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EngD Thesis

IMPROVEMENTS TO THE BIODIESEL PROCESS

by

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ABSTRACT

Biodiesel (fatty acid methyl ester, FAME) is a renewable diesel fuel made from vegetable oil and methanol. The two main problems with the process are disposal of waste streams and product purity. This thesis studies biodiesel process improvements, especially glycerol conversion to hydrogen and improved mass transfer to increase ester yield.

Experiments on steam reforming with glycerol and waste water over a platinum alumina catalyst were used to convert the combined waste product streams of a biodiesel plant. Mass spectroscopy with internal standard was chosen to measure reformer gas yield and conversion. The glycerol steam reforming was shown to depend on several reaction variables. Therefore a solid oxide fuel cell was used as a sensor to measure the effects. The results showed that good syngas yield, conversion and reformer life could be obtained using this process.

The purity of the biodiesel product was examined using real-time optical microscopy and gas chromatography to fit the FAME standard EN14214. It was observed that droplet size had a major influence on reaction end point and that the reaction was mass-transfer limited. This observation was confirmed by developing a mass-transfer based reaction model using the data from the batch reactor which agreed with results from other researchers. The model predicted better conversion with more mixing intensity. Finally, on the basis of these results, a high mixing intensity continuous reactor was developed which achieved the 96.5% standard with high flow rate and short reactor length.

The conclusion was that significant cost effective improvements could be made to the conventional FAME process.

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NOMENCLATURE

a	m^2/m^3	Total surface area per volume of reaction
AR		Static mixer aspect ratio
C_a	mol/m^3	Concentration of reactant a
C_{ao}	mol/m^3	Initial concentration of reactant a
C_b	mol/m^3	Concentration of reactant b
C_n	mol/m^3	Concentration in tank n
C_f		Friction factor
d	m	Diameter of impeller
D	m	Diameter of tank
d_{max}	m	Maximum stable droplet diameter
d_o	m	Droplet diameter
D_{32}	m	Sutra mean droplet diameter
E		Enhancement factor
Fl		Volume fraction of phase
fd		Darcys friction factor
$-\Delta G°$	kJ/mol	Gibbs free energy at 298 kelvin
$-\Delta H°$	kJ/mol	Enthalpy of formation at 298 kelvin
H	m	Tank height
Ha		Henry's law constant
K	$(mol/m^3)s^{-1}$	Reaction rate constant
K_{al}	$m^3/(m^2.s)$	Mass transfer coefficient for liquid film
L	m	Length
n	s^{-1}	Impeller speed
N_t		Number of tanks
P	kPa	Pressure
P_w	watts	Power
P_o		Power number
Q	m^3/s	Flow rate
r_a	mol/s	Reaction rate
Re		Reynolds number

R		Gas constant
t	s	Residence time
t_i	s	Residence time in tank i
T	ºC	Temperature
$\bar{t}$	s	Mean residence time
V	m^3	Volume
V_{meth}	m^3	Volume of methanol in reactor
v	m/s	Velocity
We		Weber number
X_a		Conversion

Greek symbols

ε	watts/kg	Energy dissipation rate
Φ	J/kg	Energy dissipation
ρ	kg/m^3	Density
ρ_c	kg/m^3	Density of continuous phase
μ	kg/m.s	Viscosity
ν		Kinematic viscosity
σ		Surface tension
φ^2		Varience of tracer distribution
τ		Shear stress
θ		Static mixer voidage

Acronyms

UCOME	Used cooking oil methyl ester
UCO	Used cooking oil
Veg oil	Vegetable oil
GC	Gas chromatography
MS	Mass spectroscopy
WID	Waste incineration directive

HPLC	High performance liquid chromatography
SOFC	Solid oxide fuel cell
ROC	Renewable energy obligation certificate
LSM	Lanthanum strontium manganite
TPO	Temperature programmed oxidation
S/C ratio	steam/carbon ratio
O/C ratio	Oxygen/carbon ratio
RTFO	Renewable transport fuels obligation
CNG	Compressed natural gas
LPG	Liquid petroleum gas
PHEV	Plug in hybrid electric vehicle
FID	Flame ionization detector
RTD	Residence time distribution
Re	Reynolds number

CHAPTER 1

INTRODUCTION

1.1. Background

Biodiesel is a renewable diesel fuel made from organic oils called tri-glycerides. It is produced by reacting vegetable oil with an alcohol and a catalyst followed by separation from its glycerol by-product. Biodiesel molecules contain 11% oxygen which causes leaner fuel/air mixtures and a cleaner burn than regular diesel, giving environmental benefit (SAE, 1990).

Another significant benefit is that vegetable oils can be grown all over the world so could reduce western dependence on Middle Eastern oil, besides giving a massive boost to agriculture either locally or in developing nations where labour is cheap. But by far the single most important benefit of biodiesel is the fact that it is made from plant materials which absorb carbon dioxide from the atmosphere off-seting that produced when the fuel is combusted. Studies have shown that biodiesel is on average 66% carbon neutral depending upon where the raw material is from, 95% with used oils (ADEME 2002, Elsayed 2003, ENVOC 2005, IEA 1999, JRC 2003, Levington 2000). This could potentially allow all diesel vehicles to become low carbon vehicles and reduce their contribution to the greenhouse effect. Because of these benefits the UK government has given biodiesel a 20p/litre tax incentive to encourage its use.

Biodiesel can be made from many different sources of tri-glycerides, including but not limited to, rapeseed oil, soya oil, palm oil, jatropha oil, and tallow. Biodiesel made from different feed-stocks, different production processes or different land use situations will have different carbon emission reductions (Royal society, 2008), as discussed later in chapter 2. It is possible to run a diesel engine on unmodified cooking oil, however this is not recommended because the fuel is too viscous and studies have shown it can lead to degradation of the engine such as gumming of pistons and injectors (Ramadhas *et al* 2004, Pryde 1983 and Ryan *et al* 1983)

1.2. Biodiesel Problems

My work at the companies Green Biodiesel Ltd and BHR Biofuels Ltd uncovered a range of interesting process problems which are discussed below, including by-product conversion and improved product yield. Some of these problems have been solved in the later chapters of this thesis.

The water and glycerol waste of biodiesel production are costly to dispose of and should be fully utilized in order to maximize the carbon reductions biodiesel can offer. Glycerol and waste water both need to be either utilized or avoided with a more advanced production process. Historically waste glycerol was mixed with other waste oil and burnt, but this practice was stopped in 2005 when the WID (Waste Incineration Directive) effectively banned burning of waste (European parliament and council of the European communities, 2000). Currently waste glycerol and water are likely to be treated by digestion at a water treatment plant where fuel gas yield is low and process time high. These wastes would be best converted to biofuels either through a fast chemical conversion processes or in a WID compliant co-fired power generation.

The reaction needs to be improved so that fuel quality standards such as EN14214 can be met to guarantee the quality of biodiesel and increase its selling price. Currently (2003-2008) sub-standard fuel is allowed to qualify for the biodiesel tax break, as long as it is from a transesterification process. However the law states that only 96.5% biodiesel should qualify for the tax break so this is a difficult situation for biodiesel producers because the enforcement of this tax rule could change at any time. The current reaction scheme is also slow, taking hours to even approach completion.

The separation and purification stages need to be improved. This is often the bottle-neck of the whole process. Currently there are many methods of “polishing” the biodiesel but many of these treatments contaminate the biodiesel in other ways. For instance washing the biodiesel to reduce methanol, glycerol and soaps leaves the biodiesel contaminated with water and can cause a slight reverse reaction. Heating the biodiesel to evaporate water can lead to reduced oxidative stability and increased acid value. Heating the biodiesel to recover methanol before washing can lead to viscosity increase and soap formation. Using ion exchange resin to remove soap impurities can lead to increased acid value. The purification of biodiesel to meet the standard seems to be a very difficult balancing act and in many cases it is impossible to reach the standard if the original oil or biodiesel is of poor quality.

The use of sodium hydroxide catalyst is thought to be a crude method because it leads to emulsification of product and waste. This reduces yield and necessitates expensive down stream purification. It would be a major breakthrough to find a non-soluble heterogeneous catalyst which would not leave the same problems. However, no heterogeneous catalyst has yet been developed that gives sufficient yield under normal reaction conditions. Supercritical and sub critical processes have been developed both with and without heterogeneous catalysts to give the required yield, but these seem to be very expensive and have not been widely adopted.

1.3. Objectives

The objectives set out in the beginning of the EngD were very broad. This was because the original sponsor (UK Biofuels) was a fresh start up company still learning their chemistry and they did not want to restrict research to a specific area. The initial EngD objectives were as follows.

- Testing standards and specifications and forming a quality control lab.
- Improve yield
- Improve purity
- Water saving
- Glycerol saving
- Any process gains
- Speed up process time

With experience the work soon became focused on areas where there were obvious process problems that could be improved through proper application of chemical engineering.

Utilization of waste water and waste glycerol was always a key objective and work soon focused on steam reforming of waste because this showed the most potential and had not been previously researched. Therefore, a major part of this thesis describes an investigation of glycerol reforming.

Purification of product to meet the EN standard was the second major issue which became increasingly important as product samples failed to meet the purity level expected in the market. Independent testing revealed that the reaction was not reaching completion, which was affecting product quality. Very little was known about the reaction and the mechanism was unclear so finding out why the samples were failing and coming up with a solution was paramount. This led the work to focus on real-time optical microscopy and gas chromatography ester determination to show that mass transfer was the main obstacle.

Once the by-products were dealt with and the purity was established, the objective was to demonstrate an improved design of plant which would operate more effectively. This was the final part of the study.

1.4. Layout of this thesis

This thesis consists of 7 chapters. Chapter 1 is the introduction. Chapter 2 gives an insight into the politics and driving forces of the biodiesel industry and also describes the benefits stemming from this research. Chapter 3, the literature survey, is an overview of all the work done in the field of biodiesel. Detailed literature specific to the work in this thesis is included later in the results chapters specific to that literature. Results chapters 4,5 & 6 are written in the style of research papers and can be understood separately. Each of these chapters describes a separate industry problem, but taken together, the three improvements show that significant advances can be made in the biodiesel process. Chapter 7 lists the conclusions of the thesis and objectives for future work. This is followed by a list of references.

CHAPTER 2

THE INDUSTRIAL VIEW

2.1. Tax and incentives

The selling price for biodiesel is usually the same as, or less than, the price of petro-diesel. Without tax concessions, biodiesel is not economically viable with the current oil price and therefore the success of biodiesel is dependent on government backing. The UK government currently gives biodiesel a 20p/litre tax incentive over petro-diesel. Governments give incentives for bio-fuels for many reasons but the main one is because they are seen as environmentally friendly fuels. Therefore the success of biodiesel depends on its green image.

When the petro-diesel price is high and the vegetable oil price is low then biodiesel producers make profit. The profit margin for making biodiesel in the UK has been very tight in the last few years (2003-2007) usually under 10 pence per litre and a large capital investment is required for big plants. Unfortunately many of the biodiesel producing companies in the UK are having difficulty. The original sponsor of this work (UK Biofuels and then in 2004 Green Biodiesel) has gone bankrupt and been bought out 3 times in 4 years. So far, lots of people have lost money on biodiesel and there have been few real winners, but there is no shortage of investors ready to pump in money.

In 2007 the government removed the tax on biodiesel producers making under 2500 litres/year. This made biodiesel production for personal consumption very attractive but caused a rise in the vegetable oil price which has put some of the small and medium producers out of business. This was done because it was impossible to catch individuals using and making their own fuel and it took too many resources from UK Customs and Excise. The pre-established big oil collectors, who control the raw material, are making all the money in this new industry . However the UK government declared in November 2005 that it would take part in the RTFO (road transport fuel obligation) which will come into effect in April 2008. The RTFO will make it mandatory for fuel retailers to include a percentage of biofuels in their fuel or face harsh financial penalties. The mandated blend will start at 2 % in April 2008 and go to 5 % in 2010 (Knott, 2007). This will have the effect of artificially increasing the demand for biodiesel which will increase its price beyond that of petro-diesel. With the RTFO biodiesel producers and farmers will make more money. Requirements on carbon savings and sustainability will eventually be introduced into the RTFO (Cave, 2007) which should at last guarantee the environmental credentials of biodiesel.

2.2. The price of oil

The price of fossil oil determines the selling price of biodiesel or any road transport fuel. The price of fossil oil is steadily increasing as demand increases and world oil production peaks (McKillop 2005, Alhajji 2002 and Bentley 2002). When the peak occurs there will be oil shortages and the oil price will rise, maybe dramatically. As the oil price increases, biodiesel becomes more attractive. There have been short periods of time where biodiesel did not require subsidies to be profitable because the price of oil was so high. There is still some disagreement over when peak oil production will occur, with some researchers saying that the peak has already occurred in 2003 and some say that it will occur in 2018 (Goose., 2007.) The mean of all peak oil predicted dates of is currently 2010 (McKillop 2005, Goose 2007 and Bentley 2002). The worlds remaining oil reserves are increasingly held in unfriendly countries (Bentley, 2002). Governments seek energy security by reducing their oil demand for foreign oil. Biodiesel could replace some of the demand for oil and extend the remaining world fossil oil reserves. Each unit of biodiesel replaces 2/3 of a unit of diesel (Frondel and Peters, 2007.) Investment in biodiesel creates jobs in the countries agricultural and industrial sectors.

