunflower oil with subcritical water was carried out at four different temperatures at 20 MPa and was found to be an effective method for producing FFA with yield greater than 90 % without any catalyst. This is because the FFA acts as an acid catalyst in the hydrolysis of the oil in subcritical water. Also, water acts as a catalyst due to high ionic product. The oil hydrolysis reactions exhibited an induction period which was found to decrease with an increase in the reaction temperature. This decrease can be attributed to an increase in the solubility of oil in water. The hydrolysis reaction requires greater energy to start the first reaction than the second and third reactions.

A kinetic model was developed to describe the thermal hydrolysis of vegetable oils. The hydrolysis reaction has been proven to be a simple second order irreversible reaction. The proposed kinetic model was in a good agreement with the experimental data and had a maximum variance of < 5.8 %.

CHAPTER 5

ESTERIFICATION KINETICS OF FREE FATTY ACIDS WITH SUPERCRITICAL METHANOL FOR BIODIESEL PRODUCTION[4]

5.1. Introduction

Biodiesel is produced though a transesterification reaction of typically vegetable oils or animal fats with methanol or ethanol in the presence of an alkali catalyst, such as sodium hydroxide (NaOH), potassium hydroxide (KOH) or calcium oxide (CaO). The transesterification reaction can also be catalysed with acids (Berrios

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[4] This research has been submitted to the Energy Conversion and Management, *accepted.*

et al., 2007) and enzymes (Dizge et al., Du et al., 2004). The aim of this reaction is to chemically break down the molecules of the oils/fats into methyl or ethyl esters with glycerol as a by-product (Demirbas, 2007a). This conversion process overcomes another obstacle associated with the use of vegetable oil alone as a fuel, whose viscosity is about 10 to 20 times that of moderate diesel fuel (Pinnarat and Savage, 2008). The transesterification reaction leads to an optimal reduction in the viscosity of the oil/fat feedstock and thus makes it suitable for use as a fuel.

The major problem associated with transesterification reaction is that the catalysts involve some difficult separation steps to give the final biodiesel product (Demirbas, 2003). Demirbas (2007a) conducted transesterification of rapeseed oil with supercritical methanol, using calcium oxide (CaO) as a catalyst. He reports that the presence of a catalyst favours the forward reaction, resulting in better yields of FAME. On the other hand, the esterification reaction can be conducted with (Sendzikiene et al., 2004) or without a catalyst under supercritical conditions of the alcohol (Kusdiana and Saka, 2004, Minami and Saka, 2006). In the non-catalytic reaction, ions are produced from the alcohol and the mixture of oil and alcohol is combined as a single phase, which causes the acceleration of the reaction (Pinnarat and Savage, 2008).

Non-catalytic methyl esterification is a one-step reaction where free fatty acids (FFA) react with methanol (M) to form Fatty Acid Methyl Esters (FAME) and water (W) as a by-product, according to Equation 5-1.

$$\mathrm{RCOOH} + \mathrm{CH_3OH} \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \mathrm{H_2O} + \mathrm{RCOOCH_3}$$ **Equation 5-1**

FFA methanol water FAME

Warabi et al. (Warabi et al., 2004) have reported that the alkyl esterification reaction had higher reaction rates and could be performed at a lower reaction temperature than a transesterification reaction could. Conversely, Berrios et al., (2007) state that esterification reaction did not take place in the absence of a catalyst. The authors measured acid value instead of FAME production as an indication of the progress of the reaction; however they did not consider the reaction in supercritical conditions of the alcohol.

Minami and Saka (2006) have suggested that the esterification reaction could be modelled as a second-order reversible reaction. They introduced a new concept of auto-catalytic esterification and embedded a term into the kinetic equations. In their approach, the fatty acid acts as an acid catalyst; thus, both the terms in the differential were multiplied by the fatty acid concentration term, causing an increase in the order of both forward and reversible reactions. The authors do not mention the application of their model and the values of respective rate constants, nor the goodness of fit to their experimental data. Sendzikiene et al., (2004) present their acid-catalysed esterification reaction results using a simplified model to consider a first order irreversible reaction. Even though there is a high demand for biodiesel production, few data in the literature are reported regarding non-catalytic esterification reactions. In this chapter, the factors which strongly affect the yield of biodiesel are discussed. A comprehensive critical kinetic model of FFA esterification in supercritical methanol is also generated, which to date no data have ever been reported.

5.2. Materials and methods

5.2.1. Materials used

5.2.1.1. Gases

The gases used throughout the present study were supplied by the British Oxygen Company (BOC) UK, as follows:

- Helium, purity 99.99 %.
- Hydrogen, purity 99.95 %.
- Nitrogen, purity 99.9 %

5.2.1.2. Reagents

The chemical materials used are listed below in Table 5-1. All the chemicals used in the experiments were reagent grade or higher and were used as received, without any purification. FFA was supplied by IOI Group, the Netherlands. The FFA was analysed by GC by the supplier and was found to consist of a number of FFA (see Table 5-2) that are mostly found in any vegetable oil. The short formula is expressed in Cx:y where x is the number of carbon atoms and y is the number of the double bounds.

Table 5-1. A list of chemical materials used for esterification reaction.

Material	***Cas number***	***Grade***	***Supplier***
Methanol (99.9 %)	67-56-1	A.R	Fisher
Ethanol (99.9 %)	64-17-5	A.R	Fisher
Heptane (99.9 %)	142-82-5	A.R	Fisher
Methyl heptaecanoate (99.5%)	5-163-3	A.R	Sigma-Aldrich
Sodium hydroxide	1310-73-2	A.R	Fisher
Phenolphthalein	77-09-8	A.R	Hopkin & Williams Ltd, UK
Methyl palmitate (99 %)	112-39-0	G.C.	Sigma-Aldrich
Methyl stearate (99 %)	112-61-8	G.C.	Sigma-Aldrich
Methyl oleic (99 %)	112-62-9	G.C.	Sigma-Aldrich
Methyl Linoleic (99 %)	112-63-0	G.C.	Sigma-Aldrich

Table 5-2. The composition of FFA.

FFA, Cx:y		***Composition (% wt.)***
Lauric	(C12:0)	0.25
Myristic	(C14:0)	0.1
Palmitic	(C16:0)	3.5
Stearic	(C18:0)	2.5
Oleic	(C18:1)	88.0
Linoleic	(C18:2)	4.5
Linolenic acid	(C18:3)	0.35
Arachidic	(C20:0)	0.2
Behenic	(C22:0)	0.6

5.2.2. Apparatus and methods

The esterification reaction experiments of FFA with supercritical methanol were carried out in a bench-top batch reactor (Parr Instrument Company) with a total reactor volume of 3×10^{-4} m^3.

5.2.2.1. Experimental equipment

The bench-top batch reactor is shown in Figure 5-1 and the design parameters are shown in Table 5-3. The other items of equipment used in these experiments are listed below:

- Bench-top batch reactor: (Parr Instrument Company-5500) made from 316 stainless steel equipped with an electrical heater, and a magnetic stirrer.
- Thermocouple: type-K, with accuracy of +/- 2 ^{o}C.
- Pressure gauge: Ashcroft, with accuracy of +/- 0.25 MPa.
- Butterfly valves: stainless steel.
- Rotary vacuum evaporator:
- Cooling pumps: Watson-Marlow, type-502S
- Ice water bath
- Gas regulator valve:GA-3500, 0-25 MPa

Figure 5-1. Photographs of bench-top batch reactor vessel.

Table 5-3. Stirring reactor design parameters.

Parameters	***Dimension (mm)***
Reactor inside diameter	55
Reactor inside depth	135
Impeller diameter	37
Height of impeller blades	8.5
Stirrer shaft height	90
Stirrer shaft diameter	5.5

5.2.2.2. Experimental methods

The reaction was conducted in a bench-top batch reactor; the diagram of the system is shown in Figure 5-2. The stirred batch reactor consisted of the following parts sections: a reactor base, cylindrical vessel and a reactor head, accommodating valves, gas and purge line. A stainless steel internal coil cooling line was fixed inside the reactor vessel. The stirrer was a four pitched blade turbine. A sampling line was fixed with two on-off valves (V1 and V5) in the reactor head. A total volume of 200 cm^3 of reactants of methanol and FFA was mixed in a pre-defined ratio before being fed into the reactor. Once the autoclave was sealed, the reactor vessel was pressurised by nitrogen. The reactor was heated to the pre-determined reaction conditions by an external electrical heater. The temperature in the reactor vessel was measured by an iron-constantan thermocouple (type K). The impeller speed was varied from 430-1680 rpm. Samples were periodically withdrawn from the reactor vessel through a valve (V1) and a sample line which was immersed in an ice-water cooling bath. Valve (V4) is used to purge the sample line. The volume of the sampling line on the system made sample collection during the reaction possible without considerably affecting the pressure inside the autoclave. Different sampling durations were investigated in order to maximise kinetic data while minimising the disturbance of the equilibrium of the reactions. The sample drawn from the reactor vessel was then charged into a vacuum evaporator to remove the unreacted methanol and water produced during the methyl esterification reaction (Gerpen and Knothe, 2005, Kusdiana and Saka, 2001a, b, Tesser et al., In press). The experiments were conducted at temperatures ranging from 250 ^{o}C to 320 ^{o}C and at 10 MPa pressure (methanol is supercritical above 8.09 MPa and 239.0 ^{o}C). The molar ratio of methanol:FFA was varied from 0.7:1.0 to 11.0:1.0 during the experiments. Stirring rates of 430, 850 and 1630 rpm were investagited.

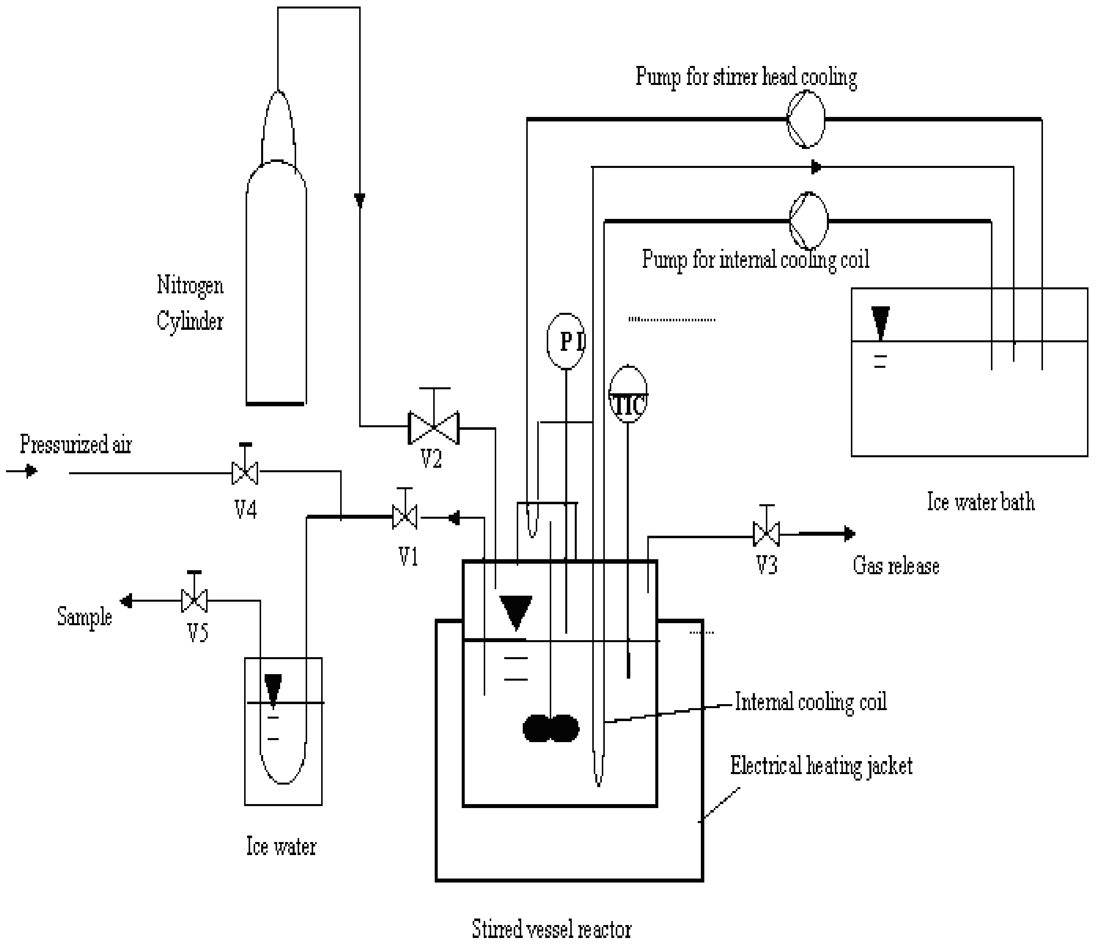

Figure 5-2. Bench-top batch reactor vessel.

5.2.3. Analytical methods

The yield and purity of the biodiesel products were examined using gas chromatography (GC) according to the FAME standard tests EN14214 (European Standard) to determine the content of the fatty acid methyl esters (FAME) indented to use as biofuel. This method is appropriate for FAME containing methyl esters of carbon atoms between C14 and C24.

The GC (6890A, Agilent Technologies, USA) was equipped with a capillary column DB-wax (J&W Scientific, USA), (length 30 m x diameter 2.5 x10^{-3} m x film thickness 0.1µm) and a flame ionization detector (250 ºC). Helium was used as the carrier gas at a constant flow (1 cm^3/min) with a split injector (340 ºC, 1:50). The oven temperature programme was constant at 200 ºC for 15 min. The sample was weighed to between 30 and 60 mg of FAME, then 1 ml of heptane which contained 10 mg/cm^3 of methyl heptadecanoate as the internal standard was added. The sample mixture of 1 µl was injected into the GC and the FAME component was identified from reference standards and its mass was calculated from a predetermined peak area response factor of the internal standard. Typical chromatograph peaks of FAME can be shown in Figure 5-3. The total yield of FAME was determined by the addition of all the FAME masses. As in FFA analysis, this method eliminates the error incurred by varying injection volumes because of the presence of internal standard. Injection errors were minimised by comparing the peak area of the internal standard to a predetermined set value, and subsequently, applying any necessary corrections to maintain quality control and assurance. This method of calculating FAME contents eliminates the error incurred by varying injection volumes because always peaks of FAME referred to the peak of internal standard that already in the sample. It was assumed that all FAME were equally detected in the flame ionization detector and that all FAME have similar response factors. All methyl esters were detected between the 3.0 to 5.0 minute residence times. The difficulty with this method is that not all the sample passes, for example heavy components can remain in the column. The calculation of FAME contents from the G C is given by Equation 5.2.

$$Esters\% = \frac{Area\ \ of\ \ esters\ \ \ peaks}{Area\ \ of\ \ internal\ \ \ s\tan dard\ \ peak} x \frac{Weight\ \ of\ \ internal\ \ s\tan dard}{Weight\ \ of\ \ sample} x100$$ **Equation 5-2**

In this study, the product yield of FAME is defining as the weight percent of FAME in the final product after removal the methanol layer in the product mixture (Equation 5-3) (Kusdiana and Saka, 2004, Minami and Saka, 2006).

$$Yeild\ \ of\ \ FAME\ \%\ \ = \frac{\text{Weight}\ \ of\ \text{FAME}}{\text{Weight}\ \ \text{of}\ \ product} x100$$ **Equation 5-3**

The comparison between yield, conversion and concentration is shown in Appendix 9.4

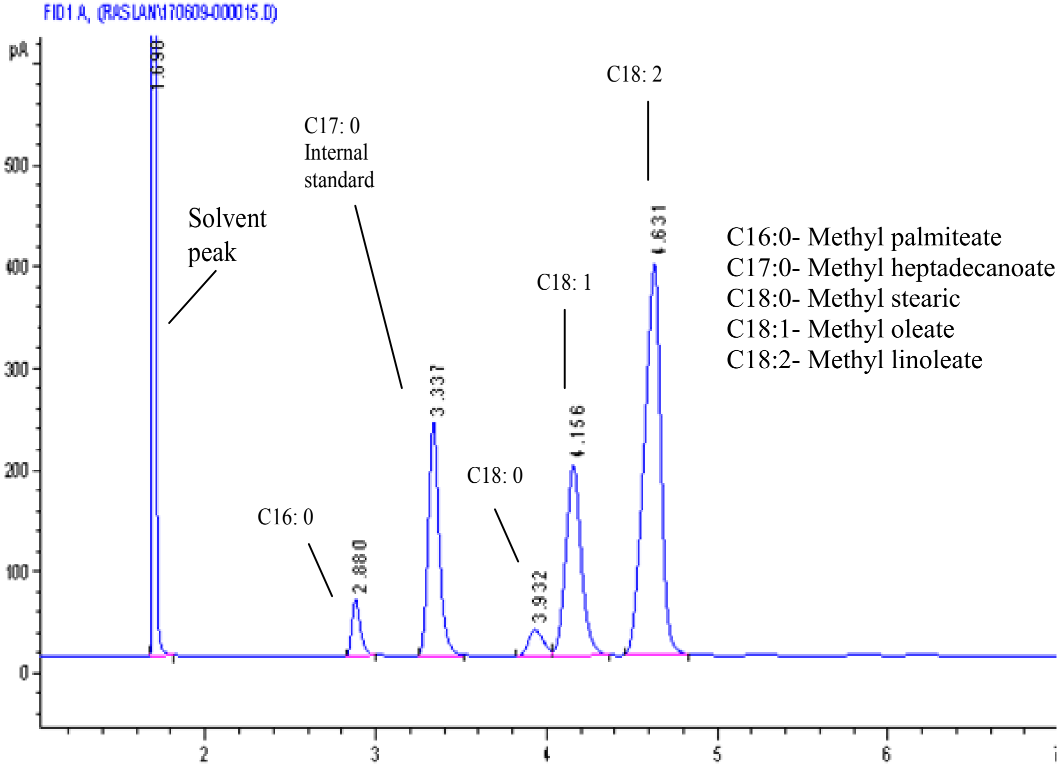

Figure 5-3. Typical chromatograph showing the peaks used to calculate the FAME content.

5.3. Results and discussion

5.3.1. Introduction

This part deals with methyl esterification of FFA that come from the hydrolysed products of sunflower oil, in supercritical methanol. This study investigated the methyl esterification reaction of FFA (see Table 5-2) that contained mainly oleic acid with supercritical methanol. The supercritical esterification experiments of methanol with FFA were carried out in a batch reaction vessel. In order to evaluate the kinetic parameters and to optimise the yield of FAME, the process variables (temperature, agaitaion speed and ratio of methanol/FFA) were varied according to those given in section 5.3.2.2.

5.3.2. Effect of different process variables on the production of FAME

In this study the effect of four process variables on the FAME yield were investigated; the initial molar ratio of methanol to FFA, stirring rate, rate of reaction temperature and the effect of reaction time, all. The influence of these processes variables will be discussed in the following sections.

5.3.2.1. Effect of the molar ratio of methanol to FFA

The molar ratio of methanol to FFA has been reported to be one of the most important variables affecting the yield of fatty acid methyl ester (FAME) (Demirbas, 2007a, He et al., 2007b). Figure 5-4 shows the effect of the molar ratio of methanol to FFA on the esterification reaction at 10 MPa, 430 rpm and 270 ^{o}C. The stoichiometric ratio for the esterification reaction requires one mole of methanol and one mole of FFA; higher molar ratios result in greater production of methyl ester (FAME) in a shorter time.

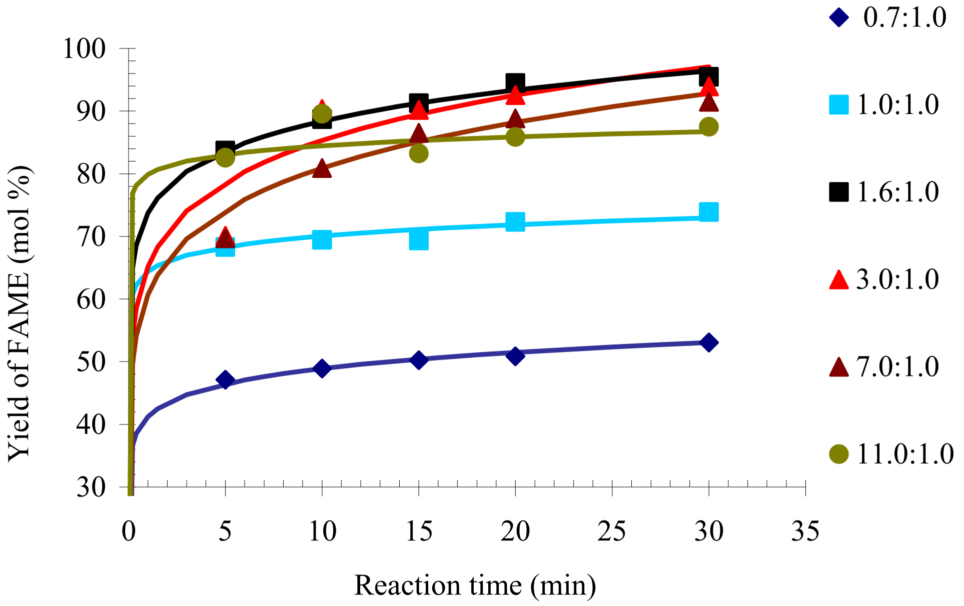

Figure 5-4. Effect of the molar ratios of methanol to FFA on the esterification reaction at 10 MPa, 270 °C and 430 rpm. (the lines are best fit to the data).

When the molar ratio of methanol to FFA is 0.7:1, the maximum equilibrium yield was 52 %. As expected, this indicated that the reaction required a greater amount of methanol to improve the FAME yield. Increasing the stoichiometric ratio to the 1:1 ratio increased the yield to 74 %. A yield of up to 97 % was obtained in 30 min when the ratio of methanol was increased to 1.6:1which is more than the required stoichiometric ratio. When the molar ratio reached 3:1, the yield of FAME did not exceed 97 %. The yield decreased to 91 % when the molar ratio of methanol was 7:1. Moreover, with high excess molar ratio of methanol:FFA (11:1) the yield further decreased to 88 %. It can therefore be concluded that the most appropriate molar ratio of methanol to FFA for esterification reaction of supercritical methanol with FFA was 1.6:1, which give an optimum yield of 97 %. The results are in agreement with the data of Minami and Saka (Minami and Saka, 2006) who observed that a higher yield of FAME was achieved when a lesser amount of methanol was added. When the ratio of methanol is higher than 1:1, it causes the equilibrium to shift to the right hand side.

At such conditions the oil is completely dissolved in the methanol and changes the reaction from heterogeneous to homogenous and increases the yield of FAME (He et al., 2007b).

5.3.2.2. Effect of stirring on the yield of FAME

The effect of stirring speed on the yield of FAME at 10 MPa, 270 °C and a 7:1 molar ratio of methanol to FFA was investigated using a Rushton turbine impeller with a diameter of 35 mm. It can be seen in Figure 5-5 that the high stirring speed had an insignificant effect on the yield of FAME. Whereas a 430 rpm affected the FAME yield in the early stages of the reaction due to mass transfer. Sanz et al., (Sanz et al., 2002) reported that 500 rpm was sufficient to minimise any mass transfer limitation in the esterification reaction. It can therefore be concluded that at > 850 rpm the esterfication reaction is not limited by mass transfer; the major factor influencing the overall conversion is the intrinsic reaction kinetics.

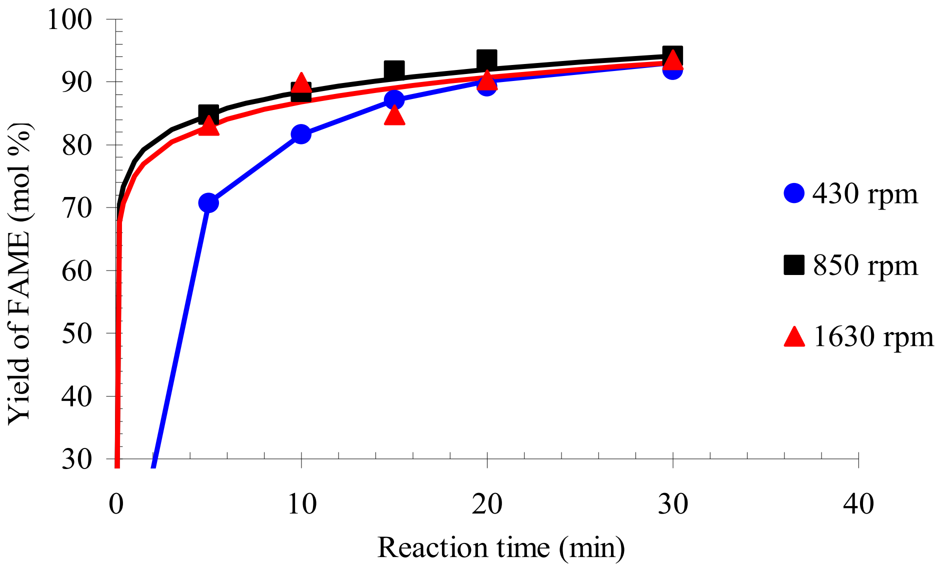

Figure 5-5. Effect of stirring speed on the esterification reaction at 10 MPa, 270 °C and a molar ratio of methanol to FFA of 7:1 (the lines are best fit to the data).

5.3.2.3. Effect of reaction temperature and time on the yield of FAME

The influence of temperature on FAME yield from 250 °C to 320 °C is shown in Figure 5-6. The reaction was carried out with a fixed molar ratio of 7:1 methanol to FFA and with an agitation speed of 430 rpm. The experimental data obtained are shown by symbols, whereas the values generated by the model (see section 5.4.3) are presented as curves. It was observed that an increase in reaction temperature had a favourable influence on the yield of methyl ester (FAME). It would do this with or without a catalyst. At a temperature of 250 °C, the maximum yield achieved was 87 % in 30 min. As the temperature increased the yield increased significantly; at 270 °C to 290 °C, the yield reached 93 % and 97 %, respectively, in 30 min. When the temperature was 320 °C, the yield of FAME reached 97 % in only 5 min. At higher temperature the solubility of oil in methanol would increase and the mass transfer limitations at the 430 rpm stirring rate would be less an issue. The yield of FAME has a tendency to increase quickly at the beginning of the reaction and then slowed depending on the concentrations of reactants and chemical equilibrium conditions. The reaction therefore approached equilibrium in the experimental temperature range in almost 20 min.

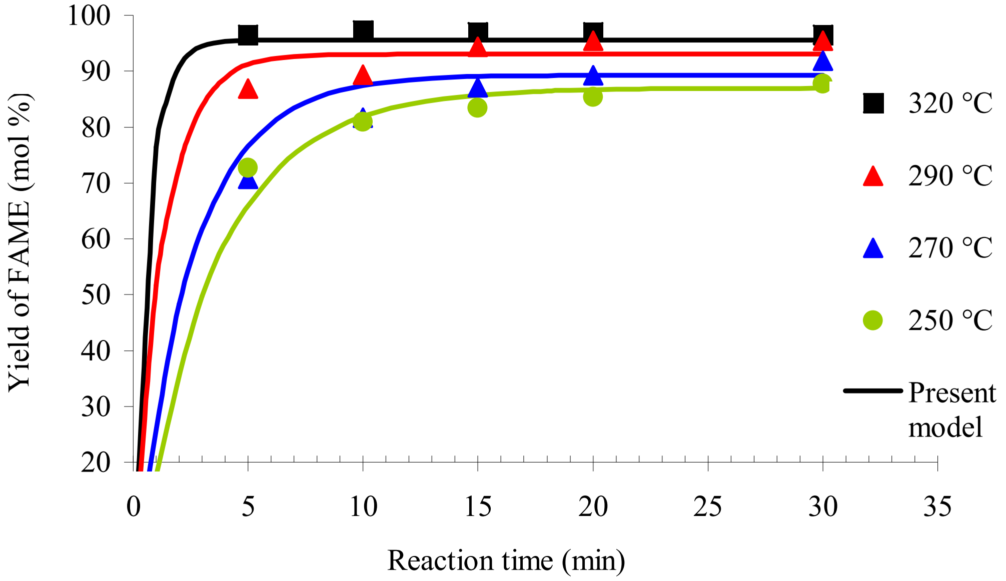

Figure 5-6. Effect of temperature on the esterification reactions at 10 MPa, 430 rpm and a molar ratio of methanol to FFA of 7:1 (the lines represent data predicted by Equation 5-4 to 5-5).

5.3.3. Continuous esterification process

The second approach in the production of biodiesel was carried out in a continuous flow system. The reaction times were varied by manipulation the flow rates of the reactants feed. In this process, the same compositions of FFA (see Table 5-2) were used. Also, the same rig used for the hydrolysis reactions in Chapter 3 was used. The best process variables as discussed in section 5.3.2 were used in order to investigate the esterification reaction in a flow system. Figure 5-7 shows data for the esterification reaction at 20 MPa, 320 ^{o}C and 1.6:1 molar ratio methanol to FFA. The yield of FAME reached equilibrium at around 90% at 7.0 min. This yield is lower than the batch reactor system by almost 7% due to better mixing in the batch reactor.

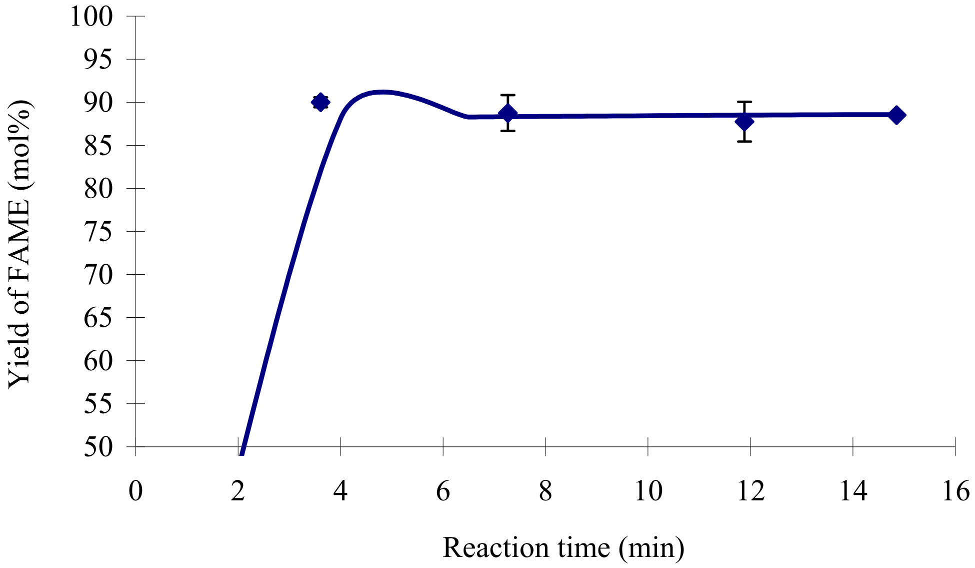

Figure 5-7. Continuous flow esterification reaction at 20 MPa, 320 °C and a molar ratio of methanol to FFA of 7:1 (The lines are best fit to the data).

5.3.4. One-step (transesterification) and two-step (hydrolysis and esterification) non-catalytic processes for the biodiesel production

Although, there is FFA production in the two-step process, these features are based on the final product of biodiesel (Kusdiana and Saka, 2004, Minami and Saka, 2006, Pinnarat and Savage, 2008). Several advantages have been achieved by the two-step non-catalytic process. The three main features are low methanol to oil ratios, reaction conditions and reaction time. Many reaction conditions with their resulting yields from non-catalytic one-step transesterification reactions are shown in Table 2-8. As shown from this table, the molar ratio of methanol to vegetable oil is about 41:1, which is much higher than the two-step esterification reaction which had a best ratio of 1.6:1.0 see Figure 5-4 in page 44. Moreover, the temperature and pressure in one-step supercritical transesterification reactions are higher compared to the two-step method, for example, in order to achieve a yield of 96 % with sunflower oil, the one-step method needs to be carried out at 350 °C and 20 MPa, while in the two-step only 320 °C and 10MPa is required. The minimum reaction time in the one-step method is 15 min to achieve a yield of 97 %, in contrast the two-step method is only 5 minutes required with less reaction temperature. Furthermore, the two-step method produces a minimal amount of mono-diglycerides and glycerol in the final product. A product that is cleaner from all these undesirable components in the biodiesel will remarkably reduce the refinery costs. Therefore, it can be concluded that the two-step esterification method operating at milder operation conditions and shorter time is more efficient than one-step transesterification; however the process economic should be evaluated.