2.3. The desire to be environmentally friendly

While some consumers do chose their fuel based on its effect on the planet, this market segment is not thought to be significant and so the selling price for biodiesel is usually the same as or less than the price of petro-diesel. However, the tax incentives that make biodiesel viable are because of its green image, so this is very important. At the beginning of this course of study in late 2003 very few people knew about biodiesel in the UK, and those who did saw it in a very positive way. Now in 2008 the biodiesel industry seems to be approaching a critical stage with the coming of the RTFO (road transport fuels obligation) and much more is known about it. With this knowledge has come a growing anti-biofuels movement worried about the competition between food and fuel and destruction of carbon sinks for biofuel plantations. Groups such as Biofuelwatch have demonstrated against biofuels at industry trade shows in 2007. Some of these concerns are warranted, like the destruction of rain forest (carbon sinks) to make way for biofuel plantations. In 2007 the Biofuelwatch website referenced several non peer-reviewed reports to support its claims of biofuels causing accelerated climate change (Boswell *et al*, 2007). Now there seems to be a growing realisation that biofuels are not as simple a solution as that they were once thought to be and recent papers are finding problems with biofuel sustainability and life cycle analysis (Royal society, 2008). Not all biofuels are the same, corn ethanol from maize for example is a very poor biofuel from a CO_2 saving point of view and uses only slightly less carbon than fossil fuel. However, from the point of view of creating US jobs and increasing security of US energy supply there is a more positive benefit. There are also substantial differences in emissions between different biofuel feed stocks and farming processes. Even within the same biofuel process there can be wide variations in green house gas emissions depending upon land use changes, the use of co-products and the impact of fertilisers. This means that biofuel supply chains have to be evaluated on a location specific basis. For example ethanol from sugar beet was shown in Royal society (2008) to vary between 30 - 90 kg CO_2 equivalent per GJ of fuel, a massive variation depending on many factors. Petrol and diesel were for comparison around 100 kg CO_2 equivalent per GJ. Ethanol was reported to have, at worst case, 40 kg CO_2 equivalent per GJ of fuel if it was produced from wood, but if it was produced from beets, straw or cereal the figures were 90, 70 or 80 respectively. The issue of by-products, such as cake or glycerol, is another problem. Because the total green house gas needs to be allocated between products, there are a number of different ways of accounting for this which leads to arbitrary or subjective decisions (Royal society, 2008). Another problem is that land use changes to make biofuels from traditional carbon sinks such as peat land or tropical forests can mean a net release of carbon. Use of fertilizers can release substantial amounts of N_2O, a potent green house gas, and these need to be carefully controlled to maximise green house gas savings (Royal society, 2008). So it is by no means a simple story that biofuels reduce carbon emissions. All the different types of biofuels affect carbon emissions differently and some may even increase carbon emissions. Therefore each biofuel application needs to be examined by its own merit before it is supported.

Government subsidies and the RTFO may exacerbate this problem because they are based on the volume of fuel and not the carbon savings given, therefore making profitable the use of unsustainable feedstock's such as palm oil. The problem is that important green house gas savings could be missed with existing policy frameworks and targets. Unless biofuels development is supported by appropriate policies and economic instruments then there is a risk that we may become locked into inefficient biofuel supply chains that could create more harm that good (Royal society, 2008). Another problem with biofuels is that it promotes the "business as usual" idea, leading some people to believe they can use large polluting vehicles and biodiesel will make this environmentally acceptable. Since biofuels are not 100% carbon neutral and in limited supply this approach is unsustainable.

Most current research shows the life cycle analysis of biodiesel is very positive, and future advances should further improve this situation. Recent studies (ADEME 2002, Elsayed 2003, ENVOC 2005, IEA 1999, JRC 2003, Levington 2000) have shown that biodiesel from virgin oil is, at present, 2/3 carbon neutral. This is a big CO_2 reduction, which will secure the future of biodiesel to combat climate change. Work by North Eastern Biofuels Ltd (2007) has shown that 97% energy savings and 94% green house gas savings can be achieved when farming practices are optimised for the purpose of biofuels manufacture instead of food production. Several recent studies have attempted to quantify the externalities i.e. environmental benefits, of biodiesel in monetary terms, to examine whether government incentives are value for money. The studies (Wassell *et al* 2006, Demirbas 2007 and Frondel and Peters 2007) all conclude that biodiesel is worth the monetary incentives given to it. However there is still disagreement over whether biodiesel is the best green house gas abatement strategy, (Frondel and Peters, 2007). This may be true but the nature of the road transport application i.e. non-centralized, limited by space and weight and the fact that it accounts for over 23% of green house gases (Kyoto GHG Data, 2006) means that biodiesel will be a very important part of the solution. In conclusion, the current view is that biodiesel can be a very good way to mitigate climate change (Kirschbaum, 2003). However, there is some disagreement and much more research needs to be done (Pearce and Aldhous, 2007). A complete and accurate life cycle analysis of biofuels is a very difficult task to undertake and one that is only recently being properly undertaken.

2.4. Future challenges to biodiesel and other alternative fuels

Other low carbon transport fuels need not threaten the growth of biodiesel because land use will limit biodiesel to about 13% of the current road fuel market (Wassell *et al*, 2006). Therefore there is still plenty of room for other alternative fuels. Since no single current alternative fuel can replace 100% of demand for oil, it would be best that all alternative fuel technologies should be developed with the aim to stop climate change. Only by developing all the alternatives can we find the best solution to sustainable transport, which will probably be a combination of approaches.

There is still disagreement over which fuels will be best because the knowledge and technology is evolving all the time. Following the RTFO, biofuels are certain to be a big part of reducing emissions from road transport. The most popular alternative fuel is biodiesel because of the aforementioned advantages, economics and ease of use. Other popular alternative fuels are Bio-ethanol, Bio-methane, CNG (compressed natural gas), LPG (liquid petroleum gas), hydrogen fuel cell, electric vehicles, 2nd generation biofuels (e.g. biomass-to-liquid, using Fischer Tropsch) and gas-to-liquid. Ethanol was popular but recent studies have shown that some ethanol processes are only 13% carbon neutral (Frondel and Peters, 2007.) Bio-methane is potentially very good because it can be produced from waste and almost any biomass feedstock can be used. Therefore it offers good carbon reductions. However the fermentation process is slow and is currently not as profitable as biodiesel. Bio-methane can be blended with CNG or LPG and this will become more commonplace as natural gas is used for cars. However significant vehicle modifications are needed to run on gas, but the infrastructure for natural gas already exists. CNG and LPG are said to be much lower carbon than gas-to-liquid because the chemical conversion for gas-to-liquid is very energy intensive (Baldwin, 2007.) BP and Dupont have invested in Bio-butanol because of its easier blending with petrol (Harman, 2007.) There is a lot of hype about so called second generation biofuels from lignocellulose, however these are still far from being commercial. By the time these fuels become available the world may already be committed to a level of catastrophic climate change. Another possibility is battery and fuel cell electric vehicles. We are starting to see more electric vehicles on UK roads from the smart electric, g-wiz and NICE mega down to the humble electric bicycle. Running battery electric from solar power is obviously carbon neutral and sidesteps the monitoring uncertainty issue with sustainable biofuels. The limited range of the battery could easily be overcome with a series hybrid to charge the batteries the odd time when a long journey is needed. A plug in hybrid electric vehicle (PHEV) would reduce the cost of the batteries needed because the range could be shortened to just the average daily city drive and would not need to hold capacity for rare long range journeys. An electric drive train is twice the efficiency of conventional cars (Ahman, 2001) and the engine-generator could be set to run at its speed of optimum efficiency. Biodiesel could be used to part fuel these plug in hybrid vehicles. Fuel cells could also replace the engine in a PHEV offering a further weight advantage and quiet operation. PHEV's would offer the most CO_2 reduction especially if the electricity or fuel could be generated from renewables (e.g. wind power or biofuels.) Currently only hybrids and small low power electric vehicles are sold but this does not have to be the case and performance electric sports cars are planned such as the Chevrolet Volt and Tesla Roadster. This author believes that PHEV's are the best low carbon option and will have a bigger role to play in future road transport.

2.5. Industry benefits of this EngD

The biodiesel company sponsor has received the following benefits from this EngD:

- Installation of a Biodiesel quality control laboratory.
- 2 years worth of quality control work, checking their raw materials and product.
- 2 years worth of research and development by a graduate chemical engineer.
- Possible savings of 4p/litre benefit from dealing with waste streams onsite using steam reforming other than paying for contractors to come and collect.
- Possible extra profit of 2p/litre because increased purity of biodiesel will generate a better selling price.
- Possible savings of 1p/litre on energy bill because continuous process makes heat exchange possible. This makes the fuel greener which could in future be taken into account with RTFO subsidies or carbon credits.
- Safe guarding the essential tax break by ensuring quality standards are meet. The tax break is only given to biodiesel, which is defined by law as fuel which meets the EN14214 standard.
- Removing liability and risk from potential law suits arising from poor quality fuel harming vehicles.

CHAPTER 3

LITERATURE SURVEY

3.1. Background

The purpose of this literature survey is to give an overview of biodiesel properties and processes. More detailed literature is found later in the relevant results chapters. At the beginning of this study in 2004 there were 134 biodiesel papers and by the end of the course in 2008 there were 670 biodiesel research papers. The number of papers published each year is exponentially increasing (see Figure 3.1.) which indicates the growing interest in this field. However the total amount of research is still much less than other energy related fields, such as fuel cells with 12,229 papers in 2008. This may be because biodiesel seemed to be more commercial than fuel cells which will require more research breakthroughs in order to make them commercial. However there is still much to learn about biodiesel and many things that need to be re-examined. It seems strange that comparatively so little biodiesel research has been done yet biodiesel is about to become standard across Europe with the onset of the RTFO.

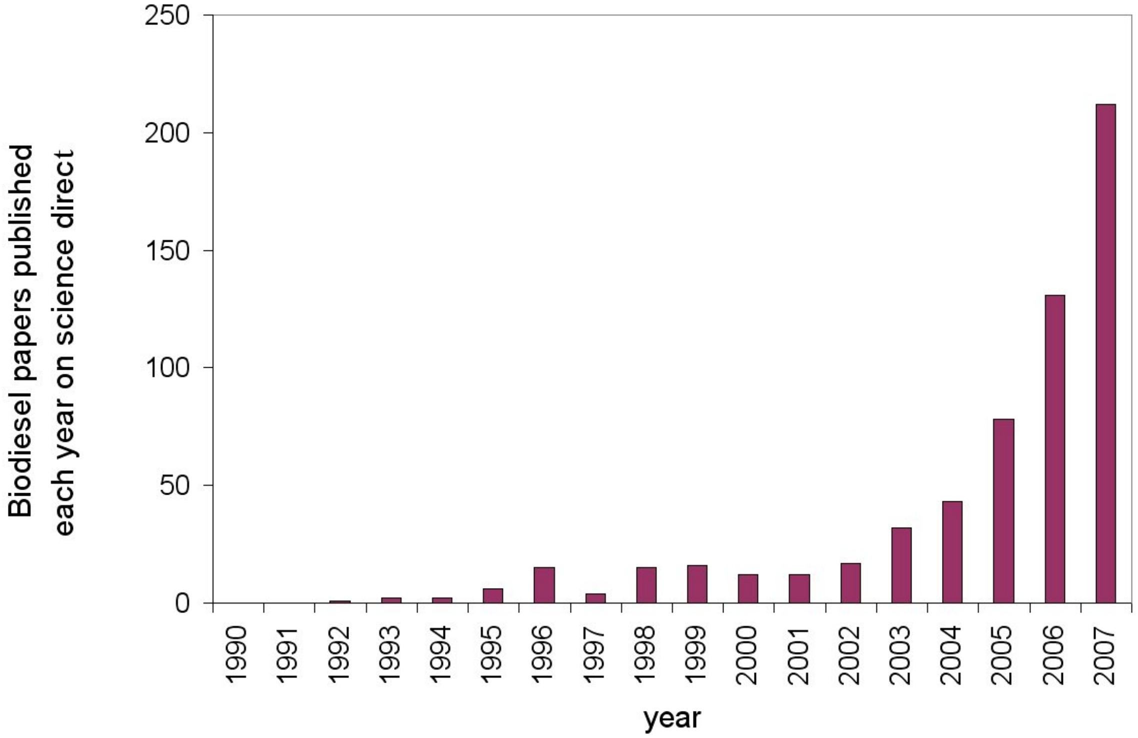


Figure 3.1. The number of biodiesel papers published year on year is exponentially increasing. In the first two months of 2008 there have already been over 100 biodiesel papers published.

3.1.2. Introduction to biodiesel

Biodiesel can be used alone or mixed in any amount with regular diesel (Tickell, 1999). Because of this biodiesel can be used in any diesel engine or infrastructure without the need for modification. Engines run normally on biodiesel because the fuel has similar properties to regular diesel. Biodiesel has a high cetane rating which improves engine performance. Biodiesel is more lubricating than regular diesel fuel and it can be used to replace sulphur compound lubricating agents which when burned produce sulfur dioxide which is the main cause of acid rain, whereas biodiesel contains no sulphur (Tickell, 1999) Much research has been done on how biodiesel effects engine performance and emissions and there are several good reviews of this work (Graboski and McCormick 1998, Lapuerta *et al* 2007, EPA 2002).

Biodiesel substantially reduces un-burnt hydrocarbons (by 70%), carbon monoxide (by 50%) and particulate matter (by 50%) in exhaust fumes compared to petro-diesel (EPA, 2002). biodiesel is +10% NO_x emissions (Lapuerta *et al,* 2007.) Biodiesel fuel consumption is on average 10% higher for pure biodiesel than petro-diesel (EPA, 2002.) The long term effects of biodiesel are still relatively unknown. Some work has been done (Staat, 1995) but studies can not take into account the effects of all the different impurities which are often found in different biodiesels.

Other biofuels for use in diesel engines have been tested. Straight vegetable oils (Pryde, 1983) and various micro-emulsions of alcohol/veg oil/pyrolysis oil/diesel fuel have all been tried (Carrol *et al*, Chiaramonti *et al*, Caro *et al*, and Lima *et al*). Biodiesel is the most successful of these biofuels, probably because it is the simplest to make and use.

3.1.3. Description of biodiesel process

(Detail of green biodiesel process is discussed in section 5.1.1)

In most industrial biodiesel processes the oil is delivered to the factory by road tankers. With used cooking oils it is often delivered hot and kept hot to prevent it from setting solid. Water and fatty acids are usually the main impurities and these parameters will be laboratory tested before the load is accepted. The oil can be initially treated to remove water or fatty acid prior to alkali catalysis reaction, by either centrifugation, acid esterification or drying depending upon the spec of the oil (see process modifications page 20-21). Methanol is also delivered by tanker, it is stored at room temperature in special flammable liquid storage tanks. Sodium hydroxide is delivered by the pallet load containing bags of NaOH in pellet form.

The methanol is measured out and dosed into a mixing vessel by a control system. The sodium hydroxide is added to this mixing vessel to make methoxide. This is a dangerous and unpleasant task so it is preferable to be automated. ATEX regulations must be followed when handling flammable methanol which is an ATEX zone 1 environment. When mixed the sodium hydroxide reacts with the methanol to make methoxide and the temperature increases to around 40°C. Reaction vessels and mixing can vary widely between companies but they are usually un-pressurized batch reactors in the range of 1-33m^3. By regulation large biodiesel plants should have sealed reactors with condensers to trap methanol vapours, and the best biodiesel reactors are pressure vessels which can allow higher temperature reactions. Mixing is usually poor with Reynolds numbers of around 2000 common. Hot oil is loaded first into the reactor and methoxide then pumped into the reactor start the reaction. The oil is usually mixed with 20% methoxide (by volume of oil) and mixed for 1-3 hours at just below the boiling point of methanol (~60ºC). Usually 3.5g of NaOH are used per litre of oil, but extra may have to be added to neutralise acidity. With the standard process it is impossible to reach 96.5% ester content. This author has visited 5 boidiesel plants and tested countless samples from different biodiesel plants in the UK and none have reached 96.5% ester content. Usually the conversion is about 90%.

After reaction the products are allowed to settle in big tanks. The settling process usually lasts several hours, even days hours. The waste glycerol settles on the bottom and is drained off and pumped into storage tanks waiting to be tankered away for disposal. The settled fuel is pumped into washing tanks and mixed with 10% water (by volume of oil) and mixed, usually using compressed air jets or sprinkling systems. This increases the interfacial-area of the fuel and water and transfer impurities into the water. The mixture is then allowed to settle again, and the waste water is then disposal of. Most big biodiesel plants have waste water treatment facilities on-site. The washing-settle process is very ineffective and often needed to be repeated multiple times to remove enough impurities to get complete emulsion separation and give clear fuel. 30% water (by volume of oil) is used and the process lasts several days. After this process the fuel looks clear but still contains several thousand ppm (parts per million) water, so further drying solutions are needed.

There are several other processes and modifications to the biodiesel process. Other processes that were available were acid esterification, high temperature/pressure reaction with heterogeneous catalyst and supercritical reaction with or without heterogeneous catalyst. Modification can include oil pre-treatments such as drying, centrifugation, filtration, acid pre-esterification or alternate clean up processes such as dry-washing, centrifugation, adsorption, additives packages, even distillation.

The most common process modification is the acid pre-esterification stage to convert the fatty acid oil impurities to biodiesel. This process can significantly increase the yield when using high fatty acid oils and is essential with fatty acids >10%. However it does not increase the ester content of the fuel and it is still difficult to reach the standard 96.5%. Usually in this process the oil is first dried and centrifuged to remove water because the acid process is very sensitive to water (Freedman *et al*, 1985). Water is the product of reaction and slows down the rate it there is too much. The type of drier is usually a falling film evaporator and centrifuges are usually disc stack centrifuges. The acid pre-esterification stage only aims to react the fatty acid impurities which make up only usually 7% of the oil and it takes two - four hours (Hancsók et al, 2004). Acid esterification can also be used as an alternative to alkali transesterification to react the oil to methyl-ester. This process usually uses 1% concentrated H2SO4 or hydrofluoric acid as a catalyst. However the reaction takes unfeasibly long times and unfeasibly high methanol ratios to reach completion. 70 hours with 30:1 methanol/oil molar ratio and 65°C was observed by Freedman *et al* (1984) to reach completion. Higher temperatures can offer faster reaction rates but this necessitates the use of pressurized vessels. Some processes are based on using high temperature (up to 250°C) and pressure acid processes in combination with solid catalysts to eliminate the need and problems associated with NaOH. One commercial process available is Esterfif-H® (Bournay *et al*, 2005). This author is not aware of any commercial supercritical processes because their high cost renders them uneconomical, but there is much research done on the subject. The supercritical process uses temperatures up to 300°C, pressures of up to 200bar and methanol ratios of 40:1 methanol/oil molar ratio (Saka and Kusdiana, 2001). This process is very energy intensive although there are benefits that feed impurities water and fatty acid do not degrade reaction and reaction is fast 2-25 minutes. There are lots of papers focusing on the break down of the oil at this temperature as this has been problematic. Various papers have looked at adding catalysts and co-solvents to the supercritical reaction that would allow lower temperatures to be used.

Many alternate clean up processes are available for the alkali catalysed reaction. The washing process is considered to be very wasteful by many and there are a number of different products that can be used to adsorb the soap glycerol and methanol impurities instead. Ion exchange resins such as Amberlite, PD206 from Purolite or BD10 from Rohm & Hass can reduce soap levels by a factor of 10 and will reduce free glycerol down to EN14214 acceptable levels, 0.2% with a flow rate of 3l/hr per kg adsorbent.

Magnasol Adsorbent (Magnesium Silicate) will achieve similar results and can also remove methanol with a dose of 1% (m/m) biodiesel (Berrios and Skelton, 2008). However all the adsorbants tested had problems removing methanol water and mono- and di-glycerides. A primary good separation stage, such as centrifugation, is needed before the adsorbants can be successfully used. A disadvantage with the adsorbents is that none can be regenerated and so this replaces the waste water problem with a waste adsorbent problem. Water washing is still more effective at removing glycerol and methanol. Another interesting separation technology for biodiesel is electrostatic field separation. A high DC voltage, at least 1000v, is applied across two electrodes immersed in crude pre-washed biodiesel, and after several second the soap and glycerol begin to clump together and fall out of solution at the positive electrode (Laming, 2008). Very little work has been done on this process it looks highly promising and it is now freely available in the public domain. In another process Molecular-sives (zeolite) can be used to dry biodiesel after a washing. The zeolite can be regenerated, using heat to evaporate the water. This saves having to heat up the bulk biodiesel in order to evaporate the less than 1% of water.

3.1.4. Overview of biodiesel process research

There are many different research topics underneath the umbrella of biodiesel research such as: new catalysts, new reactors, new processes, reaction variables, analysis techniques and fuel standards, engine testing and other non-transesterification biodiesel fuels. There are several good biodiesel review papers which cover these fields (Ma *et al* 1999b, Zhang *et al* 2003, Meher *et al* 2006, Schuchardt *et al* 1997). Meher *et al* (2006) looked at aspect of biodiesel production by transesterification by used only 8 lines to cover the topic of mixing in the reaction and only one reference. The authors quote ma *et al's* (1999a) work "mixing is no longer needed after the reaction is started" this is wrong as the reaction is mass transfer limited and mixing has a big effect on conversion. There is no counter argument offered. They did have lots of coverage of co-solvents increasing reaction rate and stated the reason this worked was because oil was insoluble in methanol. They did not realise the relevance the insolubility would have on mixing and they failed to ask why co-solvents were seen to be effective but not mixing. Ma *et al* (1999b) conducted a review of biodiesel production. They examined several methods of using vegetable oils as fuels including transesterification to biodiesel and a very detailed discussion of direct use and blending of vegetable oil. They failed to mention the effect of mixing on transesterification in their review even though they wrote a paper on the subject in the same year. They confine their discussion of variables affecting biodiesel to that of concentrations of reactants, time and temperature.

The first most obvious biodiesel research focused on the main variables in the standard biodiesel process. Most of the papers which examine reaction variables are old e.g. Freedman *et al* (1984) and Tomasevic *et al* (2002) Both these papers fail to mention biodiesel as a two phase mass-transfer limited reaction and no attention is given to mixing so they fail to understand the underlying mechanism. Freedman proposed both pseudo-first order kinetics and second order kinetic mechanisms depending on reaction conditions. A special shunt mechanism was offered to explain why intermediate concentrations deviated from the standard second order reactant profile. Freedman failed to realise that the reason their butanol reactions were initially much faster than their methanol or ethanol reactions was because the butanol/oil mixture is single phase. They reasoned it was because the higher boiling point allowed them to react at higher temperatures. The research made few useful advances except for slight adjustments to reaction conditions to achieve slightly better results. Tomasevic *et al's* (2002) paper was particularly dull because it failed to propose any theory and just examined concentrations of reactants with a very limited amount of experimental data. However they were pioneers in the field because there was so little biodiesel research being done at that time. Many of these parameters they examined would be uneconomical to change in real life such as using expensive sodium methoxide catalyst, very high methanol ratios or much longer reaction times. Therefore we have to look further to achieve a breakthrough result, than simply adjusting reaction conditions and observing what happens.

Other papers examine physical variables like viscosity, boiling point or melting point to try to cherry pick fractions of the ester mixture to improve cold flow (Gonzalez-Gomez *et al*, 2001) or to correlate between measurements of biodiesel properties for easy measurement (Kerschbaum and Rinke 2003, Goodrum 2001). This research was too obvious, involved very little theory, and it did not led to any great advance in biodiesel processing. Gonzalez-Gomez *et al* (2001) proposed the useless process of ‘winterisation’ in which the biodiesel is freeze distilled by filtration to yield a biodiesel with lower freezing point. This process would be very energy intensive an also halve the yield of the biodiesel product because the solid saturated oil biodiesel by-product would be useless for most seasons and countries. It would be much better to develop a freezing point depressant additive or cold flow improver that might have a similar effect. Goodrum, 2001 used TGA (thermo gravimetric analysis) to measure the vapour pressures and boiling points of biodiesel mixtures. This work was justified as a new method of quality control. However these parameters are not as important as in petroleum based fuels because there is less variation of these properties in biodiesel feedstocks. No evidence is given that fuel with off spec boiling point or vapour pressure can cause a problem. Similar parameters are measured by tests that are already on EN14214 e.g. flash point. Kerschbaum and Rinke’s (2003) paper is more useful because it examines the trends in viscosity with temperatures. Despite the fact it is just observations of a physical parameter it is usefull because viscosity is an important parameter, it is the reason biodiesel is made from vegetable oil in the first place. This paper examines the idea of micro heat exchanges possibly onboard vehicles to alter viscosity through temperature change and draws conclusions on the best temperatures to use.

3.2. Problem areas global

3.2.2. Sustainability of biodiesel

The problem with biofuels is that scarce arable land is needed to produce them unlike solar panels which can be positioned anywhere (deserts, roofs, etc). Recent papers have highlighted this problem (Royal Society, 2008). Because of government incentives, farmers will make more profit on biofuels, so they will produce biofuels in place of traditional food crops. In theory this could increase the price of food so that some people would not be able to afford to eat. Since overpopulation is one of the causes of global warming, an increase in the food price might reduce the rate of global warming. However, food shortages would not be acceptable from a humanitarian point of view and this would count against biofuels. High food prices would increase the pressure on land use and this might lead to faster destruction of rain forest to plant new farm land. This destruction of rain forests, marsh land and other virgin land would release carbon held in these "carbon sinks" and could accelerate climate change. This whole argument serves to highlight the unsustainable nature upon which our current exponential growth depends. Global population and consumption growth will have to at some point be limited by either resource scarcity or global warming. At this point of resource limitation global consumption will peak and then decline, much like the growth phases of microbes in a fermentation vessel. Hopefully this will happen a long way off in the future and hopefully there will be new technology advances, or social changes that will cushion the effect. In conclusion it is not the biofuels that are unsustainable, but our global exponential growth in consumption. Hence biofuelwatch saying that biofuels are unsustainable is the same as saying that solar power is unsustainable, because it cannot sustain infinite population growth. Nothing on earth can sustain infinite growth, on a finite resource world but this does not mean that biofuels can not be sustainable.

3.2.3. Optimisation of biomass production

Crop production methods need to be optimised to biofuel production so that maximum yields can be produced with as short rotation as possible. Crops have historically been optimised, through selective breeding, to optimise food production. Biofuel production systems will have different optimum efficiency requirements to human digestion systems. Therefore it will be necessary to re-engineer the organisms either through genetic manipulation or through selective breeding or a combination of both (Gressel *et al*, 2008). It will make sense to use an organism that has the highest yield over a given land area over a given time. This organism will probably turn out to be one that can breed the fastest and has the shortest life cycle. These organisms tend to be the smallest like algae, bacteria or yeast. So it is likely that the solution to the problem of biodiesel sustainability will be photo bioreactors which could be used anywhere and would not compete for arable land (Chisti, 2007). These photo bioreactors would then directly compete with solar panels and it would be interesting to see which has the highest conversion efficiency.

3.2.4. Separation and purification

The purification stage of the biodiesel process must be improved to meet strict quality standards. Currently the purification of biodiesel is very slow, taking several days to complete. There are many methods for biodiesel clean-up but many of these treatments also contaminate the biodiesel. For instance methanol recovery by evaporation can lead to soap formation and viscosity increase. Using ion exchange resin to remove soap impurities can lead to increased acid value. Washing the biodiesel to reduce methanol, glycerol and soap increases the fuels water content. Heating the biodiesel to evaporate water can lead to reduced oxidative stability. The purification of biodiesel to meet EN14214 standard is very difficult and in many cases it is impossible if the original oil or biodiesel is of poor quality. This problem could be solved if better reaction technologies are implemented that reduce or eliminate soap and emulsification problems. This problem could be side-stepped if future diesel engines were optimised for "unpolished" biodiesel use and standards were relaxed to a more practical level.