5.3.5. Kinetic parameters of the process

A new approach to implementing a kinetics model for the reversible esterification reaction of FFA with supercritical methanol has been developed. Kinetic parameters were investigated under the following reaction conditions: temperature range 250 °C to 320 °C, a 7:1 molar ratio of methanol to FFA and a stirring speed of 430 rpm. In this model, FFA, M, FAME and W indicate the concentrations of RCOOH, CH_3OH, $RCOOCH_3$, H_2O, respectively. The kinetic differential equation governing the esterification reaction of FFA with supercritical methanol is expressed by Equation 5-4.

$$\frac{d[FAME]}{dt} = -\frac{d[FFA]}{dt} = k_1([FFA].[M]) - k_1^{'}([FAME].[W]) \qquad \textbf{Equation 5-4}$$

The rate of formation of methyl ester (FAME) is equivalent in magnitude to the rate of FFA reacted, but is denoted by negative sign and presented as dx/dt (see Equation 5-5).

$$\frac{dx}{dt} = k_1((n/1) - x)(1 - x) - k_1^{'}(x)(W_0 + x)$$ **Equation 5-5**

Where x is the moles of FAME produced or moles of methanol or FFA reacted, t is the reaction time (min), n/1 is the ratio of methanol to FFA and W_0 are the moles of water per mole of FFA in the feed. The first order differential equation was solved using a fourth-order Runge–Kutta (Kreyszig, 1999) programmed in Excel (Microsoft Office 2003) using initial values of $FFA_0 = 1$, $FAME_0 = 0$, $W_0 = 0$, and M = n as the molar ratio of methanol to FFA in the feed.

For the limited experimental data, a power exponential equation was fitted Equation 5-6 to represent the entire reaction behaviour during the reaction time, by applying Curve Expert 1.3. CurveExpert 1.3 is a powerful curve fitting system. CurveExpert can be programmed to compare the experimental data to each model from its library and enable selection of the best curve(CurveExpert, 2009). The equation allows the regeneration of as many data points as required for evaluating all the reaction parameters.

$$FAME = A(1 - e^{-Bt})^p$$ **Equation 5-6**

Where A, B are constants, p is the power (optimised by Microsoft Excel solver) of the function and FAME is yield of FAME in mol%.

The values of k_1 and $k_1^{'}$ were initially guessed to start the programme and were later estimated, using Microsoft Excel's non-linear optimisation built-in function

"*Solver*", for the best possible representation of the experimental data. The choice of step size was designed to reduce unnecessary computation, without affecting the accuracy of the results. The only constraint added was that all the rate constants should be greater than zero (positive). Using the above approach, the numerical interpolated data from the power exponential function (Equation 5-6) were used to obtain all the rate constants for the complete kinetic regime.

In defining the objective function for the esterification of FFA with supercritical methanol, the FAME product is equivalent to the sum of one times the moles of FFA reacted or equivalent to the total moles of alcohol consumed. The sum of the squares of percentage error between the experimentally measured (exp.) and numerically calculated amounts (cal.) of FAME was minimised, by the objective function (OF) given in Equation 5-7.

$$OF = Minimise \sum_{j=1}^{N} \left(\frac{[FAME]_j^{exp} - [FAME]_j^{cal}}{[FAME]_j^{exp}} \times 100 \right)^2 \qquad \textbf{Equation 5-7}$$

where N is the number of experimental data points and $[FAME]_j$ is the fatty acid methyl ester concentration at a given time for the isothermal conditions. Using this approach, the experimental data were used to obtain the two rate constants for the complete kinetic regime under investigation. Figure 5-8 shows the algorithm used to estimate the parameters of chemical kinetics for the esterification reaction. The minimised average errors between the experimental and calculated data were found to be 2.4 % for 250 °C, 2.7 % for 270 °C, 3.7 % for 290 °C and 0.33 % for 320 °C. Alenezi et al. (2009) have provided a detailed description of solving Equation 5-3 for the hydrolysis of sunflower oil.

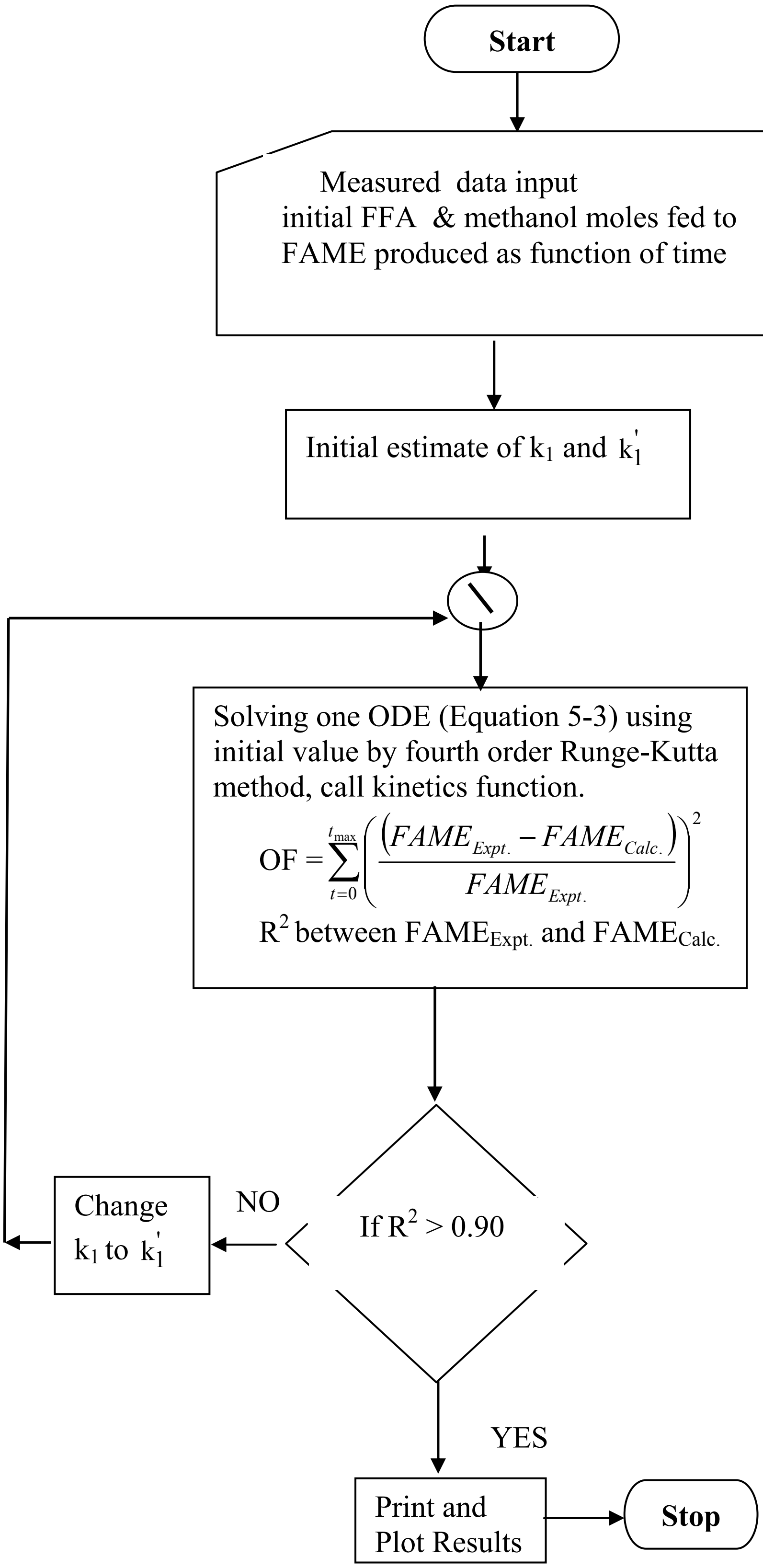

Figure 5-8. Flowchart of parameter estimation programme for chemical kinetics of esterification of FFA in supercritical methanol.

The optimum values of the rate constants, k_1 and $k_1^{'}$ representing the experimental data for the esterification reaction are shown in Table 5-4 and are plotted versus 1000/T (K^{-1}) in Figure 5-9. The rate constants k_1 and $k_1^{'}$ are found to increase as a function of temperature, confirming Arrhenius' observations. The computed activation energy values from Equation 4-12, E_{a1} and E_{a2} are obtained from the slope of the Arrhenius plot.

It is evident that the E_{a1}, value for the forward reaction from FFA to FAME is almost 3 times higher than the reversible reaction. This is because the esterification reaction is an endothermic type and requires high energy to start the reaction. The activation energy for the reversible reaction FAME to FFA, E_{a2} is much less than that of $E_{a1,}$ reflecting the ease of reaction at high temperature. The value of the equilibrium constant would approach near to unity and the overall conversion reaches almost 97 %. Moreover, the low value of the activation energy of the reverse reaction (FAME to FFA), speeds up the approach to equilibrium.

The activation energy value of 72 kJ/mol for the forward reaction was found to be in agreement with the value, for similar reactive systems. Tesser et al., (Tesser et al., In press) reported 67 kJ/mol, for free fatty acids esterification and by Song et al., (Song et al., 2010) 32 kJ/mol, the esterification of oleic acid in subcritical methanol using a zinc acetate catalyzed. However, both set of workers have simplified the kinetic reaction equation and neglected the reverse term of the equilibrium reaction.

Table 5-4. The kinetic parameters for the esterification of FFA with supercritical methanol where the methanol to FFA molar ratio is 7:1.

No.	*T*	k_1	$k_1^{'}$
1	250	0.035	0.037
2	270	0.050	0.041
3	290	0.110	0.054
4	320	0.230	0.063
	R^2	0.98	0.97
Arrhenius Constants	A_0	$5.0x10^{5}$	7.9
Activation Energies	E_a	72	23.2

T, temperature (^{o}C); k_1 and $k_1^{'}$, rate constants (min^{-1}[mol/mol of FFA]$^{-1}$); E_{a1} and E_{a2} energies of activation (kJ/mol); A, pre-exponential factor (min^{-1}[mol/mol of FFA]$^{-1}$).

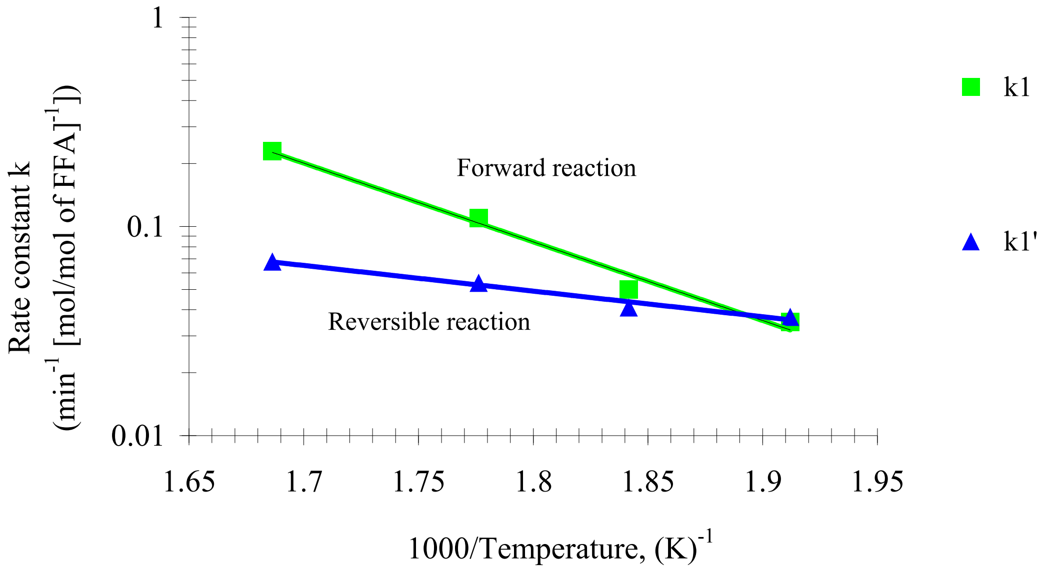

Figure 5-9. Arrhenius plot for the esterification reaction.

5.4. Conclusion

The non-catalytic esterification reaction of FFA with supercritical methanol was investigated at four different temperatures, stirring rates and different time intervals. The proposed kinetic model represented the experimental data very well, with minimum deviation. The model is in very good agreement with the experimental measured values of the FAME product for all the data and the maximum absolute computed deviation between the experimental and numerically evaluated value at any time is less than 3.7 %. The esterification reaction is a second order reversible endothermic reaction. The forward reaction requires a substantial amount of energy, but, predictably, the reversible reaction occurs more easily as evidenced by the energy of activation value of these consecutive step reactions. The use of supercritical methanol in the esterification reaction has been found to be an effective method to produce a high yield of FAME (biodiesel). It was found that the esterification yield depends on the reaction temperature and the initial ratios of FFA and methanol but the stirring speed has no further effect on the yield of FAME at high temperature. At 320 ^{o}C and 430 rpm; only 5 min was required to achieve a yield of 96.7 % of biodiesel and separation of the final product from the catalyst is not necessary. This result also surpasses the technical regulations of EN14214 European-Standard (2008) for the FAME content.

CHAPTER 6

DOWNFLOW GAS CONTACTOR REACTOR (DGCR) FOR BIODIESEL PRODUCTION

6.1. Overview of the DGCR

A wide range of industrial applications depend on the efficient contact between different phases and within the same phase (with reference to gases, liquids and solids). In the past few years, stirred tank reactors have been most popular for carrying out catalytic and non-catalytic reactions. Stirred tank reactors have several advantages, for example, their temperature is easy to control, their cost is moderate, and they are flexible and relatively easy to operate. Despite these advantages, however, they suffer from scaling-up which are dependant on the mechanical stirring (power) for large configuration and have mass transfer limitations. In order to overcome these problems, the downflow gas contactor reactor (DGCR) was introduced by Boyes and Ellis (1976) as a gas-liquid contactor and further developed as a three-phase chemical reactor. The state-of-the-art DGCR has a number of advantages (see section 2.4.4). In this study, the DGCR is used for the first time as a two phase liquid-liquid contactor reactor.

The DGCR is a simple reactor consisting of a single column with an orifice at the top of the reactor through which liquid is introduced. The critical feature of the DGCR is the high velocity of the liquid stream or jet which is generated by a pump and introduced into the top of the flooded column. The DGCR is operated in batch mode with recycle loop.

6.2. Materials and methods

6.2.1. Materials used

6.2.1.1. Gases

The gases used throughout the present study were supplied by the British Oxygen Company (BOC) UK, as follows:

- Helium, Purity 99.99 %.
- Hydrogen, Purity 99.95 %.

6.2.1.2. Reagents

The chemical materials used are listed below in Table 6-1 . All the chemicals used in the experiments were of reagent grade or higher and were used as received, without any purification. Deionised water was used to prepare all the chemical solutions.

Table 6-1. A list of chemical materials used.

Material	*Cas number*	*Grade*	*Supplier*
Methanol (99.9 %)	67-56-1	A.R	Fisher
Ethanol (99.9 %)	64-17-5	A.R	Fisher
Heptane (99.9 %)	142-82-5	A.R	Fisher
Methyl heptaecanoate (99.5 %)	5-163-3	A.R	Sigma-Aldrich
Sodium hydroxide	1310-73-2	A.R	Fisher
Phenolphthalein	77-09-8	A.R	Hopkin & Williams Ltd (UK)
Sunflower oil	8001-21-6	A.R	Leading supermarket chain (U.K)

6.2.2. Apparatus and methods

Experimentation with biodiesel using the DGCR with a total reactor volume of 1.13×10^{-3} m^3 was carried out at WRK Design and Services. The DGCR is operated in batch mode with recycle loop.

6.2.2.1. Experimental equipment

The DGCR and other pieces of equipment used in this research are listed below:

- Glass column reactor: made from QVF glassware, length 0.5588 m and diameter 0.0508 m

- Centrifugal pump: Midland pump MANFG company limited, with AEG motor
- Orifice: diameter of 5-10 x10^{-3}m.
- Relief valve: stainless steel Swagelok
- Butterfly valves: stainless steel Swagelok
- Regulating valve: stainless steel Swagelok
- Pressure gauges: standard bourdon gauges ranging from 0-0.7 MPa with accuracy of 1.25x10^{-2} MPa
- Stainless steel pipe connections: a 6.0 x10^{-3} m o.d. and a 1.26 x10^{-2} mm o.d. with thickness of 1 x10^{-3} m and 1.63 x10^{-3} m, thus giving i.d. of 4 and 9.3 x10^{-3} m, respectively.
- Glass reservoir (break vessel): Volume 2.5x10^{-3} m^3
- Oil heating bath: Volume 5x10^{-3} m^3
- Heating coil with a temperature controller and gear pump: Techne (Cambridge) Limited Company, TE-8A
- Thermocouple: HANNA Instrument, K-thermocouple
- Thermometers: mercury type
- Flow meter: Platon Rotameter with maximum flow rate 4x10^{-2} m^3/min with increment scale of 1x10^{-2} m^3/min
- Pyrex measuring cylinders: 5x10^{-4} m^3 and 6x10^{-4} m^3
- Heating and stirring plate: Heidolph Company, MR-3001K
- Plastic magnetic stirring:
- Balance: A &D company limited, K0001
- Plastic hose connections: Griflex Reinforced flexible hose with o.d. of 1.26 x10^{-2} m

6.2.2.2. Experimental methods

The experimental setup of the apparatus is shown in Figure 6-1. The rig comprised a centrally mounted QVF glassware holding column that had a total volume of 1.13×10^{-3} m^3 including the associated stainless steel pipes and reinforced flexible plastic hoses. Standard fibre gaskets and flanges were used to join and seal the two glass sections of the column. A stainless steel plate was fitted at each end of the reactor, sealed with rubber gaskets. The top part of the column inlet is shown in Figure 6-2.

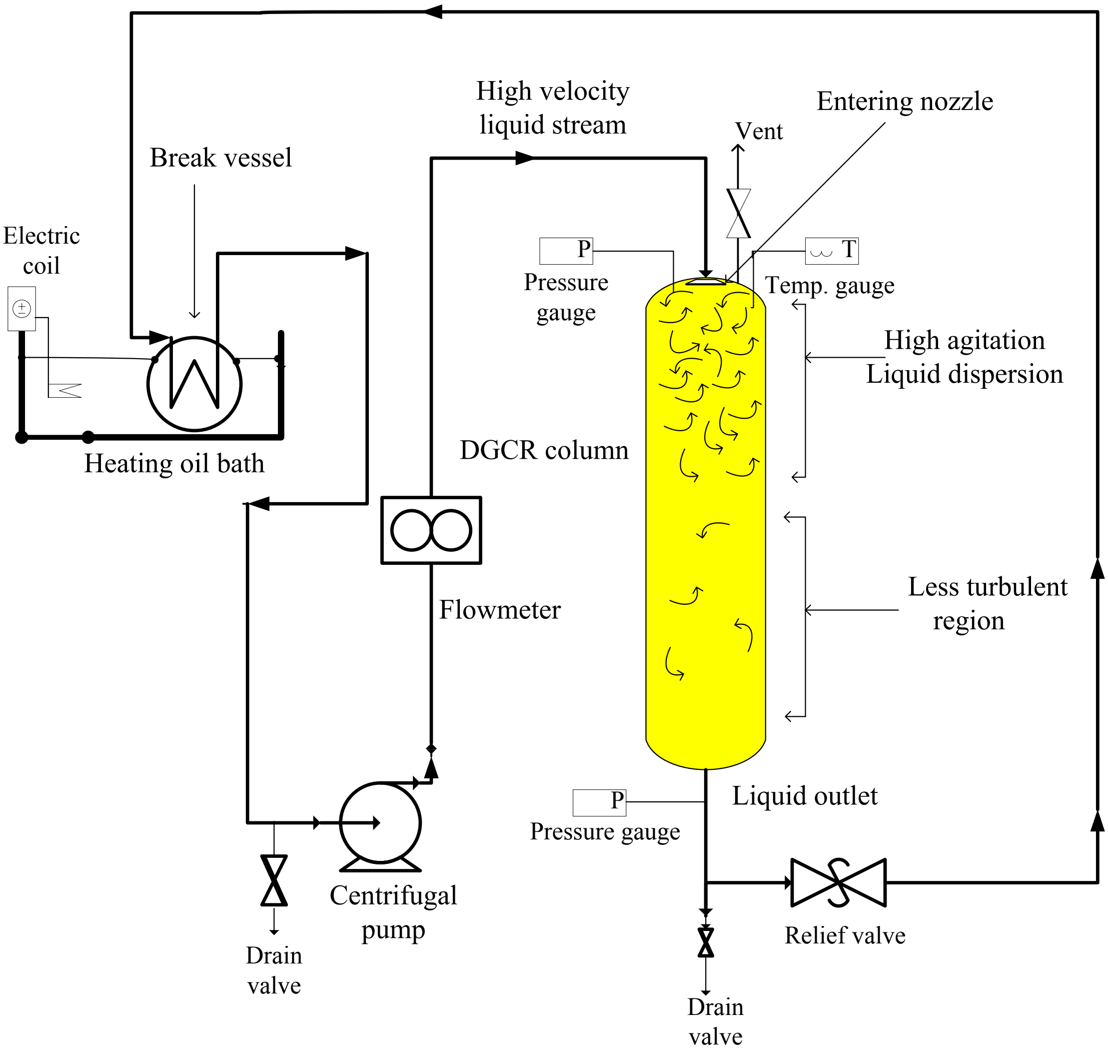

Figure 6-1. Schematic diagram of experimental apparatus used for the DGCR rig.

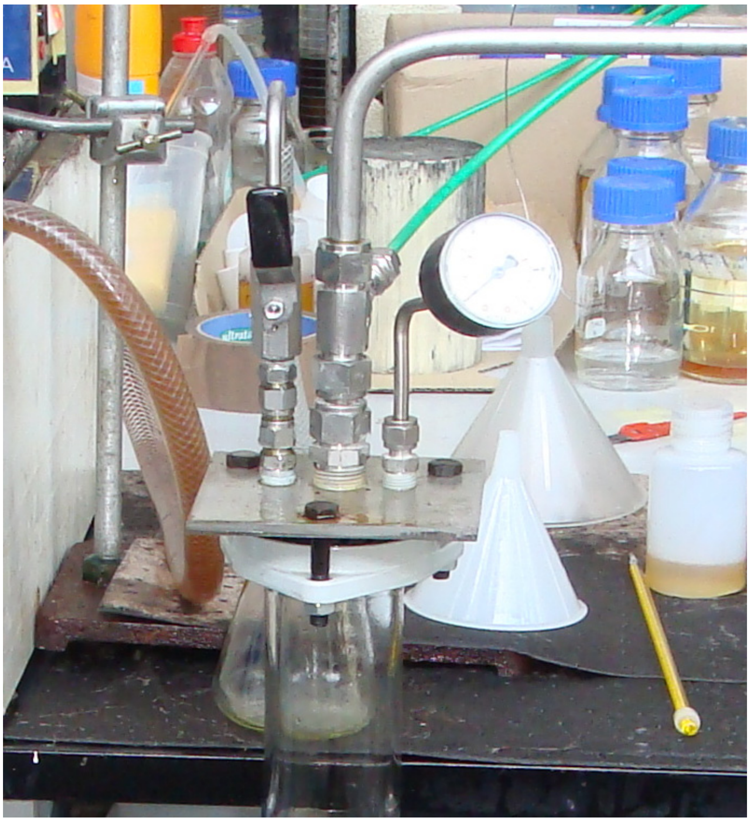

Figure 6-2. The top part inlet of the DGCR rig.

In the upper part of the column, the stainless steel plate incorporated a centrally situated 1.2 x10^{-2} m i.d. inlet, the inside of which was threaded, allowing orifices of different sizes (1-10 x10^{-3} m) to be used. An orifice plate is attached to the underside of the plate. The top part also included a 6 x10^{-3} m o.d. stainless steel pipe vent which was used to vent out the air and fill the column with reactants. At the bottom of the DGCR, three T-pieces are connected with 6.0 x10^{-3} m to stainless steel pipes and fixed with butterfly valves to allow the column and the pipe system to be drained. Standard bourdon gauges were fitted to the top and bottom plates of the column with 6.0 x10^{-3} m o.d. stainless steel tubing; these were used to measure the pressure and pressure drop in the column. For safety reasons a pressure relief valve was situated at the bottom part of the column. The reaction temperature was monitored by a thermocouple inserted within the liquid in a break vessel (a glass reservoir). In addition, the reactor temperature was measured by an external thermometer when a sample was drawn from the reactor. A break vessel was incorporated into the reaction system to accommodate the volume expansion within the column. This break vessel contained the oil at the start of the experiment. This vessel was placed in an oil bath which was heated by a heating coil with a temperature controller and a gear pump in order to circulate the heated oil through the bath (as shown in Figure 6-3). The connecting plastic hoses were further connected to stainless steel pipes, all with an i.d. of 9.3 x10^{-3} m. A centrifugal stainless steel pump was installed to circulate the liquids from the break vessel to the column and vice versa. A 0.127 m i.d. including a regulating valve was fitted to the pump, to allow smooth operation and control of flow rate to the column. The discharge of the pump was connected to the column though a needle valve and a Platon Rotameter to measure the flow rate of the reactants, which entered the column.

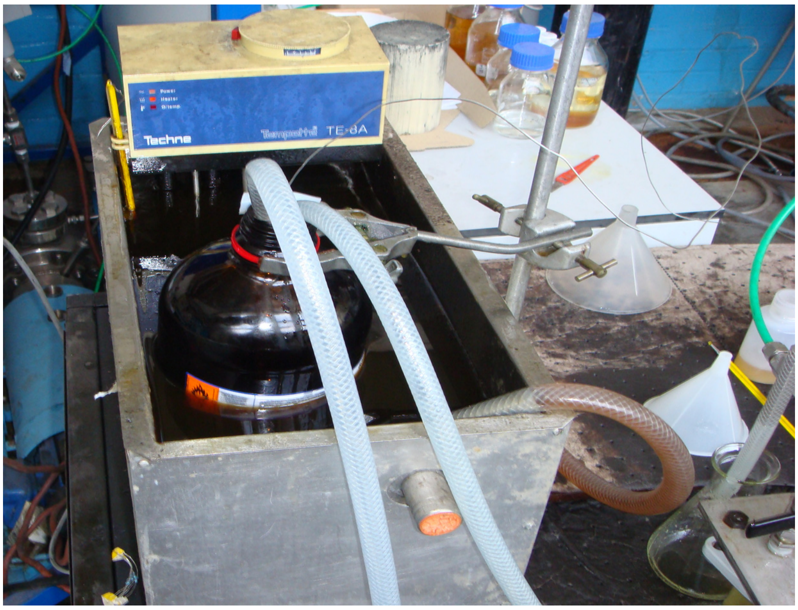

Figure 6-3. Heating coil inside oil bath and break vessel showing hose connections to and from the DGCR column.

Figure 6-4 shows a photograph of the DGCR rig in operational mode. The sunflower oil reactant was measured by a 5x10^{-4} m^3 measuring cylinder and stored in the break vessel. Once the break vessel was half full (1.5x10^{-3} m^3), the oil transferred from the break vessel to the column using the centrifugal pump. The vent lines for the DGCR reactor were opened until the air inside the reactor vent escaped and the reactor drain lines were closed. The oil in the bath heated the break vessel that contained the sunflower oil (as shown in Figure 6-3). The desired amount of methanol was measured by a 6x10^{-4} m^3 measuring cylinder and the desired amount of sodium hydroxide was measured by a balance. Both the measured amounts of methanol and sodium hydroxide were added into a 1x10^{-3} m^3 conical flask. The conical flask was placed on a heating and stirring plate to increase the solubility of the sodium hydroxide in the methanol. This process continued until the sodium hydroxide was completely dissolved in the methanol. The temperature of the solution was monitored not to exceed 40 °C.

Figure 6-4. Photograph of the DGCR rig.

The detailed procedures for starting up and shutting down the DGCR are described in the following sections.

6.2.2.2.1 Start-up procedure for the DGCR

In this experimental study, the following procedure was followed for the DGCR:

1- The three bottom drainage valves (as seen in Figure 6-1) were checked to ensure that they were fully closed.

2- The vent, column outlet valve and pump by-pass valve were fully opened.

3- The sunflower oil feed to the DGCR was measured by a $5x10^{-4}$ m^3 measuring cylinder and stored in the break vessel.

4- The centrifugal pump was started once the break vessel was half full to transfer sunflower oil from the break vessel to the column.

5- The vent line in the upper part of the column reactor was opened until the air inside the reactor vent had escaped and then the valve was closed.

6- The desired amount of sunflower oil was continued to be added in the break vessel, while the oil was kept circulating between the break vessel and the column to leave space for other amount of oil.

7- The thermocouple line was inserted into the break vessel and the thermocouple was switched on.

8- The flow rate of sunflower oil entering the column was adjusted by two valves, a by-pass regulating valve and a needle regulating valve, and measured by a Platon Rotameter.

9- The oil in the bath heated the break vessel with sunflower oil inside, as shown in Figure 6.3.

10- The sunflower oil was kept in circulation for about 30 min until the desired temperature was reached.

11- The desired amount of methanol and NaOH were measured.

12- Both the measured amounts of methanol and sodium hydroxide were poured into a 1x10^{-3} m^{3} conical flask which was placed on the heating and stirring plate.

13- The solution in the flask was stirred and heated until the sodium hydroxide was completely dissolved in the methanol. The temperature of the solution was monitored to not exceed 40 ^{0}C.

14- Once the circulating sunflower oil reached the required temperature, the solution of methanol with dissolved sodium hydroxide was added to the break vessel and the time taken by a stop watch.

15- Samples were drawn from the DGCR vent line at different time intervals, typically 2.5, 5, 10, 15, 20, 30, 40, 60 and 80 min.

6.2.2.2.2 Shut-down procedure for the DGCR

The following procedure was used for shutting down the process.

1- The electric power for the heating coil and the thermocouple was switched off.

2- The liquid supply to the column was shut off by switching off the centrifugal pump.

3- The vent valve was opened.

4- The drainage valve was opened and the product was collected in a container.

5- The break vessel was removed from the heating oil bath and emptied into the product container.

Table 6-2 shows the operating conditions of the DGCR.

Table 6-2. DGCR operation conditions

Parameters	***Values***
Orifice diameter	0.005-0.010 m
Recirculation rate	8 x10^{-3}-10 x10^{-3} m^3/min
Reactor temperature	30-40 °C
Reactor pressure	0.1-0.11 MPag

6.2.3. Analytical methods

Reaction samples were analysed by GC in a similar manner to that give in section 5.2.3. In this study, the mass yield (kg FAME per kg oil) has been measured by measuring the mass fraction of FAME in the oil layer after removal the glycerol and catalyst layer in the product mixture (Equation 5-3) (Gui et al., 2009, Minami and Saka, 2006, Saka and Isayama, 2009, Vicente et al., 2007). This is a reasonable approximation provided the molecular weight of the oil is approximately three times the molecular weight of the FAME (see Appendix 9.4).

6.3. Results and discussion

6.3.1. Introduction

This section discusses the results of experiments performed to study the production of biodiesel in the DGCR. The reaction studied was the transesterification of sunflower oil with alcohol (methanol and ethanol). Although DGCR has been used for many industrial applications, such as hydrogenation, the treatment of industrial waste effluent and oxidation reactions, this is the first time that DGCR has been used for the production of biodiesel. The main objective of this work was to investigate the effect of various operating variables (molar ratio of alcohol to oil, reaction temperature and time, catalyst loading and type of alcohol) in order to establish the optimal conditions for obtaining the highest yield of biodiesel.

The turbulence in the top part of the column was calculated to be around 13000 (see Appendix 9.4). This indicated that very high level of dispersion in this area and efficient mass transfer.

In the EU countries, biodiesel is sold according to the technical regulations of EN14214 (European-Standard, 2008), which stipulates a 96.5 % ester content (European-Standard, 2008). All over the world in the area of biodiesel production, researchers are using simple chemical methods to produce biodiesel without fulfilling some of the technical requirements such as kinematic viscosity, ester content and density (Lois, 2007). The results described in this Chapter detail how 96.5 % ester content was reached in the DGCR. Moreover, other tests were made to verify other specifications of the EN14214 (European-Standard, 2008), such as kinematic viscosity, density, iodine value and acid value (see section 6.3.4). This chapter discusses a range of each process variables to find their effect on the yield of FAME and to examine the performance of DGCR in the transesterification reaction.

6.3.2. Effect of different operating parameters on the production of biodiesel

In the transesterification reaction of biodiesel a number of parameters can be varied. The studies reported in the literature have investigated almost the same process variables but these have varied over different times in order to optimise the yield of biodiesel (Bambase et al., 2007, Dizge et al., 2009, He et al., 2007b, Minami and Saka, 2006, Varma and Madras, 2007).

Recently, some authors (Leung and Guo, 2006, Pinnarat and Savage, 2008) have stated that in general the main process variables needed to achieve high biodiesel conversion are reaction temperature, pressure, quantity of catalyst, reaction time and the alcohol to oil ratio.

These process variables studied are listed below:

- Reaction temperature and time
- Catalyst loading
- Molar ratios of initial oil/fat to alcohol
- Type of alcohol used

The yield of an individual FAME increased almost in the same rate as the total FAME observed in the hydrolysis reactions (section 3.3.2). The proportion for each FAME can be shown in Table 6-3.