3.2.5. Alternative processes

The use of alkali hydroxide catalysts (NaOH or KOH) is bad because it creates emulsions which affect the process yield. It would be a major breakthrough to find another catalyst that would not leave the same problems. Published work has focused on: non-soluble heterogeneous catalysts (Furuta *et al,* MacLeod *et al*, Gryglewicz *et al*, Arzamendi *et al*, Albuquerque *et al*, Shibasaki-Kitakawa *et al)*, however, none has yet been found that gives sufficient yield under economical reaction conditions. Supercritical and sub critical processes have been developed both with and without heterogeneous catalysts to give the required yield, but these seem to be very expensive and have not been widely adopted. Another possibility would be to find a cheap homogeneous catalyst which has reduced emulsification problems and fast reaction. Another possibility would be to ignore the transesterification route completely and opt for a different process. Vegetable oil could be hydrotreated at refineries and blended with fossil diesel. Alternatively, other completely original catalytic processes could be used (Stumborg *et al*, 1996) and (Huber *et al*, 2007).

A good heterogeneous catalyst for biodiesel would be a breakthrough because it would simplify the downstream separation stages needed to make EN14214 specification biodiesel and may increase the purity (and value) of the by-products. Lots of work has been done in this area but the industrial catalyst of choice is still sodium hydroxide. This may be because the alternatives all have uneconomical reaction conditions, residence times or catalyst costs required to reach conversion. Although maybe manufacturers have not "chemical engineered" the process yet and are sticking with processes they know to work for reasons of capitol cost. There are companies selling heterogeneous catalysts commercially e.g. Esterfif-H (Bournay *et al*, 2005) who claim to be able to reach 98% purity ester and glycerol, but are very secretive about the reaction conditions temperature and pressure.

Many heterogeneous materials have shown promise as catalysts for the biodiesel reaction. The two main approaches have been to use either insoluble compounds with some activity and try to improve their activity or to take homogeneous catalysts and try to immobilize them on a support. Schuchardt *et al* (1997) reviewed the different catalysis methods for the biodiesel reaction both acid and alkali and explained these in terms of their reaction mechanisms. Their work focused on the chemistry of the reaction and in depth look at catalysts including enzymes. They found KOH, NaOH and sodium and potassium methoxides were the only catalysts that could give the desired conversion in one hour reaction. Several authors (MacLeod *et al*, Gryglewicz *et al*, Arzamendi *et al*, Albuquerque *et al*, Liu *et al*, Granados *et al* and Zhu *et al*) have studied alkali earth metal compounds as catalysts for biodiesel. Gryglewicz (1999) studied CaO, $Ba(OH)_2$ and $Ca(MeO)_2$ under normal conditions 60°C and a catalyst/oil loading of 0.84% (m/m). Calcium methoxide was found to be the best, excluding NaOH and barium hydroxide was better but they decided it was too toxic. Unfortunately they fail to specify what type of mixing was used, but it was presumably a low powered magnetic stirrer because all their reactions including their NaOH reaction were slow. After sufficient time all their catalysts reach conversions of around 90% but could not beat NaOH. They then explored the methods of ultrasonics and co-solvents to try to puch the reaction further. Their paper is a good examination attempt at finding better, cleaner catalysts. MacLeod et al (2008) took alkali sodium potassium and lithium based catalysts and immobilized them on CaO, MgO and γ-Al2O3 metal oxide supports. Suppes *et al* (2003) studied an impressive number of zeolite catalysts impregnated with sodium, potassium, titanium and aluminium among others. They used very high catalyst loadings 11%(m/m), high temperatures 150°C and long reactions 24hours and under these conditions were able to reach 96.5% conversion using zeolites catalysts. Their best catalyst was ion exchanged NaX faujasite zeolite (NaO_x/NaX) which achieved 96.5%. No mixing was used, the reactions were performed in sealed glass tubes inside a furnace. With mixing the results might have been even better. Furuta *et al* (2004) examined super acid catalysts of sulphated tin, zirconium oxides and tungstated zirconia. They reacted at 300°C for 20hours with extremely high catalyst loading and high methanol ratio. They used a flow reactor with very low flow rate 3g/hour, mixing was not discussed. tungstated zirconia was their best transesterification catalyst and it reached only 90% conversion under these extreme conditions. They also looked at esterification of fatty acids where they could get better results with milder reaction conditions. Their best catalyst was sulphated tin oxide which they claimed could reach 100% conversion after 20hours at 175°C. Ion-exchange resin was investigated as a heterogeneous catalyst for biodiesel by Shibasaki-Kitakawa *et al* (2006). They used anion-exchange resin as a catalyst in a shaken, flow reactor immersed in a bath at 50-100°C for 2-4 hours. They reached conversion of around 80% with these mild conditions, which show much more promise than other research. Their catalyst had to be regenerated after use and it degraded after multiple uses, catalyst loading was 20-40%(m/m). This area of research remains very promising and hopefully we will see some of these new catalysts being used in industry.

3.3. Problems addressed in this thesis

3.3.2. By-product use

(see chapter 4 for detailed discussion of catalysts and poisoning)

The biodiesel process produces two waste products, water and glycerol. Few people have realised the problem that waste glycerol presents for increasing biodiesel production.

Production of 100kg of biodiesel yields approximately 10kg of glycerol, which is impure and of low economic value. With the even-growing production of biodiesel and by-product glycerol, it has been suggested that the open market value of crude glycerol may be eventually stabilize at the low price of $0.11/kg, but the cost to refine this crude glycerol will cost approximately $0.441/kg (US Department of Energy, 2004). The projected production volume of crude glycerol will exceed the present commercial demand for purified glycerol, and that purification for sales of medical glycerol will not be a viable option for the biodiesel industry, therefore some alternative uses for the glycerol will need to be found (Chi *et al*, 2007).

Historically waste glycerol was mixed with other waste oil and burnt, but this practice was stopped in 2005 when the WID (Waste Incineration Directive) effectively banned burning of waste (European parliament and council of the European communities, 2000). This was bad from a carbon emissions perspective because it made it harder and more expensive to effectively recycle waste oils. Currently waste glycerol and water are likely to be treated by digestion at a water treatment plant where fuel gas yield is low and process time high. Several recent papers have examined the possibility of fermentation of biodiesel wastes and a review paper has been published by Yazdani *et al (*2007). The products involved in recent research were docosahexaenoic acid (Chi *et al,* 2007), glycolipid biosurfactants (Morita *et al,* 2007), hydrogen and ethanol (Ito *et al,* 2005), 1,3-propanediol (Gonzalez-Pajuelo *et al,* 2006) and (Zheng *et al,* 2006) and lipid (Papanikolaou and Aggelis, 2002), (Narayan *et al,* 2005). However these researchers fail to realise that the waste product is not optimal for supporting fermentation of microbes because it contains soap, salts, or acids and high pH which most micro-organisms do not like. Yield is typically low with long residence times, so high value products are favoured in these processes.

Few thermo-chemical routes have been explored for the conversion of biodiesel wastes. Steam reforming to make hydrogen or syngas has been explored by (Slinn *et al* 2007, Shabaker *et al* 2004, Zhang *et al* 2007 and Adhikari *et al* 2007). Shabaker *et al* (2004) investigated low temperature subcritical aqueous phase reforming of oxygenated biomass compounds using tin modified Raney nickel catalysts (Ni:Sn atomic ratio 14:1). They found good activity, selectivity and stability for H_2 production, comparable to good platinum catalysts. They altered the mix of tin to nickel in the catalyst and found it reduced the rate of methane formation and increased H_2 selectivity. However their process requires very dilute feed concentrations below 16-165 steam/carbon ratios (S/C) and very high pressures 1500-5000 kPa. Thermochemical propylene glycol production has been explored by (Dasari *et al,* 2005) and (Chiu *et al,* 2006). This author believes that if biodiesel is expected to become main stream then the glycerol waste would be best converted to biofuels or energy with a fast chemical conversion processes or in WID compliant co-fired power generation.. This is because, with the quantity of glycerol expected, making high value low demand products would soon flood the market and the price would crash.

3.3.3. Biodiesel reaction and reactor design

(see chapter 6 for detailed discussion of reactor research)

The reaction needs to be improved so that fuel quality standards such as EN14214 can be met to guarantee the quality of biodiesel and increase its selling price. Currently (2003-2008) sub-standard fuel is allowed to qualify for the biodiesel tax break, as long as it is from a transesterification process. However the law states that only 96.5% biodiesel should qualify for the tax break so this is a difficult situation for biodiesel producers because it could change at any time. The current reaction scheme is also slow, taking hours to even approach completion.

There are few papers investigating biodiesel kinetics, and those that do exist are based upon the incorrect assumption that the biodiesel reaction occurs in-side a single liquid phase mixture of reactants and is only limited by the rate of reaction. Only two recent authors Boocock *et al*., (1996) and Olivera *et al*., (2007) have realised the importance of the two phase mass transfer limited mechanism and published on it. There is no model of this theory and there is currently no theory in any paper that can be used to predict the conversion of a biodiesel reaction. Boocock *et al*., (1996) noticed that transesterification using butanol at 30ºC was 15 times faster than using methanol at 40 ºC. They concluded that this was because the methanol transesterification was a two phase system compared to the single phase butanolysis reaction. These realisations led them to develop a co-solvent system that used THF in 1.25 times the volume of methanol to form a single phase. The process dramatically increased the initial rate of reaction although there was still difficulty reaching the desired conversion. Olivera *et al*., (2007) studied the effect of agitation intensity on alkali catalysed methanolysis of sunflower oil. They found droplet size distribution became smaller and narrower during reaction or with increased impeller speed. They observed the drop size to stay constant then reduce then level out which corresponded to the slow fast slow parts of the biodiesel reaction. They put the slowing of the reaction down to the nearing of a state of equilibrium.

Many of the papers investigating biodiesel reaction variables used unrealistic reaction conditions that would be too costly to use in industry. For instance Freedman *et al* (1984) used pure sodium-methoxide instead of using sodium hydroxide as is typical of industry. Pure oil is always used and reaction vessels are small and highly mixed. This gives much better results and therefore is seams to have been assumed that reaching the 96.5% EN14214 standard is not a problem. However in the biodiesel industry there is a real problem trying to reach 96.5% ester from the raw materials and reactors used.

Much effort has been put to the problem of developing new biodiesel reactors that can offer separation advantages for the down stream processing such as cleaner glycerol. Some new reactor papers have focused on achieving high conversion but these have all been flawed in some way. None of these reactors have been scaled up for industrial testing. There is very little published work about down stream purification of biodiesel, perhaps because this is business sensitive information that companies do not want to reveal or do not want to admit they have a problem with quality.

3.3.4. The Future of Biodiesel

There are many interesting new technologies that are now in their infant stages which could one day prove very useful for making biodiesel. There are now several ion exchange resin adsorbents on the market for biodiesel clean up. They are still not as good as water washing but in combination with other separation stages could replace water washing with much less waste. Ion exchange resins have also be examined closely as catalysts and catalyst supports. These new resin products will draw extra attention to ion exchange resin based catalysts, and we may see a new break through there. Laming's (2008) electrostatic soap and glycerol separation process looks very promising. As a chemical engineer this author often wondered about the possibility of using an electrostatic field to separate biodiesel elusions but did not have the electrical knowledge to try it out. This has only recently come into the public domain and in combination with ion exchange resins could succeed in replacing water washing without compromising the quality standard. This author does not believe that distillation or supercritical reaction will enter the main stream of biodiesel production processes because they are just too energy intensive and will never be economical. To heat a distillation column it would require a not insignificant fraction of the energy that is present in the biodiesel product. There is however, a promising place for the fast reacting static mixer reactors examined in this thesis. They can produce quality biodiesel in less than 5 minutes compared to the several hours that is required in a batch reactor. This continuous reactor could allow heat exchange opportunities and substantially reduce the heating energy used to make biodiesel and offer big cost savings.

On the social-political side this author believes that biodiesel will always have a place. There will always be millions of diesel vehicles in operation and the price of oil will only increase so sooner or later biodiesel will become established. Hopefull there will be big developments in algae photo bio-reactors that will ensure a plentiful supply of biomass for biodiesel. There will be a lot of work to be done in developing this process and turning the product into dry oil, and then biodiesel.

3.4. What does it mean for thesis?

The following research areas show the most promise for new research from a chemical engineering position.

- Thermo-chemical routes for waste product use i.e. steam reforming.
- Underlying mechanism and kinetics of biodiesel reaction.
- New reactors for increased conversion of biodiesel.

CHAPTER 4

STEAM REFORMING OF BIODIESEL BY-PRODUCT TO MAKE RENEWABLE HYDROGEN

4.1. Introduction to Steam reforming

Currently most by-product glycerol is sent to water treatment for digestion but this process is slow, expensive and has a low yield (Nopharatana *et al*, 2006). Glycerol has been purified by distillation and used in both food and pharmaceuticals. However, distillation is a costly process and the low price of glycerol makes it uneconomic (Zhang *et al*, 2003). By-product glycerol often contains up to 50% impurities such as biodiesel and methanol (Norman Tate *et al*, 2003), a major issue for processing. For large scale production the best option would be to use the by-product as a fuel directly (Ito *et al*, 2005). However glycerol is a poor fuel which does not burn in either petrol or diesel engines (Scharmer *et al*, 2006). Up until recently (2006) by-product glycerol was blended with fuel oil and burnt as fuel. However, a new European directive (Waste Incineration Directive) has put an end to this recycling because of fear of pollution from unburnt combustion products (European Parliament and Council of the European Communities, 2000).

An alternative method could be steam reforming; a high temperature endothermic process which uses a catalyst to react the glycerol with water to produce H_2. The H_2 can be used to generate electricity directly in either a fuel cell or a gas turbine. The advantage of this is that the waste heat from the turbine/fuel cells can be used to supply heat in the fuel reforming which improves the efficiency of the whole burning process. This electricity is renewable energy, which would also create extra funds through Renewable Energy Obligation Certificates (ROCs) (Wordsworth and Grubb, 2003). The high temperature reforming process would also fulfil the new Waste Incineration Directive. Steam reforming is used to reform both naphtha and natural gas. Biodiesel by-product is chemically very different to these, with a C:O ratio of 1:1, a higher boiling point and high impurity levels.