Table 6-3. Pupation of each FAME

FAME	*Formula*	*Proportion (%)*
Methyl palmitate	C16:0	5
Methyl stearate	C18:0	4
Methyl oleate	C18:1	28
Methyl Linoleic	C18:2	60

The influence of these processes variables will be discussed in the following sections:

6.3.2.1. Effect of methanol to sunflower oil molar ratio on the yield of FAME

The molar ratio of alcohol to vegetable oil is one of the most important variables in the transesterification reaction affecting the yield of FAME (Demirbas, 2007a, Fangrui and Hanna, 1999, Kusdiana and Saka, 2001a, Pinnarat and Savage, 2008). The presence of sufficient methanol during the transesterification reaction of vegetable oil is crucial to break-up the glycerine-fatty acid link as shown in Figure 2-3 in page 14 (Al-Widyan and Al-Shyoukh, 2002). It is easy to increase the methanol ratio to modify the reaction and increase the yield of FAME in a shorter time. This way is very effective as the methanol fraction directly increases the interfacial area of the two phases (up to 50 % v:v) (Kusdiana and Saka, 2001a, Slinn, 2008). Many authors have studied different methanol oil ratios and each offers a different optimal ratio for this reaction. Starting from a higher ratio, Miao and Wu (2006) have reported the production of biodiesel from microalgal oil and a large quantity of methanol, with a molar ratio of about 70:1 and 84:1 methanol:oil which slow down the separation of the ester from glycerol phases during the production of biodiesel. In their study, a 56:1 molar ratio of methanol to microalgal oil was reported to be the best for the biodiesel reaction. More recently, Sharma et al. (2008) found that an excess molar ratio of methanol to oil of more than 6:1 made the ester recovery difficult and increased the cost of the total process. The vegetable oil was transesterified using a 6:1-40:1 alcohol-vegetable oil molar ratio in a catalytic reaction and at supercritical conditions for the alcohol reaction (Demirbas, 2007a, Kusdiana and Saka, 2001a). Other researchers (Sharma and Singh, 2009) further noted that the molar ratio of methanol to alcohol depended on raw oil and its acid value and a 10:1 molar ratio is used most often.

In this work, the initial molar ratio of methanol to oil was optimised for the transesterification process in the DGCR. Figure 6-5 and Figure 6-6 show the effect of initial molar ratio of methanol to sunflower oil in the DGCR system at 40 ^{o}C and 0.29 wt.% NaOH catalyst load based on oil mass. As shown from these figures, when the molar ratio is 2.4:1 only 76 % of methyl ester is achieved in 20 min of reaction time.

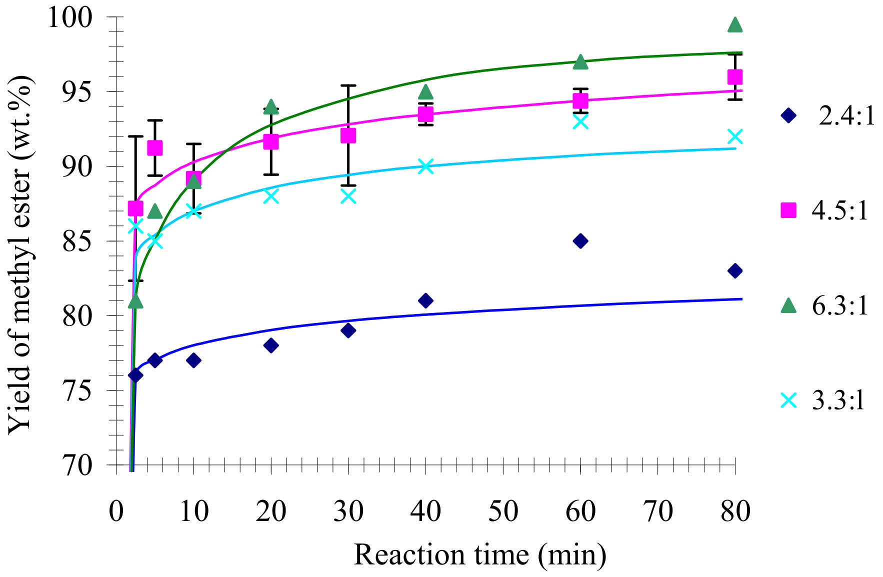

Figure 6-5. Effect of methanol to sunflower oil molar ratio on the yield of FAME (reaction conditions: 40 °C and NaOH catalyst load 0.29 wt. % based on the oil. Data points are experimental results and the lines show the best fit to the data).

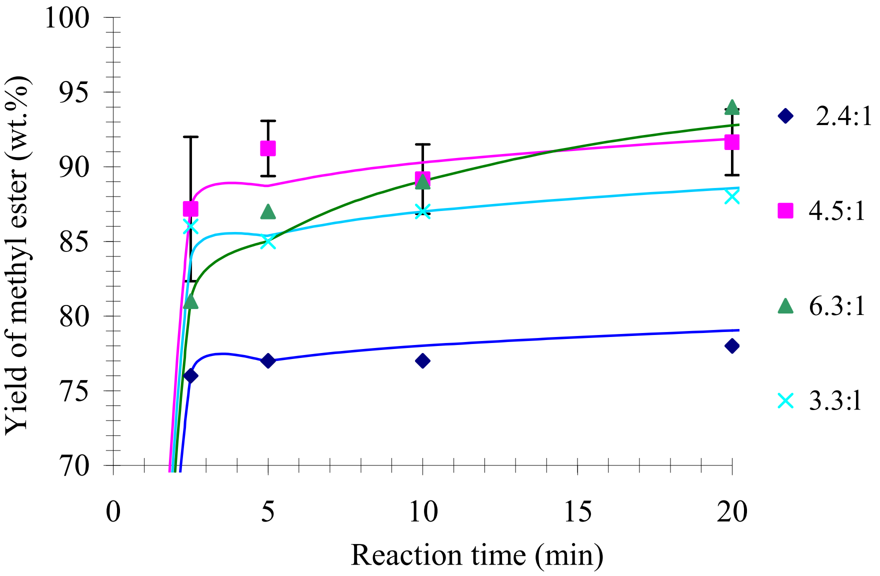

Figure 6-6. Expansion of Figure 6.5 showing earlier reaction times. Effect of methanol to sunflower oil molar ratio on the yield of FAME. (reaction conditions: 40 °C and catalyst load 0.29 wt.% based on the oil mass. Data points are experimental results and the lines are best fit to the data).

This is interesting result as the stoichiometrical molar ratio for the transesterification reaction requires 3 moles of alcohol and 1 mole of oil to yield 3 moles of FAME and 1 mole of glycerol. In practical terms, the alcohol molar ratio needs to be higher in order to drive the equilibrium to yield the maximum (Fangrui and Hanna, 1999). This explains why the maximum 85 % yield was achieved with this molar ratio. Moreover, when the molar ratio was further increased to the ratio (3:1), the yield of FAME rose considerably to 88 % and 93% after 20 and 60 min of reaction time, respectively. Moreover, an 85 % yield of FAME was reached in only 5 min. This yield of FAME is higher than what is reported in the above literature for the same transesterification reaction of vegetable oil with methanol. Increasing the molar ratio to more than the stoichiometric reaction ratio of 4.5:1 provided only little improvement in the yield of FAME. A yield of 96.6 % was reached for this stoichiometric reaction ratio in 80 min, while 91.6 % and 94.5 % of FAME yield occurred after 20 min and 60 min, respectively. The two yields approach the Technical regulations EN14214 (European-Standard, 2008). In this molar ratio, the error bars show little difference between each run especially when the run time was increased with a maximum variance of 2.7 %. Another run was undertaken at a higher molar ratio of 6:1 to investigate this molar ratio reported by other researchers (Demirbas, 2007a, Fangrui and Hanna, 1999, Kusdiana and Saka, 2001a, Meher et al., 2006, Sharma et al., 2008). For this molar ratio 94 %, 97 % and 99.5 % was reached in 20, 60 and 80 min, respectively. These yields of FAME were not considered to be significantly practical compared with the previous molar ratio of 4.5:1. In general, a higher alcohol to oil molar ratio was needed to gain a higher yield, but eventually a point is reached where a higher molar ratio of alcohol was not proportionately effective. However, a 99.5 % is very impressive and demonstrates the advantage of the DGCR toward the biodiesel reaction.

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6.3.2.2. Effect of catalyst loading on the yield of FAME

The type and load of catalyst are important factors in the transesterification of oil/fat with alcohol. The catalysts commonly used in this reaction are classified as alkali, acid and enzyme. Among these catalysts alkaline catalysts such as sodium hydroxide, sodium methoxide, and potassium hydroxide are the more effective and more commonly used (Fangrui and Hanna, 1999, Ma et al., 1998, Sulaiman, 2007). An acid-catalyst used in the production of biodiesel has received less consideration because it is 400 times slower than an alkali catalyst (Sulaiman, 2007).

The transesterification reaction of beef tallow was discussed by Ma et al. (1998), who compared two types of catalyst, sodium hydroxide and sodium methoxide. They found that sodium hydroxide was significantly better in achieving a higher yield, however, this result is not the same as that reported by Freedman et al., (1984). They reported that sodium methoxide is more effective than sodium hydroxide for laboratory use.

Sodium hydroxide (see Table 6-4) was used in this study, because it was less hazardous, more effective and cheaper than the sodium methoxide (this is made inside by adding NaOH and MeOH), acid or enzyme catalysts (Boocock et al., 1998, Leung and Guo, 2006).

Table 6-4. Unit price of catalyst as of 2005 (Leung and Guo, 2006)

Item	***NaOH (purity: 99 %)***	***KOH (purity: 92 %)***	***CH_3ONa (purity: 99 %)***
Price (US$/ton)	400	770	2300

Figure 6-7 and Figure 6-8 show the relationship between the reaction time and catalyst loading at 40 ^{o}C and a methanol to sunflower oil molar ratio of 4.5:1. It can be seen that the loading of the sodium hydroxide can accelerate the yield of FAME. The yield of FAME in Figure 6-7 at 80 min is higher the 100 % because of two reasons. First the assumption that all FAME have the same response factor in the analytical method (European Standard Method EN-14213). Second there are very small errors about 1-1.5% in each sample analysed from the GC.

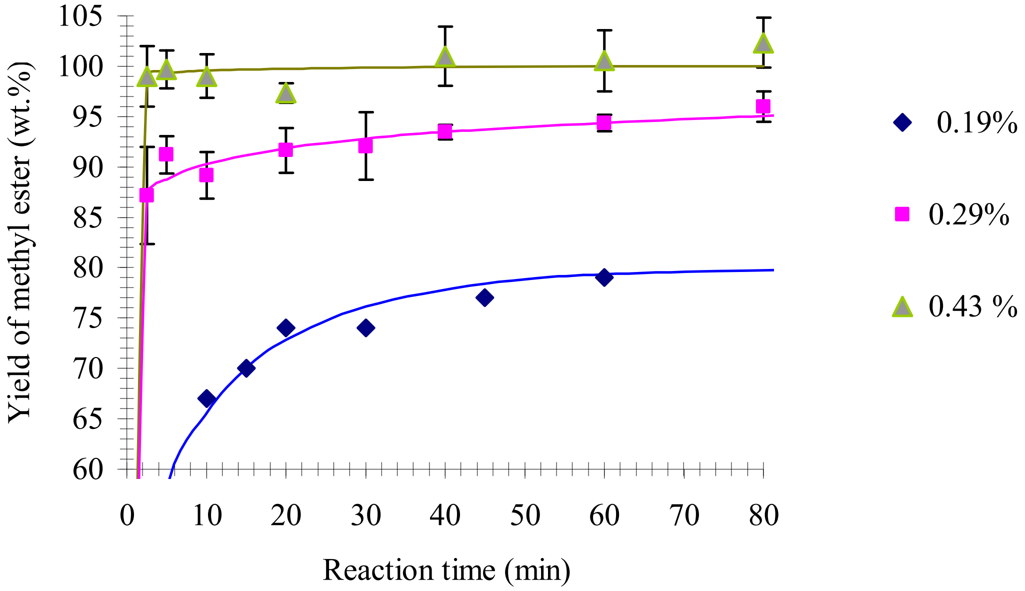

Figure 6-7. Effect of catalyst loading based on the oil on the yield of FAME (reaction conditions: 40 °C and molar ratio methanol to sunflower oil 4.5:1.0. Data points are experimental results and the lines are best fit to the data).

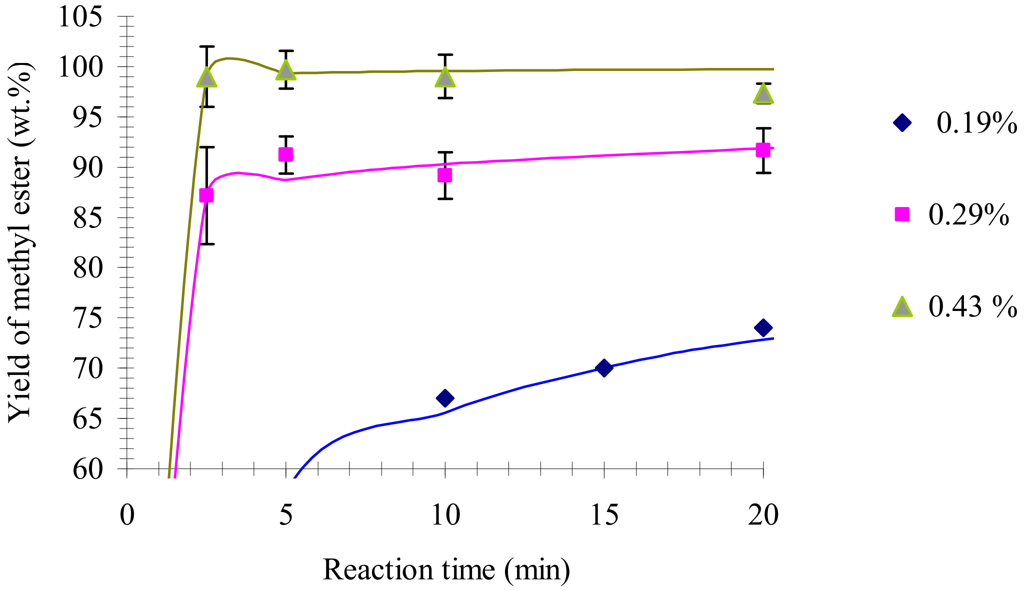

Figure 6-8. Expansion of Figure 6.7 showing earlier reaction times. Effect of catalyst loading on the yield of FAME (reaction conditions: 40 °C and molar ratio methanol to sunflower oil 4.5:1.0. Data points are experimental results and the lines shown are best fit to the data).

When catalyst loading was 0.19 wt.% (based on the oil mass), yields of only 74 % and 79 % were reached at 20 and 60 min, respectively. As the catalyst loading was increased to 0.29 wt.% yields of 88 % and 93 % were attained at 20 and 60 min, respectively. For a catalyst load of 0.43 wt.% an extraordinary result was recorded; after only 2.5 min 99 % of FAME yield had been achieved. This catalyst loading, methanol to oil ratio and reaction temperature have not been reported in the literature before as achieving such a high yield of FAME in so short a time. This result also surpasses the technical regulations of EN14214 (European-Standard, 2008) for the FAME content.

The residual catalyst settled down with the glycerol layer, as shown in Figure 6-9. The residual catalyst and glycerol was separated by gravity without the need for water washing. Boocock et al. (1998) reached a 95 % yield of FAME in a flat-bottom flask with a magnetic stirrer after 15 min with a NaOH catalyst load of 1.3 wt.% based on oil mass and a 4.2:1 molar ratio of methanol to soybean oil with tetrahydrofuran as cosolvent and 23 ^{o}C. They also reported that a dramatic increase in reaction rate was achieved by increasing the sodium hydroxide load from 1.0 to 2.0 wt.% based on the oil mass, which resulted in a 98.8 wt.% of FAME content in only 3 min. This indicated that the catalyst load has an important effect on the reaction rate. The DGCR reactor when used in the liquid mode as a chemical reactor provides a high degree of liquid-liquid mass transfer. The greatest mass transfer occurs in a specialised mixing nozzle, and the immediate zone which can be found in the upper section of the DGCR reactor, for gas-liquid reaction system (Khan, 1995). As a result, the transesterification reaction of sunflower oil with methanol in the DGCR system proceeded appropriately as the catalyst loading was increased up to 0.43 wt.%.

Figure 6-9. Sample product of biodiesel from DGCR rig. The upper layer is biodiesel and the lower layer is residual catalyst with glycerol.

6.3.2.3. Effect of reaction time and temperature on the yield of FAME

As a rule, the conversion rate increases with time for the transesterification reaction (Fangrui and Hanna, 1999, Meher et al., 2006, Vyas et al., 2009). Ma et al. (1998) studied the effect of the reaction time on the transesterification of beef tallow with methanol. They reported that the reaction rate was very slow during the first minute, due to the slow dispersion of methanol in the beef tallow, but after 5 min the reaction proceeds very rapidly and reached a maximum in about 15 min. Other authors (Leung and Guo, 2006) have indicated that the reaction time required for the completion of transesterification reaction depends not only on the reaction temperature, but also on the intensity of the mixing in the process. For the reaction temperature, it was observed that increasing the reaction temperature had a favourable influence on the yield of FAME, (as expected). Transesterification reactions take place at different temperatures, depending on the type of oil used (Meher et al., 2006), however the boiling point of alcohol should be considered, for example, the boiling point of methanol is 64.7 °C. At atmospheric pressure a reaction temperature higher than this will cause the alcohol to boil and form a large number of bubbles, which inhibit the reaction and reduce the yield of FAME (Liu et al., 2008, Sharma et al., 2008). Moreover, a higher temperature also favours the formation of saponified products.

To determine the effect of the temperature and time on the formation of FAME, transesterification reactions were carried out with a fixed molar ratio of 6:1 methanol to sunflower oil and a catalyst loading of 0.29 wt.%, (based on the oil mass). Figure 6-10 and Figure 6-11 show typical examples of the relationship between the reaction time and the temperature. A higher reaction temperature produced a higher yield of FAME, however, for the reaction time there is no significant increase in the yield over the temperature studies. At 30 °C, the yield of FAME was 84 % and 88 % at 20 and 60 min, respectively, while at 35 °C there was a slight increase in the yield. As the temperature rose to 40 °C the yield of FAME increased to 92% and 95% at 20 and 60 min, respectively. A 96.5 % yield of FAME was achieved at 80 min. Generally, a rapid reaction rate could be obtained at higher temperatures, but at too high a temperature, as mentioned previously, methanol starts to boil. For this reason extra care should be considered when raising the reaction temperature.

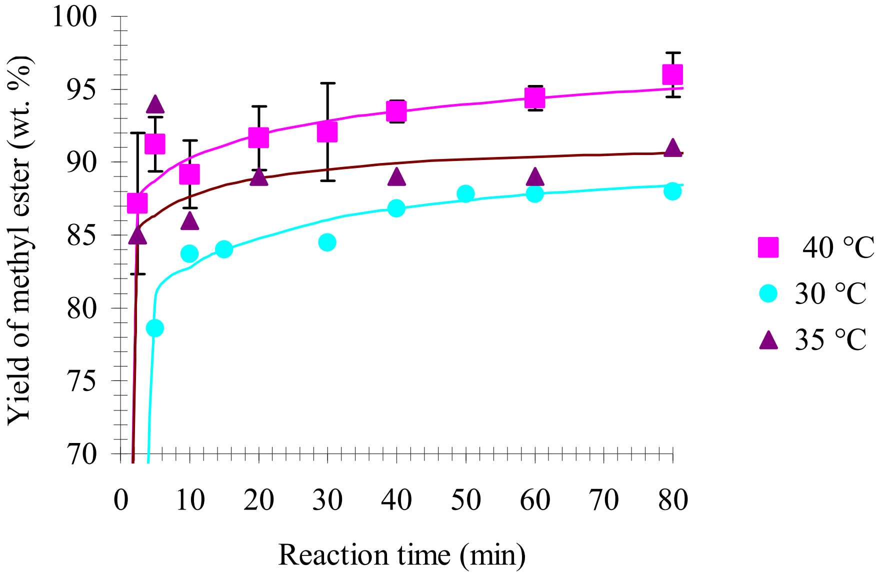

Figure 6-10. Effect of reaction time and temperature on the yield of FAME (reaction conditions: 0.29 wt.% catalyst loading based on the oil mass, and a molar ratio of methanol to sunflower oil of 4.5:1.0. Data points are experimental results and the lines show the best fit to the data).

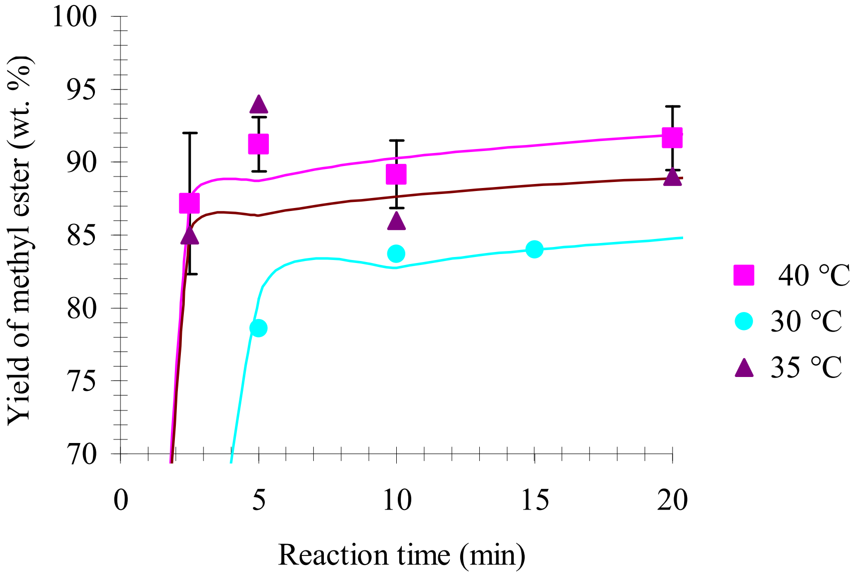

Figure 6-11. Expansion of Figure 6.10 showing earlier reaction times. Effect of reaction time and temperature on the yield of FAME (reaction conditions: 0.29 wt% catalyst loading based on the oil and a molar ratio methanol to sunflower oil of 4.5:1.0. Data points are experimental results and the lines show the best fit to the data).

6.3.2.4. Effect of solvent type on the yield of biodiesel

Methanol and ethanol are the most frequently alcohols used in transesterification reactions and are immiscible with oil/fat at ambient temperatures. In this reactant the reaction mixture needs to be stirred to enhance mass transfer. Because of its low cost and chemical and physical advantages (polarity and shortest chain alcohol), methanol is preferred (Fangrui and Hanna, 1999, Tapanes et al., 2008). However, ethanol is sometimes preferred since it can be derived from agricultural products and is renewable. Tapanes et al.(2008) have reported that because the effect of the ethyl group is stronger than the effect of the methyl group, it is more difficult to break an ethyl molecule to form ethoxide anions than to break methanol to form methoxide anions. The transesterification reactions would not be possible without these anions.

In this study, methanol and ethanol transesterification reactions were carried out, and the yields of biodiesel were very promising. Figure 6-12 shows yields of fatty acid methyl/ethyl ester (FAME/FAEE) for transesterification reaction at 40 °C, 0.29 wt.% (based on the oil mass) and a molar ratio of alcohol to sunflower oil of 4.5:1. The highest yield, 96.5 %, was obtained at 80 min of reaction with methanol while with ethanol it was only 90%. The results demonstrate that yields of FAME and FAEE were not significantly different in the DGCR system, as confirmed by other researchers with other reactor designs (Fangrui and Hanna, 1999). It can be seen that there is always a difference in the yield of FAME. Comparatively, FAME has been shown to be more suitable for use in biodiesel production than FAEE.

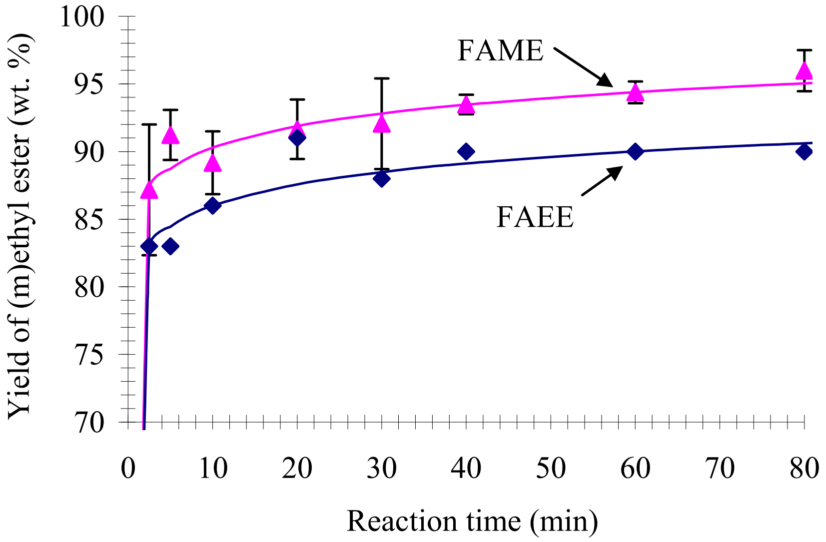

Figure 6-12. Effect of type of solvent on the yield of FAME/FAEE (reaction conditions: 0.29 wt.% catalyst loading based on the oil, a molar ratio methanol to sunflower oil of 4.5:1.0 and 40 °C. Data points are experimental results and the lines show the best fit to the data).

6.3.3. Separation of the FAME/FAEE products

After the samples were obtained from the DGCR rig, the reaction mixtures were allowed to cool down to the ambient temperature to generate two phases: a crude FAME/FAEE phase at the top layer and glycerol on the bottom layer (see Figure 6-9). This separation occurred quickly and can be observed within 10 min. However, the FAME/FAEE layer still had some opacity, representing that the separation was still incomplete. The opaque sample phase went translucent, when it is given enough time to settle completely (Leung and Guo, 2006). A complete separation of the two phases could take as long as 1 to 5 h. In fact, the transesterification process was still continuing during the settling time. The effect of settling time on the product yield is shown in Figure 6-13. Allowing the sample to settle for four months increased the yield of FAME in 10 min reaction from 86 to 92 wt.%. For each point data in Figure 6-13, the results were analysed three times. As a result, the longer the settling time, the more encouraging is the separation and the yield of FAME/FAEE. Figure 6-14 shows the increase of yield for longer reaction times. The increase of yield in 40 min is similar to that in 10 min (Figure 6-13).

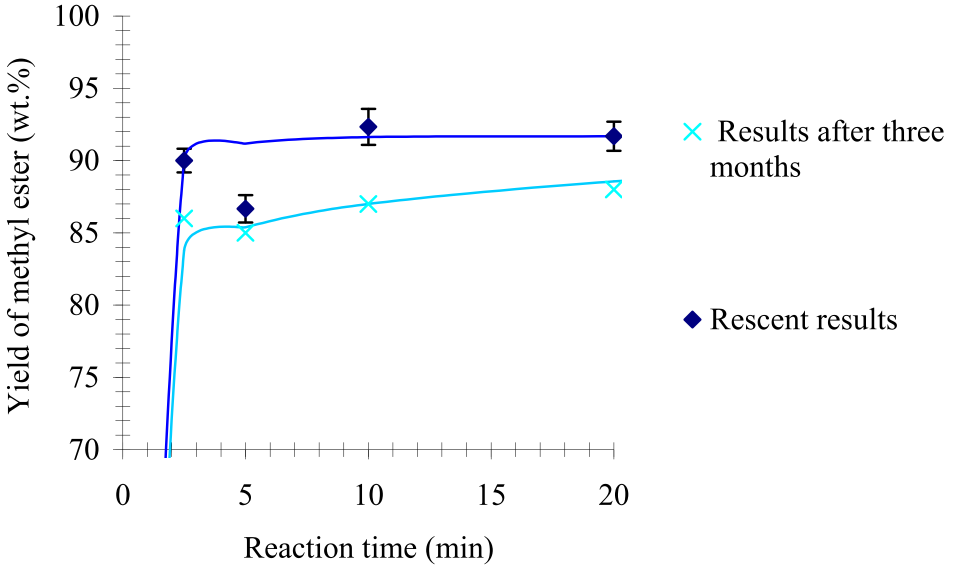

Figure 6-13. Effect of settling time on the yield (reaction conditions: 0.29 wt.% catalyst loading based on the oil, a molar ratio methanol to sunflower oil of 4.5:1.0 and 40 °C. Data points are experimental results and the lines show the best fit to the data).

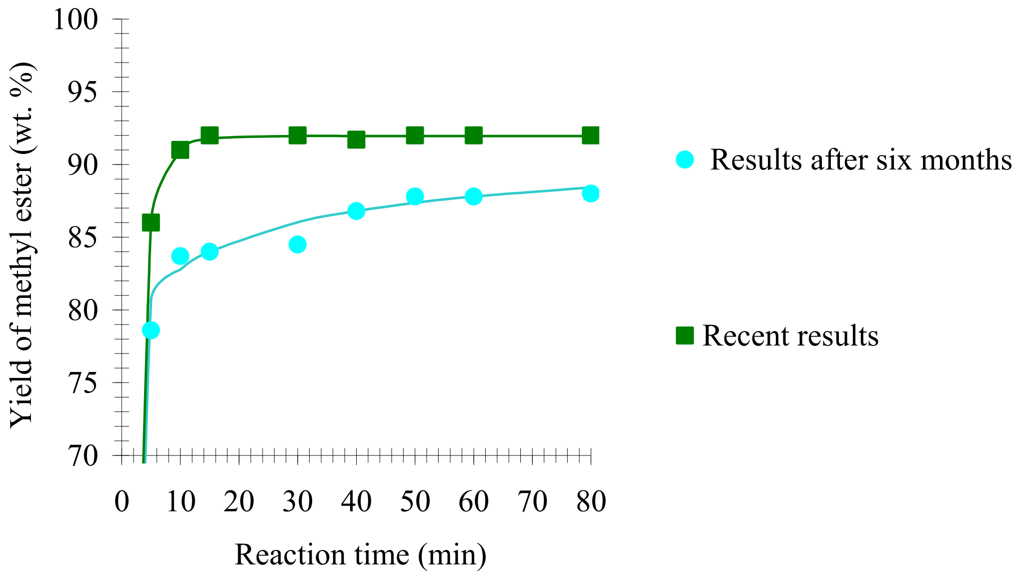

Figure 6-14. Effect of settling time on the yield (reaction conditions: 0.29 wt.% catalyst loading, based on the oil, and a molar ratio of methanol to sunflower oil of 4.5:1 at 30 °C. Data points are experimental results and the lines show the best fit to the data).

6.3.4. Properties of biodiesel

Biodiesel is characterised by numerous parameters, for this work only five items were examined, which were ester content, density, kinematic viscosity, acid value, and iodine value. The viscosity of vegetable oil and ester contents are the most important issue in the biodiesel product. The major problem in using vegetable oils in diesel engine is the kinematic viscosity, which is between 27.2 and 53.6 mm^2/s (Demirbas, 2006). The kinematic viscosity, density, and acid value was measured as detailed in sections 3.2.2.3.1, 3.2.2.3.2,3.2.2.3.3, respectively.

The conversion factor for the correction of density, determined by EN ISO 3675 over a range of temperatures from 20 °C to 60 °C, to density at 15 °C is reported by European-Standard (2008). The following Equation 6-1 can be used for the calculation of density of FAME at 15 °C.

$$\rho(15) = \rho(T) + 0.723(T - 15)$$ **Equation 6-1**

The calculation of Iodine Value is adapted for biodiesel from the AOCS recommended practice Cd 1c – 85 (European-Standard, 2008). The percentage by mass obtained from GC is then used to calculate the sample's iodine value, being the sum of the individual contributions of each methyl ester, obtained by multiplying the methyl ester percentage by its respective factor given in Table 6-5.

Table 6-5. Factors of Methyl ester.

Methyl ester	*Factor*
Methyl ester of saturated fatty acids	0
Methyl hexadecenoate (Methyl palmitoleate) C16:1	0.950
Methyl octadecenoate (Methyl oleate) C18:1	0.860
Methyl octadecadienoate (Methyl linoleate) C18:2	1.732
Methyl octadecatrienoate (Methyl linoleate) C18:3	2.616
Methyl eicosenoate C20:1	0.785
Methyl docasenoate (Methyl erucate) C22:1	0.723

The properties of biodiesel in produced from the DGCR and the Two-steps batch method are compared with technical European Standard EN-14214 (2008) in Table 6-6. The ester content for both methods satisfies the standard requirement, as do the density and kinematic viscosity. In the acid value property, the two-step method is higher than the standard limit due to the use of FFA in the feed of the esterification reaction. The DGCR method slightly exceeds the limit for the iodine value. This is because the sunflower oil feedstock contains 0.5 wt% FFA of which 67.5 % is C18:2 which contribute to the iodine value property.

Table 6-6. properties of biodiesel as in European standard EN-14214 (European-Standard, 2008).