Another benefit of this steam reforming process is that it could use the waste water from the biodiesel washing step. This waste water stream contains a number of impurities which prevent easy disposal. Therefore, an extra cost to the biodiesel process is tankering the waste water to a disposal site, or setting up a waste water treatment operation on the biodiesel site. By combining the glycerol and waste water in the reforming step to produce hydrogen, two costly steps could be removed (Slinn and Kendall 2006).

4.2. Steam reforming theory

There are two main reactions which can occur in a high temperature steam/fuel mixture (Table 4.1); steam reforming and pyrolysis. However many reactions occur simultaneously on the reformer including many side reactions, (Table 4.1). Side reactions transfer high thermodynamic stability by coupling exothermic and endothermic reactions.

1	$C_3H_8O_3 + 3H_2O \Leftrightarrow 7H_2 + 3CO_2$	+128 kJ/mol
2	$C_3H_8O_3 \Leftrightarrow 4H_2 + 3CO$	+250 kJ/mol
3	$C + H_2O \Leftrightarrow CO + H_2$	+131 kJ/mol
4	$CO + H_2O \Leftrightarrow CO_2 + H_2$	-41 kJ/mol
5	$C + 2H_2 \Leftrightarrow CH_4$	-75 kJ/mol
6	$CO + 3H_2 \Leftrightarrow CH_4 + H_2O$	-206 kJ/mol
7	$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O$	-165 kJ/mol
8	$C + CO_2 \Leftrightarrow 2CO$	+172 kJ/mol

Table 4.1 Reactions involved in steam reforming glycerol. Adapted from Sutton, Kelleher, and Ross, 2001

4.2.2. Reaction pathways

The reaction mechanism for glycerol reforming is shown in Figure 4.1. First the glycerol dehydrogenates and chemisorbs onto the catalyst surface. The C-C bond cleaves (347kJ/mol ΔH_{298}^{f}) (Harrison, 1972) and this is followed by dehydrogenation which leaves CO bonded onto the catalyst. The CO can then either desorb, water-gas-shift or undergo methanation.

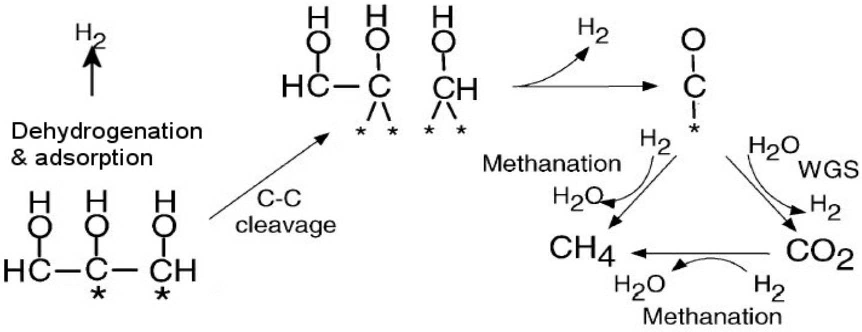


Figure 4.1: Reaction mechanism for glycerol reforming. Adapted from (Davda *et al*, 2005)

Other metal catalysed reactions are possible if a C-O group (358kJ/mol ΔH_{298}^{f}) adsorbs onto the catalyst with C-O cleavage producing smaller alcohols and alkanes. Rearrangement and dehydrogenation reactions can lead to C=C formation producing alkenes and carboxylic acids. These reactions degrade the total percentage H_2 yield and cause carbon formation.

4.2.3. Carbon deposition

Carbon deposition takes place where polymerisation, thermal decomposition and other reactions occur, leading to blockage of catalyst pores and in extreme cases complete failure of the reactor. The oxygen/carbon ratio (O/C) can be calculated to predict carbon deposition in both gasification and combustion. In pyrolysis $O/C \leq 1$, gasification $O/C < 2$ and combustion $O/C > 2$. Gasification and reforming systems can be represented graphically in an equilibrium phase diagram Figure 4.2.

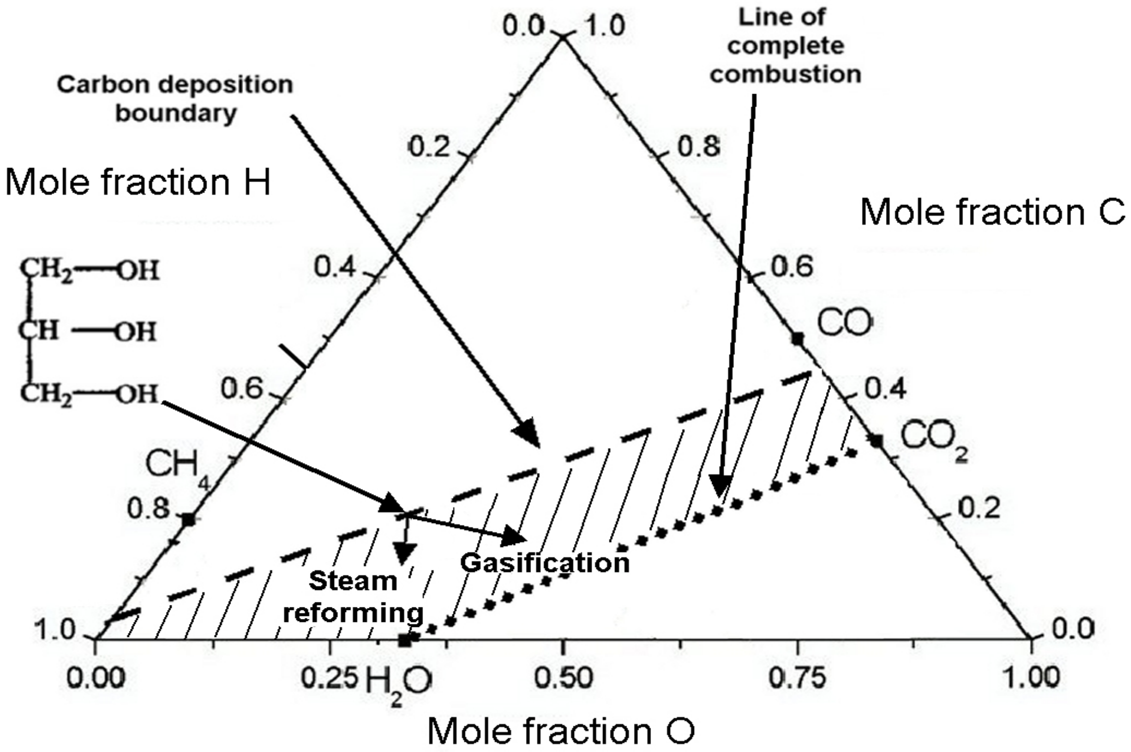


Figure 4.2: Carbon-Hydrogen-Oxygen equilibrium phase diagram. (Prins et al, 2003)

The phase diagram shows that, above the carbon deposition boundary (dashed line), solid carbon particles exist in equilibrium with the gaseous components. Below this carbon deposition boundary (shaded section) carbon is present as either CO, CO_2 and CH_4. To avoid additional carbon formation either oxygen or H_2 must be added to shift the point below the defined carbon deposition boundary. Further addition of H_2 or oxygen will shift the equilibrium position over the line of complete carbon combustion where free oxygen is produced (Prins et al, 2003).

Fossil fuels have lower oxygen within their molecular structure and they would be placed above the carbon boundary in equilibrium with solid carbon. Glycerol contains a higher oxygen content and has an oxygen/carbon ratio of 1 so it is already at the carbon boundary and does not need any extra oxygen or hydrogen. This can be seen in equation 4.2 (Table 4.1), by the fact that no additional oxygen is needed to break the glycerol down to CO and H_2. In effect the glycerol is already partly combusted so it will need more of reaction 4 (Table 4.1) which is exothermic and less of reaction 3 (Table 4.1) which is endothermic. Steam reforming of oxygenated hydrocarbons is thermodynamically favourable at lower temperatures than non oxygenated hydrocarbons (Davda *et al*, 2005), so the steam reforming of oxygenates can take place at lower temperatures because it is more exothermic (Sutton *et al*, 2001). However, this phase diagram assumes thermodynamic equilibrium, which might not always be the case. Therefore, there may be more carbon than predicted.

A novel concept was to use a SOFC (Solid Oxide Fuel Cell) as a carbon deposition sensor. A fuel cell is a device which converts fuel and oxygen directly into DC electricity. Solid Oxide Fuel Cells are high temperature fuel cells (800°C) which are more resistant to fuel poisoning and therefore can run on several different fuels (Kendall *et al*, 2006). These fuel cells consist of a cathode (LSM), electrolyte (Zirconia) and anode (nickel). O^{2-} ions are formed by the cathode and travel through the electrolyte layer and through the anode where they react with the high temperature fuel to produce DC electricity. Carbon deposition will affect a fuel cells performance thus allowing it to be used as a carbon deposition sensor.

4.2.4. Catalysts

For steam reforming the platinum group metals have often performed better as catalysts than the other transition metals. However, most researchers (Garcia 2000, Courson 2000, Courson 2002, Sutton 2001 and Davda 2005) have focused on nickel catalysts because these are commercially available and cheaper than platinum group catalysts. Their objectives were usually to find good catalyst - dopant - support combinations for the reforming of biomass. A good catalyst for glycerol reforming would need to posses good C-C bond cleavage, water-gas-shift activity as well as minimal methanation activity. Good biomass reforming catalysts are most likely thought to be among the group VIII transition metals (they have typical properties of metals, metallic luster, tensile strength and rigidity) including Pt, Ni, Pd, Ru, Ir, Fe, Co (Sutton 2001 and Davda 2005). Davda and co-workers (2005) investigated tin modified Raney nickel catalysts (Ni:Sn atomic ratio 14:1) and found good activity, selectivity and stability for H_2 production using their aqueous phase reforming process comparable to a platinum catalyst of 3% Pt/Al_2O_3. The addition of tin to the nickel catalyst reduced the rate of methane formation and increased H_2 selectivity, which they attributed to its Ni_3Sn alloying effect or selective poisoning of Ni-defect sites which catalyse methanation. They are the leading researchers in the field of low temperature subcritical aqueous phase reforming of oxygenated biomass compounds. However their process requires very dilute feed concentrations below 16-165 steam/carbon ratios (S/C) and very high pressures 1500-5000 kPa making them impractical for some applications.

Garcia and co-workers (2000) identified carbon deposition as a key issue in gasification and tested four support modifiers to try to reduce deposition on commercial nickel catalysts. Magnesium and lanthanum oxides were used in an effort to enhance steam adsorption and facilitate partial oxidation of coke precursors. Cobalt and chromium were used to try to slow surface reactions leading to the formation of coke precursors due to cracking, deoxygenation and dehydration of adsorbed intermediates. They worked at very low residence times 26 ms at above 825ºC with 5-11 Steam/Carbon (S/C) ratios. The presence of lanthanum resulted in a significant decrease in methane and benzene the lowest levels of which were achieved with Ni-Co/MgO-La_2O_3-Al_2O_3 and Ni-Cr/MgO-La_2O_3-Al_2O_3 although most of the commercial catalysts were better H_2 producers due to their water-gas-shift activity. Courson and co-workers (2000) studied steam and dry reforming of biomass using nickel catalysts supported on olivine, a natural mineral like dolomite but better for fluidised beds ($(Mg,Fe)_2SiO_4$) The theory was that the iron would prevent nickel sintering which causes deactivation. They worked at 800ºC with steam/CH_4 and CO_2/CH_4 ratios of 1. They achieved a methane conversion of 95% and no degradation in performance over 50 hours of operation.

The activity of the noble metal catalysts for C-C bond scission during ethane hydrogenolysis was studied by Sinfelt and Yates (1967). They reported most group VIII metals to be better than platinum and palladium and that copper had no C-C bond cleavage activity at all whereas nickel had the best activity for C-C bond cleavage. However a good reforming catalyst must also possess good water-gas-shift activity. Grenoble and co-workers (1981) has investigated the relative activities of group VIII metals for the water-gas-shift reaction. They found copper to possess the highest activity followed by cobalt, ruthenium, nickel and platinum. As there is no obvious all in one catalyst multiple catalyst beds may seem an attractive option. A good reforming catalyst should show minimal activity for methanation reactions. Vannice and co-workers (1977) have reported the activities of group VIII metals for methanation showing that platinum, palladium and iridium give the best resistance to methanation.

Of all the catalysts mentioned platinum and nickel based catalysts seem like the best options for study. Penchev (1976) reported the effects of thermal treatment of platinum catalysts. He says the effect of temperature is critical for chemisorption of H_2 on platinum with the reduction rate decreasing with increasing temperature so that at above 350 ºC no reduction takes place. Also the rate of chemisorption of hydrogen even at room temperature is said to be rapid and irreversible with no difference in platinum crystal size noted at 15 min, 5 or 25 hours.

4.2.5. Supports

Support interactions can critically affect the mechanism and rate of reforming and can be either positive or negative in their action. Rioche and co-workers (2005) tested a variety of different metal - support combinations for the steam reforming of bio-oil including platinum, ruthenium, palladium with supports Al_2O_3 and $CeZrO_2$. Their work showed that ceria zirconia ($CeZrO_2$) consistently out performed Al_2O_3 as a support for hydrogen production and that ruthenium gave higher yields than platinum for model compounds and bio-oil which contradicts the work done by (Davda *et al*, 2005.) Davda and co-workers (2005) tested 10 different supports for platinum for their activity and selectivity for hydrogen production by aqueous phase reforming. They reported highest production of H_2 over platinum-black and TiO_2 supported catalysts, followed by carbon and Al_2O_3. CeO_2 and ZrO_2 supports both performed badly. SiO_2 was the worst performer which was attributed to hydrothermal degradation of the support material. In another paper by that group Huber and co-workers (2004) report that the acidity of SiO_2 solid acid catalyst as a support correlates well with the selectivity for higher alkanes and thus the loss of H_2 production. It is also well known that acid catalyst supports tend to promote polymerisation reactions (Stiles, 1987).