Properties	***Units***	***EN-14214 Limits***		***DGCR method***	***Two-step batch method***
		Min.	Max.		
Ester content	wt.%	96.5	-	99.0	96.7
Density; 15 ^{o}C	kg/m^3	860	900	891	890
Kinematic viscosity; 40 ^{o}C	mm^2/s	3.5	5.0	4.2	4.1
Acid value	mg KOH/g	-	0.5	0.03	8.0
Iodine value	g iodine/100 g	-	120	127	83

6.3.5. Calculation of diffusivity coefficient

The diffusivity coefficient of methanol in sunflower oil can be calculated from the correlation of Wilke and Change (Geankoplis, 1972) as follows :

$$D_{AB} = 7.4x10^{-8} \frac{(\Phi M_B)^{0.5} T}{\mu \upsilon_A^{0.6}} \qquad \textbf{Equation 6-2}$$

Where: D_{AB} = Diffusivity coefficient of methanol in sunflower oil (cm^2/s)

Φ = Solvent association parameter, for methanol 1.9, ethanol 1.5 (Geankoplis, 1972)

M_B = Molecular weight of the solvent (g/mol)

T = Absolute temperature (K)

μ = Viscosity of solvent, cp

υ_A = Molar volume, (323.8 cm^3/mol) (Geankoplis, 1972)

The viscosities of methanol at different temperatures were obtained from Sih et al., (2007) for DGCR and from Chen et al., (2008) for batch reactor (supercritical methanol). The measured viscosities of methanol and diffusivity coefficients calculated using Equation 6-2 in different reactor types are listed in Table 6-7.

Table 6-7. Diffusivity coefficient of oil methanol in sunflower at different temperatures

Reactor type	***Temperature (^oC)***	***Viscosity (cP)***	***Diffusivity coefficient D_{AB} (cm^2/s)***
Batch	320	$2.50x10^{-2}$	$4.27x10^{-4}$
DGCR	40	0.27	$2.00x10^{-5}$

These diffusivity coefficients are in the range of diffusivity coefficients for liquid-liquid system. Although, the diffusivity coefficient in the batch reactor is higher than that in the DGCR due to high temperature, the yield of FAME in DCGR was higher (99 % in 2.5 min) than that in batch reactor (97 % in 5 min). This indicated that the efficiency of mass transfer in the DGCR is higher than that in batch reactor, and therefore, DGCR is very efficient for biodiesel production.

6.4. Comparison between reported processes and the DGCR for biodiesel production

A survey of the operating conditions applied in transesterification reaction is given in Table 6-8. The yield from the DGCR reached 99.0 wt.% of FAME in the very short time of 2.5 min at a temperature as low as 40 ^oC, with a lower molar ratio of methanol to sunflower oil of 4.5:1.0 Moreover, a low catalyst loading of 0.43 wt.%, based on the oil mass of NaOH was used, while in the other reported processes a yield of 97.0 wt.% of FAME was obtained between 60-90 min at a temperature of 60 ^oC, with a molar ratio of methanol to oil of 6.0:1.0 and a catalyst loading between 0.5-8.0 wt.%, based on the oil mass of used. Sulaiman (2007) has documented that in he alkali catalytic method, the transesterification reaction proceeded at the following conditions: reaction temperature 30-65 ^{o}C, duration 60-360 min and yield of esters 96 wt.%. This comparison between these literature and DGCR processes for the production of biodiesel highlights the power of the DGRC as a state-of-the-art apparatus for manufacturing the reaction of biodiesel.

Table 6-8. Operating conditions applied in studies on the effect of feedstock, Reactor Type, molar ratio (alcohol: oil), type alcohol, catalyst, catalyst quantity, reaction temperature and product yield.

Feedstock	*Reactor volume (cm^3)/Type*	*Type agitation/ speed (rpm)*	*Duration (min)*	*Molar ratio (alcohol: oil)/ type alcohol*	*Catalyst/ quantity % of oil*	*Temperature (^oC)*	*Yield %*	*Reference*
Soybean oil	400/five neck flask	Mechanical stirrer/-	120	30.0:1.0/ butanol	H_2SO_4/ 1.0	117	97	(Freedman et al., 1986)
Crude oil of Pongania pinnata	-/CSTR	-	90	10.0:1.0/ methanol	KOH (1.0 %) ZNO	60	92	(Karmee and Chadha, 2005)
Sunflower oil	1000/ glass reactor	Two flate-blade paddle/ 120	90	6.0:1.0/methanol	KOH/1.0	20	90	(Stamenkovic et al., 2007)
Sunflower oil	Stirrer vessel	Helix stirrer/1000	100	13.0:1.0/methaol	Activated CaO/1.0	60	87	(Granados et al., 2007)
Sunflower oil	500/erlenmeyer flask	Magnetic stirrer/600	60	6.0:1.0/methanol	NaOH/ 0.5	60	97.5	(Bambase et al., 2007)
Sunflower oil	1000/ glass reactor	Two flate-blade paddle	30	6.0:1.0/methanol	KOH/1.0	30	88	(Stamenkovic et al., 2008)
Sunflower oil	250/batch reactor	Helix stirrer/300	40	6.0:1.0/methanol	NaOH/1.0	65	95	(Vicente et al., 2005)
Soybean oil	100/glass reactor	Magnetic stirrer/100	90	12.0:1.0/methaol	CaO/8.0	65	95	(Liu et al., 2008)
Rapeseed oil	320/batch reactor	Magnetic stirrer/	40	6.0:1.0/methanol	KOH/1.59	22.8	87	(Komers et al., 2002)
Palm oil	-/liquid-liquid film reactor	-	20	6.0:1.0/methanol	NaOH/1.0	60	87	(Narvaez et al., 2009)
Sunflower oil	1130/DGCR	-	2.5	4.5:1.0/methanol	NaOH/0.43	40	99	**This work**

6.5. Conclusion

The transesterification reaction of sunflower oil with alcohol (methanol, ethanol) representing model reactions indicates that the DGCR can be used as a chemical reactor for liquid-liquid phase catalytic reactions to produce biodiesel with very promising results. The DGCR provides great potential for chemical reactions, which are normally limited by the resistance to mass transfer. The DGCR enables intense mixing which has been identified by many researchers (Bambase et al., 2007, Muniyappa et al., 1996) as the most critical requirement that must initially be met in order to achieve the highest yield of biodiesel. The experimental results demonstrated that more FAME is yielded with DGCR than is reported in the data on conventional biodiesel process. The yield from DGCR reached 96.5 wt.% of FAME and fulfilled the technical requirements of EN14214 European Standard (2008) in the very short time of 2.5 min at a temperature as low as 40 ^{o}C, with a lower molar ratio of methanol to sunflower oil of 4.5:1.0 and a low catalyst loading of 0.43 wt.%, based on the oil mass of NaOH was used. These were the optimal reaction conditions to satisfy EN 14214 in the DGCR for biodiesel production. The final product of biodiesel from DGCR does not require any kind of washing with water, although in similar biodiesel process, it does. This will have a positive influence on the cost of the final product. The biodiesel product from DGCR method fulfilled the European-Standard EN14214, except the iodine value was slightly higher than the limit.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

The research work presented in this thesis address two main objectives: first, to produce high quality FFA and biodiesel; and second, to optimise the process operation variables. The hydrolysis, esterification and transesterification reactions investigated were evaluated from the standpoint of understanding the effects of various process variables on the final product yield. Moreover, the new kinetic data acquired were subsequently used to develop reaction rate expressions for both vegetable oil hydrolysis reactions and the esterification of FFA with supercritical methanol. To achieve this purpose, many reactor systems (a continuous flow reactor, a Plug Flow Reactor (PFR), a bench-top batch reactor and a state-of-the–art DGCR) were studied in sequence, to obtain the novel experimental data presented and discussed in the course of this thesis. The PFR system was designed, constructed and operated to continuously produce FFA. The bench-top batch reactor was used in the esterification reaction of supercritical methanol with FFA. The DGCR, was operated at extremely mild conditions and shows great potential as a new technology for biodiesel production.

There are a number of objectives and conclusions to be drawn from the work presented here.

7.1.1. Continuous flow hydrolysis of vegetable oil

- The non-catalytic continuous flow hydrolysis reactions of sunflower oil with subcritical water are a promising method for producing a high yield of FFA in a shorter reaction time than enzymatic hydrolysis. It also offers the advantage of large-scale production with limited labour requirements, whilst maintaining product quality.
- The rate of non-catalytic hydrolysis is heavily affected by temperature, reaction time and the water:oil ratio; however, the reaction pressure has a minor effect on the degree of hydrolysis. The influence of temperature is directly related to the increased solubility of the water in oil.
- A high yield of up to 90 % within 10 min at 350 ºC, 20 MPa and a water:oil ratio of 50:50 v:v % can be achieved without the addition of catalysts. This therefore reduces post catalyst separation, made the process simple and

making it environmentally friendly. The products of the hydrolysis reactions, i.e. FFA, act as acid catalysts in the hydrolysis of the oil in subcritical water.

- The reaction time must be extended in order to obtain a high yield of FFA (care should be taken to avoid temperatures higher than 330 ^{o}C as this can lead to thermal degradation of the products).
- The kinetic results indicate that hydrolysis reactions require greater energy to start the first reaction than the second and third reactions, with activation energies of 108 kJ/mol, 38 kJ/mol and 90 kJ/mol, respectively. It is also found that the hydrolysis reactions can be considered to be second order irreversible reactions.

7.1.2. Esterification reaction of FFA with supercritical methanol for biodiesel production

- Supercritical methanolysis reaction is a powerful method to produce high yields of biodiesel. The undesirable intermediate products, such as mono-, di- and triglycerides are limited by this method. Moreover, the only by-product is water without the formation of glycerol, which simplifies the separation process.
- The reaction yield depends on the temperature and the initial ratios of FFA to methanol. However, the stirring speed has no effect on the yield of FAME.
- A 97 % yield of biodiesel can be achieved in 5 min at 320 ^{o}C and 430 rpm. This result also exceeds the technical minimal regulations of EN14214 European-Standard (2008) for the FAME content.

- The reaction is a second order reversible endothermic reaction. The forward reaction requires a more substantial amount of energy than the reversible reaction, with activation energies of 72 and 23.2 kJ/mol, respectively.

7.1.3. Biodiesel production from DGCR

- The Downflow gas contactor reactor (DGCR) is a state-of-the-art apparatus with great potential in chemical reactions that are limited by the resistance to mass transfer. The production of biodiesel in DGCR indicates that the apparatus is straightforward to use.

- The yield from DGCR reached 99 % of FAME which fulfills the technical requirements of EN14214 European Standard (2008) in a very short time of 2.5 min at a temperature as low as 40 ^{o}C, with molar ratio of methanol to sunflower oil of 4.5:1 and a NaOH catalyst loading of 0.43 wt.%, based on the oil mass. These results are at conditions much lower that any method reported in the literature and are extremely promising for industry and the environment.

- The final product of biodiesel from DGCR does not require washing with water. This will have a positive effect on the cost of the final product.

- The main purpose of converting vegetable oils to biodiesel products is to reduce their viscosities. In the DGCR the viscosity and other European Standard limits are attained, except for the iodine value which is slightly higher than the limit.

- DGCR is recommended for biodiesel production as it requires low energy input and is a one-step process. Although it needs a catalyst, the catalyst and the by-product glycerol can be easily and efficiently separated by gravity.

7.2. Recommendations for future work

Because of financial, equipment and time constraints several experiments and modelling could not be carried out within the present work, and hence, are recommended for future work as follows:

- Integration of the subcritical water hydrolysis and esterification processes in one continuous flow reactor system.
- Sequentially separate the FFA from glycerol in the stage between the hydrolysis and esterification processes.
- Investigation of alternative feedstocks in the production of biodiesel such as non-edible oils (Jatropha oil), beef tallow and waste cooking oils. The use of waste cooking oil can lower the final cost; however, the quality of most cooking oil is low. The high FFA content in waste cooking and non-edible oils are one of the main constraints that restrict their use in biodiesel production.
- Calculation of the specific interfacial area by measuring the droplet size of the dispersed alcohol phase with a microscope video system in the turbulent region of the DGCR. This will enable mass transfer properties to be estimated.
- Establish scale up of the DGCR since the experimental results reported have exemplified the suitability of the DGCR for the production of biodiesel in a large scale.

- Investigate the use of DGCR in a number of processes which require liquid-liquid contact, such as mineral processing, pulp and paper, oil and gas and in petrochemical processing, since its visibility has been well demonstrated and it may create new opportunities for such work.

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Chapter 9

APPENDIX

9.1. Pressure gauges and thermocouples calibrations

All pressure gauges were supplied as pre-calibrated and were checked periodically by the service available in the School of Bioscience.

The thermocouple was calibrated by used water up 70 ^{o}C. Then in the oil bath up to 270 ^{o}C against a thermometer. The thermocouples did not deviate more than +/- 1.8 ^{o}C.

9.2. Pumps calibrations

The pumps of the continuous flow rig have been calibrated by using a stop watch and measuring cylinder as shown in Figure 9-1.

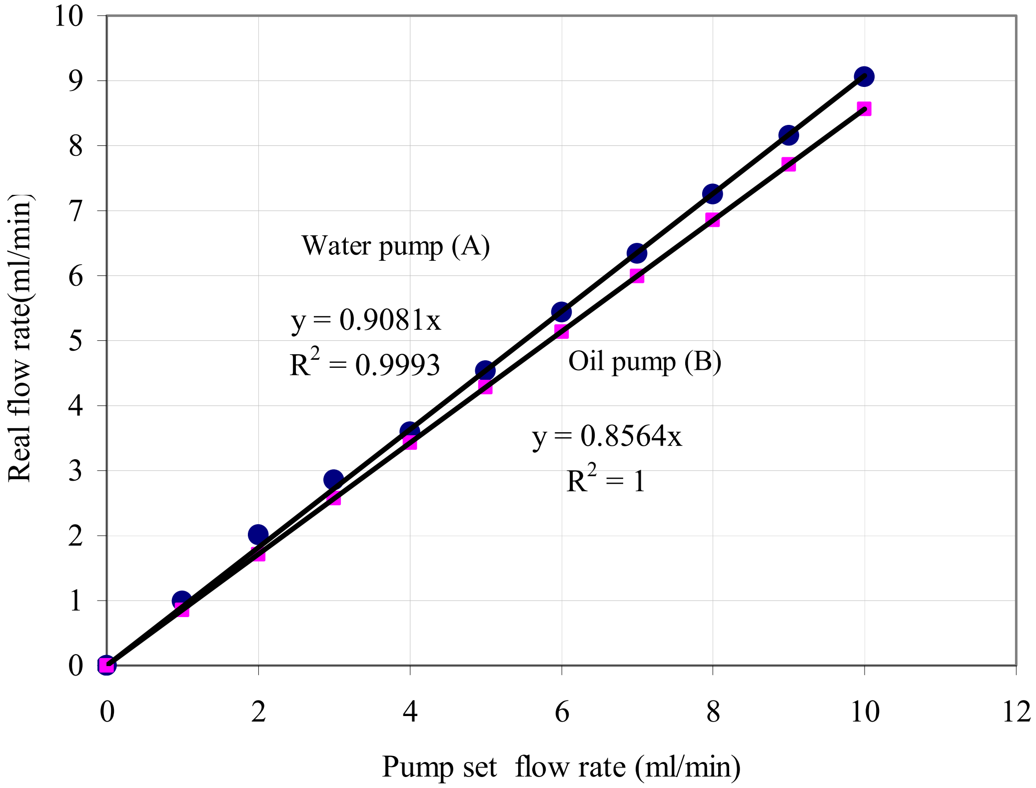


Figure 9-1. Calibrations of water and oil pumps.

9.3. Sample calculation of FAME using a fourth-order Runge-Kutta method

The concentration of FAME at any time is calculated by using Equation 5-3. The initial values of $FFA_0 = 1$, $FAME_0 = 0$, $W_0 = 0$ and $M = n/1 = 7/1 = 7$,

where $h = 0.1$, $K1 = 0.25$ and $K'1 = 0.68$ for 320 °C

$$\frac{d[FAME]}{dt} = -\frac{d[FFA]}{dt} = k_1([FFA].[M]) - k_1^{'}([FAME].[W])$$ **Equation 5-3**

$$\frac{dx}{dt} = k_1((n/1) - x)(1 - x) - k_1^{'}(x)(W_0 + x)$$ **Equation 5-4**

RK1= h*(k1*(FFA$_0$- FAME$_0$)*(n - FAME$_0$)- k$^{'}$1*(FAME$_0$ * (0+FAME$_0$))

RK1= 0.1(0.23(1-0)*(7-0)-0.068(0*(0+0)) = 0.161

RK2=h*(k1*(FFA$_0$-(FAME$_0$+0.5*RK1))*(n-(FAME$_0$+0.5*RK1))-

K$^{'}$1*(FAME$_0$+0.5*RK1)*(FAME$_0$+0.5*RK1))

RK2=0.1*(0.23*(1-(0+0.5*0.161))*7-(0+0.5*0.161)-
0.068*(0+0.5*0.161)*(0+0.5*0.161)) = 0.146293

RK3=h*(k1*(FFA$_0$-(FAME$_0$+0.5*RK2))*(n-(FAME$_0$+0.5*RK2))-

K$^{'}$1*(FAME$_0$+0.5*RK2)*(F4+0.5*RK2))

RK3=0.1*(0.23*(1-(0+0.5*0.146293))*7-(0+0.5*0.146293)-

0.068*(0+0.5*0.146293)*(0+0.5*0.146293)) = 0.147628

RK4=h*(k1*(FFA$_0$-(FAME$_0$+RK3))*(K$^{'}$1-(FAME$_0$+RK3))-

K$^{'}$1*(FAME$_0$+RK3)*(FAME$_0$+RK3))

RK4=0.1*(0.23*(1-(0+0.147628))*7-(0+0.147628)-
0.068*(0+0.147628)*(0+0.147628)) = 0.13419

FAME$_t$ = 0+(0.161+2*(0.146293+0.147628)+ 0.13419)/6 = 0.147171828

h	0.1	FFAo	1		k1	0.23
		Mo	7		k1'	0.068
					FAME (mol)	FAME (mol %)
0	RK1	RK2	RK3	RK4	0	0
0.1	0.161	0.146293	0.1476277	0.13419	0.147171828	14.71718277
0.2	0.13427127	0.122311	0.1233708	0.11241	0.270178777	27.01787771
0.3	0.11246965	0.102666	0.1035164	0.0945	0.373401572	37.3401572
0.4	0.09455286	0.086462	0.0871516	0.07969	0.460314043	46.03140428
0.5	0.07973482	0.07302	0.0735831	0.06738	0.533700851	53.37008505
0.6	0.0674134	0.061813	0.0622765	0.05709	0.595815174	59.58151741
0.7	0.05712094	0.05243	0.0528145	0.04847	0.648494937	64.84949366
0.8	0.04848977	0.044548	0.0448674	0.04121	0.69324984	69.32498401
0.9	0.04122767	0.037905	0.038172	0.03509	0.731327486	73.13274861
1	0.03510015	0.032292	0.0325161	0.0299	0.763764268	76.3764268
1.1	0.02991742	0.027539	0.0277277	0.02551	0.791425012	79.14250122
1.2	0.02552473	0.023506	0.0236658	0.02179	0.81503419	81.50341899
1.3	0.02179506	0.02008	0.0202145	0.01862	0.835200734	83.52007341
1.4	0.01862354	0.017164	0.0172779	0.01592	0.852437948	85.24379478
1.5	0.01592315	0.014679	0.0147763	0.01362	0.867179601	86.71796014
1.6	0.01362136	0.01256	0.0126429	0.01165	0.879793044	87.97930437
1.7	0.01165746	0.010752	0.010822	0.00998	0.890589948	89.05899481
1.8	0.00998049	0.009207	0.0092666	0.00854	0.899835172	89.98351719
1.9	0.00854752	0.007886	0.0079372	0.00732	0.907754097	90.77540966
2	0.00732233	0.006757	0.0068003	0.00627	0.914538738	91.45387376
2.1	0.00627425	0.00579	0.0058275	0.00538	0.920352849	92.03528495
2.2	0.00537728	0.004963	0.0049948	0.00461	0.925336207	92.53362068
2.3	0.00460934	0.004254	0.0042818	0.00395	0.929608205	92.96082051
2.4	0.00395167	0.003648	0.0036711	0.00339	0.933270898	93.32708977
2.5	0.00338827	0.003128	0.0031478	0.0029	0.936411563	93.64115626
2.6	0.00290551	0.002682	0.0026995	0.00249	0.939104877	93.91048773
2.7	0.00249177	0.0023	0.0023152	0.00214	0.941414764	94.14147638
2.8	0.00213712	0.001973	0.0019857	0.00183	0.943395957	94.3395957
2.9	0.00183308	0.001692	0.0017032	0.00157	0.945095339	94.50953389
3	0.00157238	0.001452	0.0014611	0.00135	0.946553076	94.65530758
3.1	0.00134883	0.001245	0.0012534	0.00116	0.947803588	94.7803588
3.2	0.00115711	0.001068	0.0010752	0.00099	0.948876377	94.88763771
3.3	0.00099268	0.000917	0.0009224	0.00085	0.949796733	94.97967332
3.4	0.00085165	0.000786	0.0007914	0.00073	0.950586339	95.05863393
3.5	0.00073067	0.000675	0.000679	0.00063	0.951263788	95.12637878
3.6	0.00062689	0.000579	0.0005826	0.00054	0.951845022	95.18450225
3.7	0.00053786	0.000497	0.0004998	0.00046	0.952343718	95.23437175
3.8	0.00046148	0.000426	0.0004289	0.0004	0.952771601	95.27716011
3.9	0.00039596	0.000366	0.000368	0.00034	0.953138733	95.31387331

4	0.00033974	0.000314	0.0003157	0.00029	0.953453743	95.34537428
4.1	0.00029151	0.000269	0.0002709	0.00025	0.953724033	95.3724033
4.2	0.00025013	0.000231	0.0002324	0.00021	0.953955954	95.39559541
4.3	0.00021462	0.000198	0.0001995	0.00018	0.954154954	95.41549544
4.4	0.00018416	0.00017	0.0001711	0.00016	0.954325708	95.4325708
4.5	0.00015802	0.000146	0.0001468	0.00014	0.954472225	95.44722251
4.6	0.00013559	0.000125	0.000126	0.00012	0.954597946	95.45979464
4.7	0.00011635	0.000107	0.0001081	1E-04	0.954705824	95.4705824
4.8	9.9832E-05	9.22E-05	9.278E-05	8.6E-05	0.954798391	95.47983908
4.9	8.5664E-05	7.91E-05	7.961E-05	7.3E-05	0.95487782	95.48778201
5	7.3506E-05	6.79E-05	6.831E-05	6.3E-05	0.954945977	95.49459765

9.4. Calculation of Reynolds Number for DGCR.

Calculate Reynolds Number at the jet nozzle with 0.005 m at 40 ^{o}C and molar ratio methanol:oil of 4.2:1, volume ratio 0.17: 0.83, mass ratio 0.15:0.85 by using Equation 3-2.

$R_e = \bar{\bar{\rho}} v D / \bar{\mu}$ Equation 3-2

$\rho_{m\,=}$ =775 Kg/m^3 (from (Sih et al., 2007)) density of methanol at 40 ^{o}C.

ρ'_o = 917 Kg/m^3 density of oil at ambient.

$\bar{\bar{\rho}}$ = 0.83 x 917 + 0.17x 775 = 893 Kg/m^3 average density

μ_m = 4.6x10^{-4} Pa.s (from (Sih et al., 2007)) viscosity of methanol at 40 ^{o}C.

μ_o = 1.22x 10^{-2} Pa.s viscosity of oil at 40 ^{o}C.

The viscosity of the binary mixture is calculated by using (Kern, 1950) .

$$\frac{1}{\overline{\mu}} = \frac{w_m}{\mu_m} + \frac{w_o}{\mu_o}$$

Where: w_m , w_o = 0.52, 0.48 weight fractions of methanol and oil, respectively.

$$\frac{1}{\overline{\mu}} = \frac{0.15}{4.6x10^{-4}} + \frac{0.85}{1.22x10^{-2}} \quad = 396 \ \ \text{Pa.s}$$

$\bar{\mu}$ = 2.5 x10^{-3} Pa.s average viscosity.

$\dot{V}$ = 9 dm^3/min = 1.5x10^{-4} m^3/s volume flow rate

A = 2x10^{-5} m^2 nozzle area

V = 7.6 m/s velocity

$$\text{Re} = \quad 5x10^{-3} \ x \ 893 \ x \ 7.6/2.5x10^{-3} \quad \cong \quad 13573$$

9.5. Yield, conversion and concentration (wt. fraction) assumption.

Basis: 1 mol of TG

$$\mathrm{TG} + 3\ \mathrm{MeoH} \longrightarrow 3\ \mathrm{FAME} + \mathrm{G}$$

Initial	1	3	0	0
Reaction	x	3x	3x	x
Final	(1-x)	3(1-x)	3x	x

Conversion = c = mol of TG reacted/ mol of TG initially

$$c = x/1 = x$$

yield (molar basis) = y_m = mol of FAME produced / mol of oil initially

$$y_m = 3x$$

yield (mass basis) = y_w = mass of FAME produced / mass of oil initially

$$y_w = 3xF/T$$

where F is the molecular weight of FAME (298 g/mol) and T is the molecular weight of oil (890 g/mol). The ratio of T/F is 2.99 and therefore it is very reasonable to approximate that T is three times F, hence

$$yw = 3xF/3F = x = c$$

The concentration of product FAME (in wt. %) in mixture after separation of glycerol and catalyst (assuming that the separation is complete and ideal) is

$$k\ (\text{wt }\%) = \text{mass of FAME}/(\text{mass of FAME} + \text{mass of unreacted oil})$$

$= 3xF/(3xF + (1-x)T)$

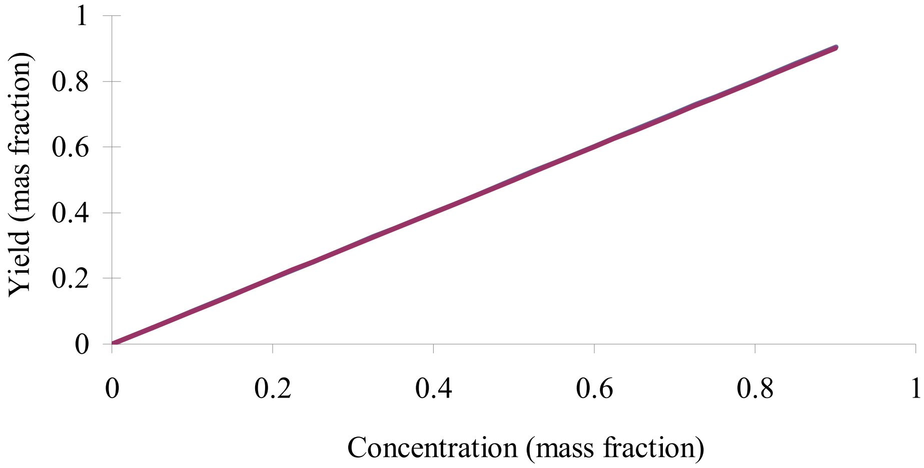
$= 3xF/(3xF + (1-x)\ 3F)$

$= 3xF/(3xF + 3F – 3xF)$

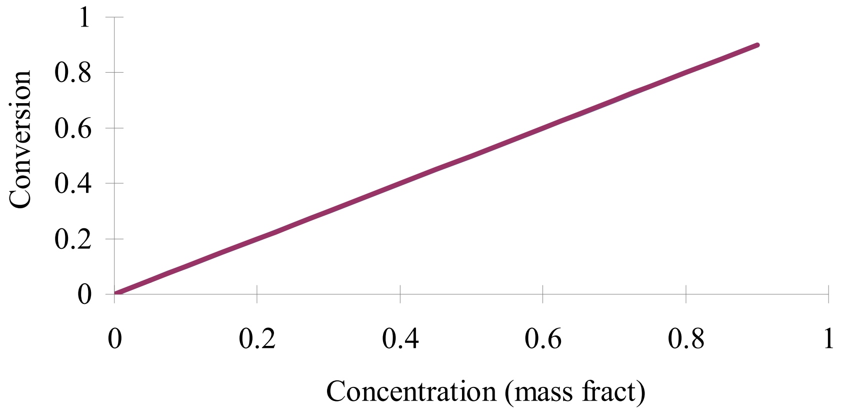
$= 3xF/3F$

$k\ (\text{wt }\%) = x = c = y_w$

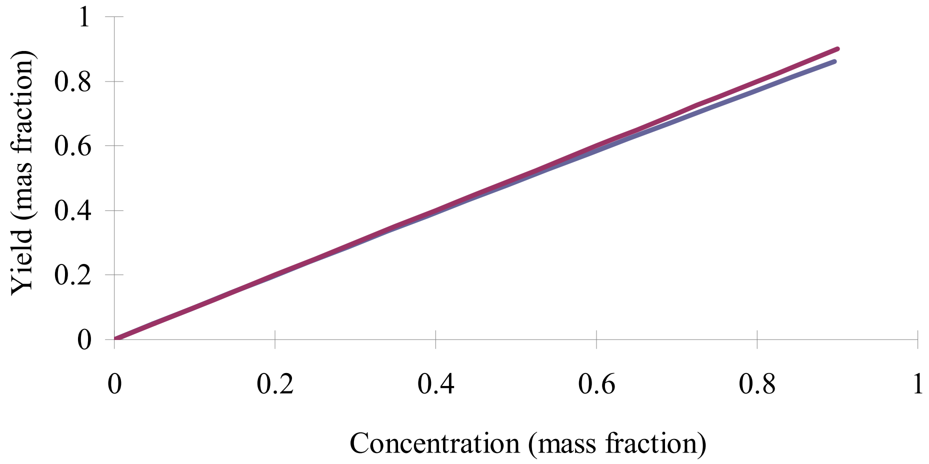
For FFA, the molecular weight is 284 g/mol and the ratio of T/FFA is 3.1 and therefore it is reasonable to use the same assumption as above, i.e. $k = c = y_w$. The figures below show the comparison between concentration, conversion and yield for FAME and FFA.



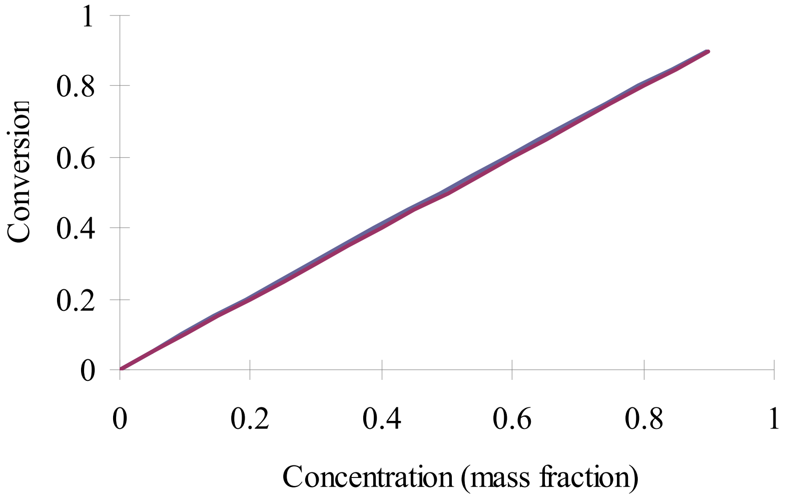
The yield of FAME vs the concentration of FAME (wt. fraction)



The conversion of FAME vs the concentration of FAME (wt. fraction).



The yield of FFA vs the concentration of FFA (wt. fraction)



The conversion of FFA vs the concentration of FFA (wt. fraction).

9.6. Publications

The outcomes from this thesis have been published in journals and conferences as follows:

1- Alenezi, R., Leeke, G.A., Santos, R.C.D., Khan, A.B. (2009) Hydrolysis kinetics of sunflower oil under subcritical water conditions. **Chemical Engineering Research and Design**, *87: (6): 867-873*

2- Alenezi, R., Baig, M., Wang, J. Santos, R.C.D. Leeke, G.A. Continuous flow hydrolysis of sunflower oil for biodiesel.(2010) **Energy Sources Part A-Recovery Utilization and Environmental Effects,** *32:(5): 460-468*

3- Alenezi, R., Leeke, G.A., Santos, R.C.D., Khan, A. B. Winterbottom, J.M. Esterification Kinetics of Free Fatty Acids with Supercritical Methanol for Biodiesel Production. **Energy Conversion and Management**, *accepted.*

4- Alenezi, R., Baig, M., Santos, R.C.D. Leeke, G.A. Continuous Flow Hydrolysis of Sunflower Oil Using Sub-critical Water. **Proceedings of the 11th Meeting on Supercritical Fluids, Barcelona, Spain,** *May 4–7 (2008).*

5- Alenezi, R., Baig, M., Santos, R.C.D. Leeke, G.A. Catalyst Free production of Biodiesel. Poster, **Universitas 21, International Conference on Energy Technologies and Policy,** Birmingham, U.K, *September 7-10. (2008)*