4.2.6. Catalyst Poisoning

Deactivation of catalysts can occur by a number of different mechanisms both chemical and physical in nature. These fall into the four categories of poisoning, coking (or fouling), sintering and phase transformation (Forzatti and lietti, 1999). Other mechanisms of deactivation include masking and loss of active elements via volatilization, erosion and attrition. Poisoning can occur in different ways also, it can block an active site or it can alter the properties of the active site to repel certain species, or it might alter the properties of the active site to produce a different product. In multi-functional catalysts, the poison might be selective to certain type of sites thus changing the equilibrium ratio of products formed. This is where doping of catalysts comes from – intentional mild poisoning that only affects certain sites to alter the equilibrium to favour certain products. Some Pt-Re/Al_2O_3 reforming catalysts are pre-treated with low concentrations of sulphur compound to limit very high cracking activity (Satterfield, 1991). a poison might be preferentially adsorbed by the strongest sites and block them first, or it might block all of a certain type of sites equally, or poisoning could equally affect all of any active sites the same. This can lead to different relationships between concentrations of poisons in the feed vs. effect it has on the activity of the catalyst. This relationship might have important implications for selective doping of specific active sites.

There is a distinction between poisons and inhibitors. Poisons are very strongly adsorbed on to the catalyst surface and are irreversible where as inhibitors are only weakly adsorbed and might be easily reversed with a change of feed composition. Poisons can also react with the feed, for instance a species may only act as a poison under a reducing atmosphere. Metal oxide based catalysts are more resilient to poisoning than metal based catalysts. It is very difficult to analyse what is happening to catalysts because a poison might be very strong and only need very dilute concentrations to have a great effect (Bartholomew, 2001). There are few options for dealing with poisons. Sacrificial catalyst beds can be used where a cheaper catalyst/reactant is used to react with and denature the poison. Combinations of catalysts can be combined to protect each other by catalysing the destruction of poisons, either on the same catalyst pellet as different active sites or as different catalyst beds that protect each other (Sato and Fujimoto, 2007). Active sites can also be incorporated into size selective catalyst pores or supports (Yang *et al*, 2006).

Coking is very different to poisoning and is only concerned with carbon compounds. Coking is a more obvious effect and deposits can build up and increase catalyst weight by up to 20% (m/m) (Rostrup-Nielsen and Trimm, 1977). Coking can degrade performance by cover just active sites or by blocking whole catalyst pores. Carbon can react with itself or with the catalyst metals in many different ways making coking very complex structurally. The carbon deposits can be affected by the conditions of temperature and pressure, the age of the catalyst, the chemical nature of the feed and the products formed (Forzatti and lietti, 1999). The different structures of carboncatious deposits were examined by (Sehested, 2005) using in situ transition electron microscope (TEM). There were three structures observed wisker formation, pyrolytic carbon and encapsulation. Encapsulation is where carbon gums form around a metal partical on the catalyst in a thin film and block any more reactants from reaching the metal. Encapsulation is increased by low temperatures and hydrocarbons with high boiling points. Pyrolytic carbon is formed when hydrocarbons are allowed exist through to very high temperatures and then under go pyrolysis which leaves carbon deposits all around surrounding area. This can result in hot bands in tube reactors. Wisker formation can occur if the steam to carbon ratio is to low for steam reforming catalysts. It is where hydrocarbons are reacted on one side of the metal particle and carbon nucleation of graphite as whiskers occurs on the other side. Coking is easier to analyse than poisoning, there are several methods for example temperature programmed oxidation, where the coke is burnt off and either the weight change or products formed can be measured. Infra-red, UV-visible or C-NMR spectroscopy can be used to chemically identify the deposits of carbon compounds on catalysts (Forzatti and lietti, 1999). Scanning electron microscopy and transmission electron microscopy can be have been used by Nikollay *et al* (2007) to examine carbon deposits. Rostrup-Nielsen (1973) observed that coking had different effects at different temperatures. At lower temperatures the effect of coking was more poisonous to catalyst activity than at high temperatures. However the amount of deposition was higher at higher temperatures. Coked catalysts can usually be regenerated by another reaction e.g. oxidisation. To prevent catalyst de-activation the catalyst can either be periodically regenerated or the reactor feed composition can be optimised to prevent coking. The best way to optimise the feed to prevent coking is to increase the carbon loving species in the feed so that the carbon preferentially reacts with that instead of clogging up the catalyst. This may mean operating the reactor under very lean conditions or high steam to carbon ratio or highly oxidising atmospheres, high air to carbon ratio, e.g. adding more water or air. To reduce coking, Nikolla *et al* (2007) used surface alloying with tin to promote carbon oxidation rather than carbon-carbon bond formation.

Sintering is a loss of active surface area by physical changes to the catalyst caused by temperatre. If the reactor is too hot then the catalyst metal may slightly melt or become mobile and attach to other similar catalyst metals thus reducing the overall surface area. Two mechanisms have been proposed for sintering: ostwald ripening and particle migration (Sehested, 2005). Particle migration involves entire crystallites containing metals to migrate over the support followed by coalescence. Ostwald ripening is transport of metal atoms thought the gas phase or support, emitted from one crystallite and captured by another. There may be interactions with the support material or in unsupported catalysts the porosity may be substantially reduced by the catalyst melting into a single big block. Solid state transformation is where the catalyst support material undergoes a change in crystalline structure at very high temperature.

4.2.7. *Thermodynamics*

Gibbs free energy calculations can be used to predict the final equilibrium composition for the reformed gas, using equations 4.1 and 4.2 as follows:

$$Ln\left(\frac{K_1}{K_2}\right) = \frac{-\Delta H^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \textbf{Equation 4.1}$$

Effect of temperature on equilibrium constant

$$K = e^{\left(\frac{-\Delta G^{\circ}}{RT}\right)} \qquad \textbf{Equation 4.2}$$

Calculating equilibrium constant

These equations have been used to develop the theory lines in Figures 4.7 & 4.9 to show thermodynamic predictions for reformer gas compositions. These equations are both derived from thermodynamic potentials. These equations assume that the substances are ideal gases. In reality the reacting species could have interactions due to electrostatic and covalent forces that would require the use of activity coefficients to take into account these non-ideal conditions. These equations assume thermodynamic equilibrium is reached. For simplicity it was assumed that all the glycerol was instantly converted to H_2 and CO with remaining excess water. The two side reactions 4 & 6 (Table 4.2) then convert these gases into CO_2, CH_4 and water until minimisation of Gibbs free energy occurs. The gas composition data is shown on a dry basis to allow comparison with experimental analysis.

4.3. Steam reforming experimental

4.3.2. Materials

The pure glycerol (1,2,3-propanetriol, glycerin) was supplied by Sigma Aldrich CAS number: 56-81-5, pure>99.0% purity (by G.C.). The by-product glycerol was obtained from Green Biodiesel Ltd. The glycerol by-product composition was 40% fatty matter, 33% glycerol, 23% methanol, 3.8% ash and 3.2% water (Norman Tate & Co Ltd, 2003). The main impurities of methanol and fatty matter, should also steam reform but are not expected to give the same yield as pure glycerol. The ash and sulphur can cause problems with fouling of catalyst surfaces. Water (aqua, H_2O) was real seven trent tap water, not distilled, to add reality to the experimentations. Helium (He) used was from BOC, pure>99% purity, CAS number 7440-59-7.

4.3.3. Apparatus and method

The diagram below (Figure 4.3) shows the experimental set-up used in this research.

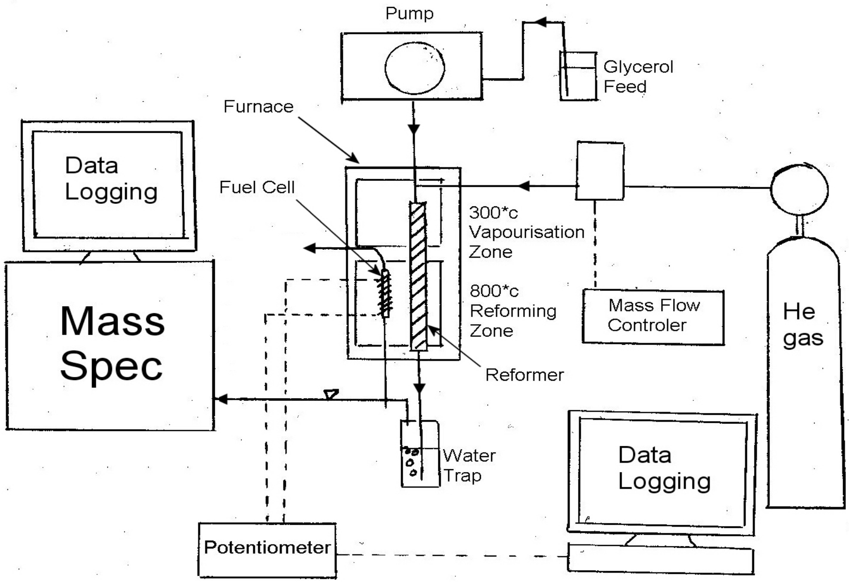


Figure 4.3: Experimental set-up

Real time gas compositions were measured using a Mini lab mass spectrometer with Process Eye software. Helium carrier gas was used (25ml/min) as an internal standard against which all gas flows and concentrations were measured. Flow rate data was checked with a bubble flow meter. The Mini Lab Mass Spectrometer (M.S.) was calibrated using both pure and calibration gases from BOC. Realtime current and voltage information was recorded by a potentiometer connected to Lab View. A water trap was used to collect any possible liquid products and to protect the mass spec from condensable gases which could block the capillary. Water trap contamination was measured using a HP5870 Gas Chromatograph (G.C.) with 30m wax HP1 capillary column. This data was checked against carbon oxygen demand measurements (COD) using on a Hack Langer Lasa30 spectrophotometer. Temperatures were set using a Eurotherm temperature controller. Gas flows were set using a mass flow controller which was calibrated using a bubble flow meter. The glycerol was diluted with water to the desired steam/carbon ratio and fed to the reactor using a micro peristaltic pump. For this experiment 3g of 0.5 wt% platinum-alumina catalyst (Johnson Matthey) was used. A platinum-alumina catalyst was chosen because other researchers had reported good results (Sutton 2001, Rioche 2005 and Davda 2005). The reactor volume was 4.8cm^3 and the total flow rate used (including internal standard) was up to 60ml/min. The fuel cells used were tubular electrolyte supported Solid Oxide Fuel Cells supplied by Adelan Ltd (Kendall *et al*, 2006).

4.4. Steam reforming results and discussion

The objective was first to compare pure and by-product glycerol, then to study temperature and flow rate effects on the process. Long set-up times made stopping and starting impractical, therefore variables were manipulated so that initial reforming conditions were good and gradually worsened until the catalyst was tested to destruction. Some of these variables took up to one hour to reach a steady state. A steam/carbon ratio of 1.35 was chosen as a standard because that was the same ratio in which the by-product glycerol and water were produced in the biodiesel process industry. Percentage gas yield is defined by atoms of carbon out, in the form of CO, CO_2 and CH_4, per atoms of carbon in the glycerol feed. This carbon yield is the best indication of overall gas yield and does not depend on S/C ratio. Percentage hydrogen selectivity is defined as percentage of hydrogen atoms in the hydrogen gas product, per total atoms of hydrogen in gas products created from glycerol. This hydrogen atom balance counts only the hydrogen atoms from the glycerol and does not depend on S/C ratio.

4.4.2. Catalysts

The first task was to find a good catalyst for the research. Previous researchers have used platinum and nickel catalysts for biomass reforming so these were included. Zeolite was also included for comparison because this is a low cost material

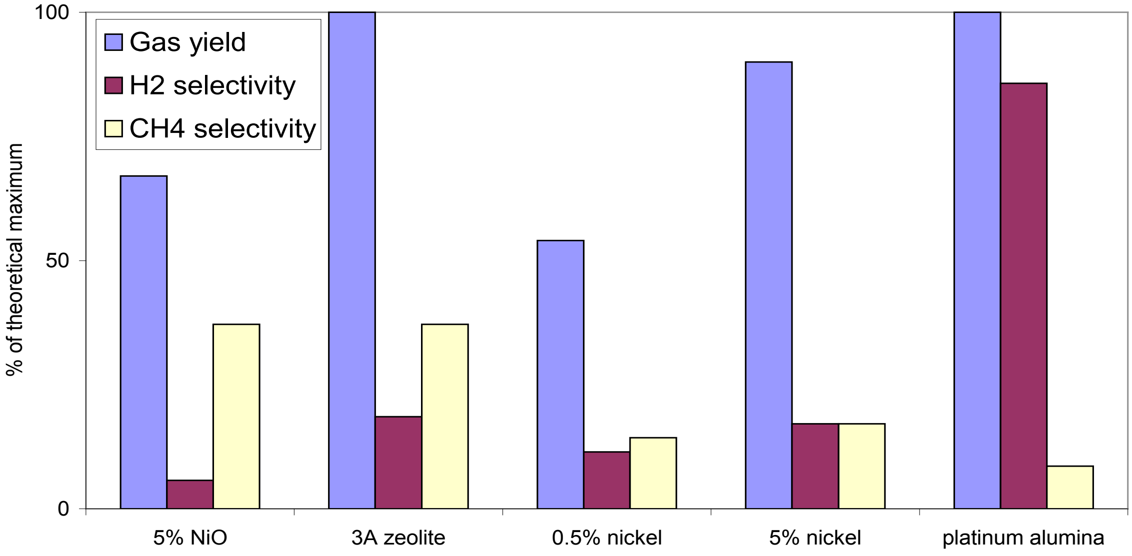


Figure 4.4: Activities of the different catalysts for reforming reactions. The catalyst active metal concentrations on x-axis are shown in weight %. The graph y-axis shows % of theoretical maximum yield and selectivity. Data is from experiment.

Figure 4.4 shows that platinum was by far the best catalyst for the water-gas-shift activity and so this catalyst was selected for use in the research. Other catalysts did show activity for methane production which can also be used in generators and fuel cells. Good gas yield was displayed by all the catalysts and this is the most important characteristic as its important not to clog the reactor with liquid products and char.

4.4.3. Performance of pure and by-product glycerol

The yield of by-product glycerol was on average only 70% of the yield of pure glycerol (selectivity was the same). This is probably because the long chain (C18) fatty acid impurities (40 %) are harder to reform, and are likely to form more carbon deposition on the catalyst than pure glycerol (C3). This experiment was supported by long run experiments where reformer lifetime and carbon deposition was accurately measured. With pure glycerol the longest run reached 30 hours (Figure 4.5), after which the reformer and fuel cell were still functional. This was achieved at S/C = 1.35, 800 ºC and a flow rate of 0.013 ml/min(glycerol). During this time 30 g of glycerol was reformed, 0.12 g of carbon deposition was observed inside the reformer (0.4% of feed stock) and the water trap contained only trace amounts of pyrolysis products 0.034 g (0.1 % of feed stock). With by-product glycerol, the longest run under constant operating conditions reached 10 hours of operation, after which the fuel cell was fully degraded by carbon deposition. This flow rate was higher than the pure glycerol result. In this time 20 g of by-product passed through the reformer and 0.4 g of carbon was deposited on the catalyst (2 %). To cope with these impurities harsher reaction conditions will be needed, for example, longer residence time, higher temperatures and a higher steam/carbon ratio.

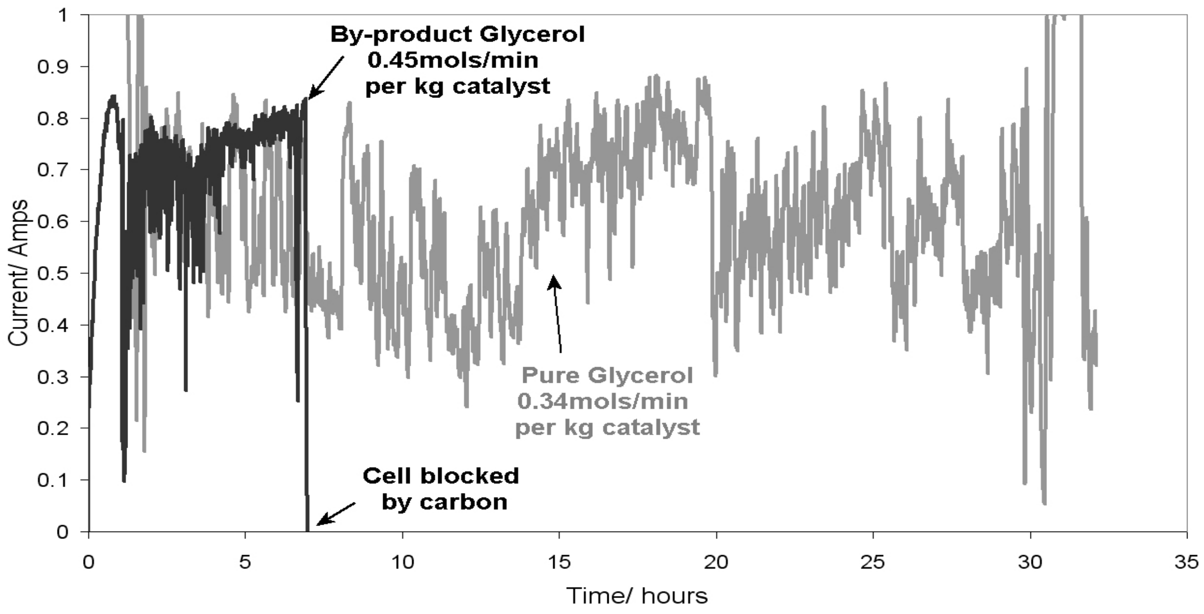


Figure 4.5: Electrical performance of long run experiments for pure and by-product glycerol.

4.4.4. Temperature

Reaction temperature governs the rate and extent of reaction and what products are formed. The effect of reformer temperature on the glycerol to H_2 selectivity and yield were shown in Figure 4.6. These results show that high yields can be reached (85%) at high temperature even with by-product glycerol. The results show a drop in gas yield at low temperatures. This is because of the formation of complex liquid products and tars which cannot be detected by the mass spectrometer. Additional GC analysis of the water trap samples at these temperatures supported this hypothesis and showed traces of unreacted glycerol at 650ºC and contamination from liquid pyrolysis products at temperatures below 700ºC. At all these temperatures the equilibrium constant for glycerol reforming was very high which means that the loss of yield is not a thermodynamic effect, but instead caused by either reaction kinetics (at low temperatures) or by production of liquids and tars.

The effect of temperature on dry gas composition is shown by the data points in Figure 4.7. This reasonably matches with the predicted effect of temperature on equilibrium gas composition (theory lines) especially at the higher temperatures (above 600°C). At higher temperatures more pyrolysis (Table 4.1) takes place which produces CO. At around 800°C there is an increase in the relative amount of CO_2 to CO in the gas product. This is because of reactions 3 and 8 (Table 4.1), which are endothermic and produce CO. Reducing the temperature will retard these reactions by Le Chatelier's principle. At lower temperatures H_2 concentration is reduced and CH_4 increased because of reactions 5,6 and 7 (Table 4.1), which are exothermic and consume H_2 to make CH_4. On Figure 4.7 the R^2 values are 0.44, -2, -5 and -1 for H_2, CO_2, CH_4 and CO respectively. Negative R^2 values show that the data points could be better fitted with a straight horizontal line (average of points) than with the theoretical line. Although, most of these R^2 values can be made to rise above 0.9 with selective deletion of just one data point which shows that maybe anomalous data points are ruining the fit. The error bars on Figure 4.7 show the standard deviation of the results which is small. The error bars increase towards the low temperature region where the data departs from theory, although the error still remains small. Several data sets supported this deviation from theory at the low temperature region so it is not random and could highlight a problem with the theory.

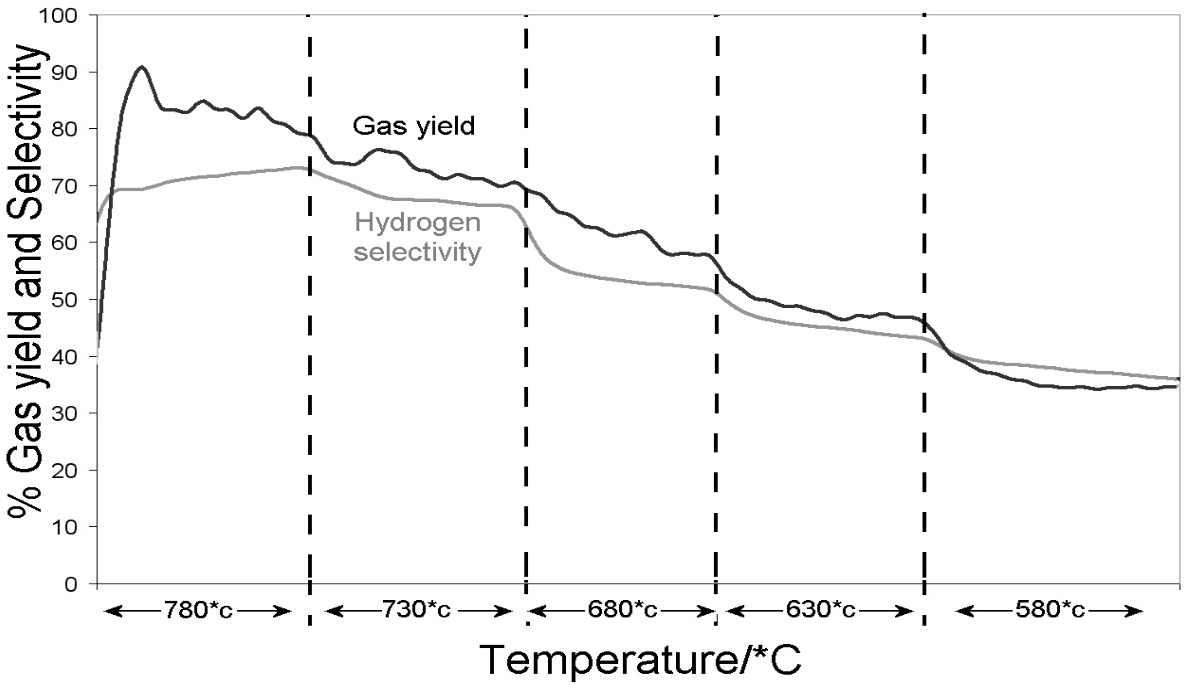


Figure 4.6: Effect of temperature on gas yield and H_2 selectivity. S/C =1.35, glycerol feed rate = 0.0065 ml/min, by-product glycerol.

The results showed less CH_4 than expected from theory, and CO increasing at lower temperature. The CH_4 difference was either due to catalyst effectiveness or reaction kinetics. Forming CH_4 is a five species collision (reaction 7, Table 4.1) and is less likely to happen than other two species collisions (reaction 4, Table 4.1). The CO increase at 600°C seems to be counter to thermodynamic theory but occurred in 2 repeats, this may be a systematic error.

For combustion applications, H_2 selectivity is not as important as gas yield because most gases burn. However some gas components may be undesirable (e.g. poisonous to fuel cells). The results are supported by the fact that the gas flows measured by the mass spectrometer match the reactant flows and the carbon atoms can be counted and balance mostly to within 5%. The results for by-product glycerol are very similar to those of pure glycerol except for a slight reduction in yield.

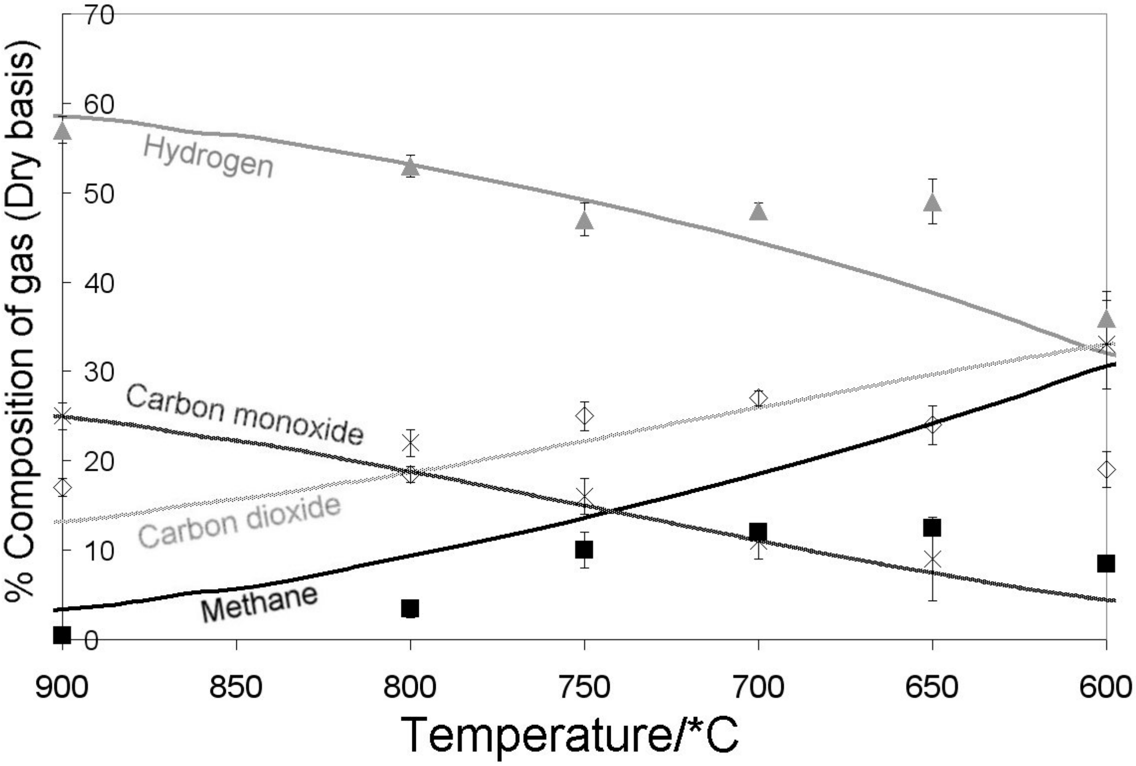


Figure 4.7: Effect of temperature on product gas stream composition. Theory lines from thermodynamic theory. Data points are results from mass spectrometer. Error bars are standard deviation of results. Key to symbols: Hydrogen, ▲; carbon dioxide, ◊; methane, ■; carbon monoxide, *. S/C =1.35, glycerol feed rate = 0.0065 ml/min, by-product glycerol.

4.4.5. Concentration of glycerol feed

The effect of feed steam/carbon ratio on selectivity, yield and SOFC performance at 850°C is shown by Figure 4.8. The liquid feed rate to the reformer was kept constant while its glycerol concentration was changed. The yield stays constant close to 100%, but the selectivity decreases with reducing S/C ratio. There was a sharp decline in SOFC performance at S/C = 0.5 because of carbon deposition. The effect of S/C ratio on reformer gas composition is shown by Figure 4.9. As the steam/carbon ratio was reduced less H_2 was produced and CH_4 production was increased. This is caused by a lack of water molecules starving the water-gas-shift reaction so methanation takes over.

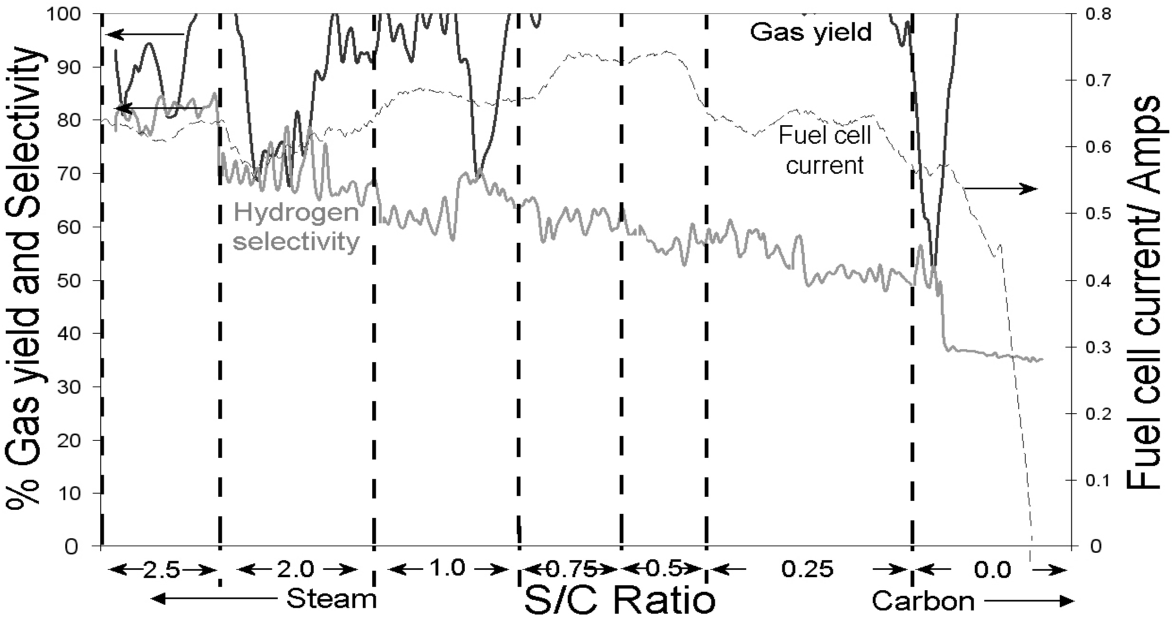


Figure 4.8: Effects of feed steam/carbon ratio on gas yield, H_2 selectivity and fuel cell current. Temperature = 850°C, pure glycerol.

The increase in CH_4 production can be explained in terms of reaction 6 (Table 4.1), where a gas stream with a high concentration of CO and H_2 and lack of water restores equilibrium by producing water and CH_4. The maximum H_2 production is at 2.5 S/C ratio. In Figure 4.9 the R^2 values for the theory lines are -5.9, -1.1, -20 and -0.06 for H_2, CO_2, CH_4 and CO respectively. These show that the theory is not a good fit and that a mean average would better fit the results. Clearly something is going on here that the theory does not take into account.

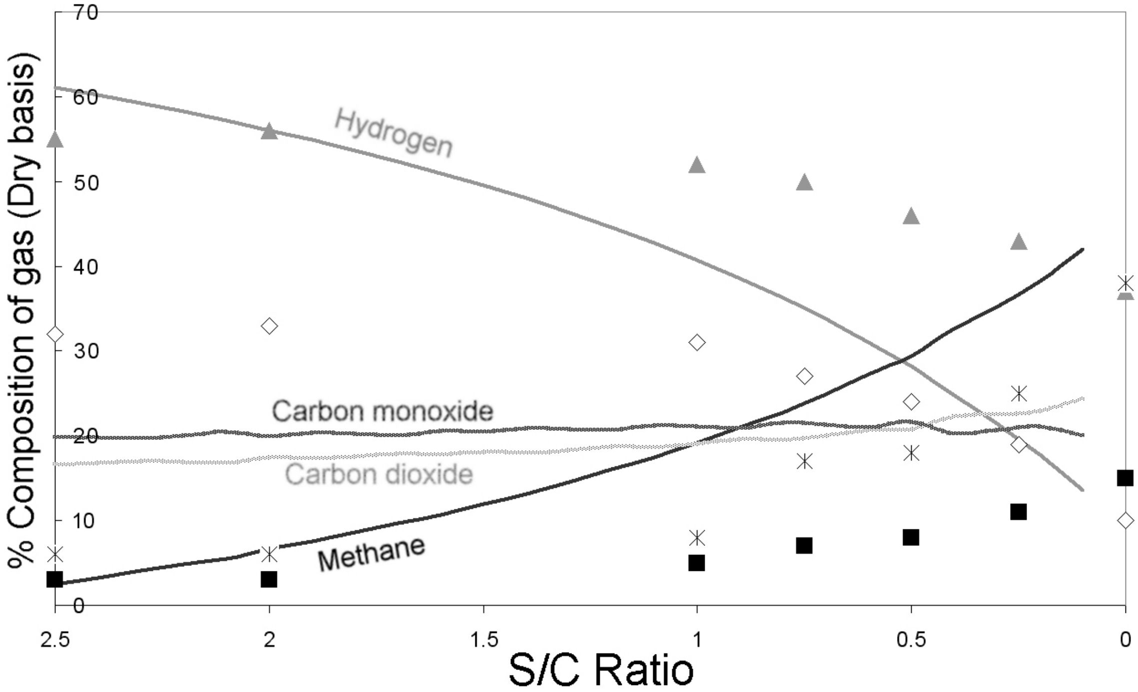


Figure 4.9: Effects of feed steam/carbon ratio on product gas stream composition. Theory lines from thermodynamic theory. Data points are results from mass spectrometer. Key to symbols: Hydrogen, ▲; carbon dioxide, ◊; methane, ■; carbon monoxide, *. Temperature = 850°C, pure glycerol.

The drop in electrical performance in Figure 4.8 is because at low S/C ratios methanation starts to take over as the dominant reaction mechanism and the CH_4 increases, which reduces performance and ultimately overloads the fuel cell. The drop in electrical performance in Figure 4.6, at 0.5 S/C, corresponds to the crossover point in Figure 4.9, where CH_4 becomes the most abundant gas. When the carbon is present as CO or CH_4 it must chemisorb on to an active site to react, however the active site will become blocked if too much of this carbon accesses the active site simultaneously leading to a high carbon concentration and carbon deposition. CO_2 does not have the same effect because it is already completely combusted and has no need to chemisorb to the fuel cell anode for further combustion. At zero S/C ratio with minimal water-gas-shift reaction the fuel cell dies in just under an hour.

A maximum in electrical performance is shown in Figure 4.8 because the total liquid flow was kept constant, so as the glycerol concentration increased, reformer gas flow would increase, causing electricity generation to increase. Therefore the degradation of electrical generation due to carbon deposition will have started at higher S/C ratios, but would have been masked by the increase in fuel gas flow rate. The optimum S/C ratio is therefore closer to 2.5 than 0.5.

4.4.6. Flow rate of glycerol feed

The variation in gas composition against the reactant flow rate at 800°C and S/C ratio 1.35 is shown in Figure 4.10. At faster flow rates the H_2 yield begins to decrease and CO increases. This is the same when flow rate is controlled by carrier flow and by reactant flow. This effect is caused by reactant gases by-passing the catalyst without sufficient time to properly react. In order to water-gas-shift, a reactant molecule needs several requirements to be met; an available active site, contact with a water molecule for a certain period of time and enough energy to overcome the activation energy barrier. If the flow rate per g of catalyst is too fast then one or all of these conditions may not be met. Without these conditions the reactant molecules may just be pyrolysing (reaction 2, Table 4.1) on the surface area of the support. The CH_4 concentration increases with flow rate, probably because the water-gas-shift reaction only occurs at the active site whereas methanation can occur anywhere on the support (trend observed in 4 repeats). With platinum alumina all the water trap samples were clean (G.C. showed no hydrocarbons present) even at the highest flow rate tested.

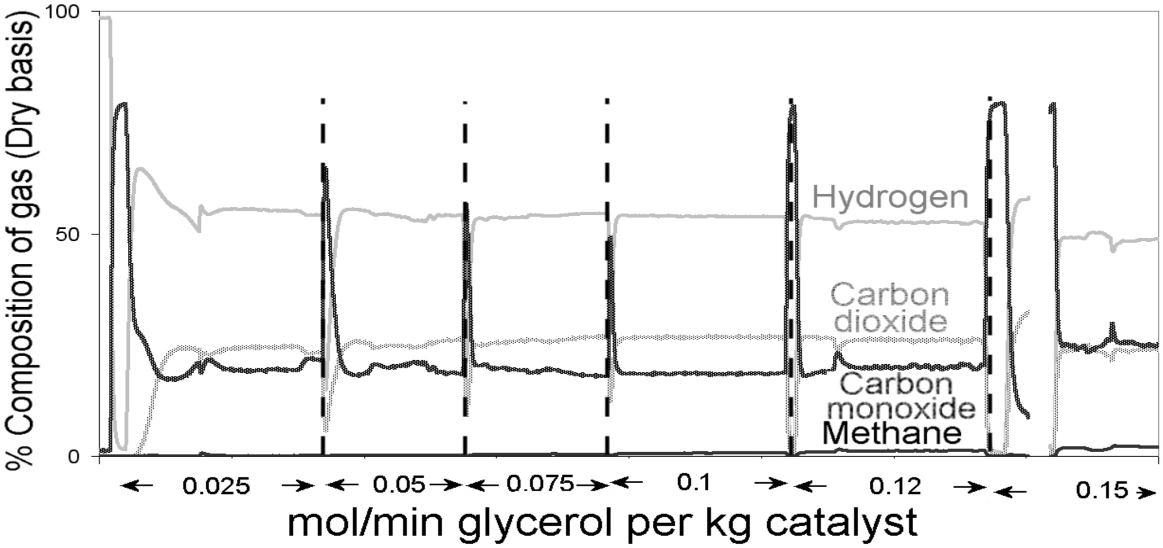


Figure 4.10: Reforming at differing flow rates. Effect of reformer flow rate on gas composition. S/C = 1.35, temperature = 800°C, pure glycerol.

The yield, selectivity and SOFC performance at different flow rates are shown in Figure 4.11. The yield is constant throughout, but the H_2 selectivity decreases with increasing flow rate. The SOFC current increases (caused by more fuel) up to a maximum followed by a decline in performance (caused by carbon deposition). The optimal electrical performance was reached at a feed rate of 0.20 mols/min (glycerol) per kg catalyst. After this point further flow actually decreased the current drawn. The fuel cell was overloaded because too much carbon flowed through the fuel cell (per weight of cell) and there were too few active sites to process it. Consequently, carbon blocked the active sites by forming high local concentrations without the O^{2-} ions coming through to react and desorb so instead the carbon reacted with each other leading to tar formation. This effect blocks the important sites where oxygen diffusion, conductivity and fuel are all available, known as the triple phase boundary, (Deng and Petric, 2005) and reduces the performance of the fuel cell. The degradation of electrical generation due to carbon deposition would have started at lower flow rates, but would have been masked by the subsequent increases in fuel gas flow rate. The optimum flow rate is therefore around 0.12 mols/min (glycerol) per kg catalyst.

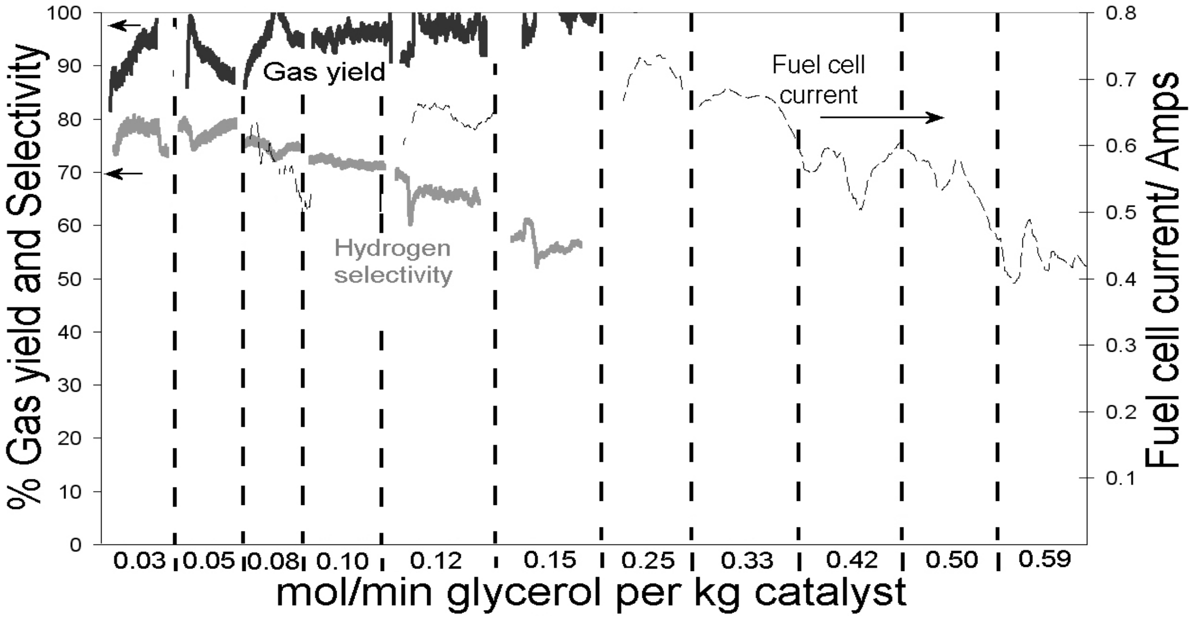


Figure 4.11: Effect of flow rate on gas yield, H_2 selectivity and fuel cell current. Catalyst and fuel cell weighed differently but had same gas flow causing graphs not to overlap. S/C = 1.35, temperature = 850°C, pure glycerol.

4.4.7. Fuel Cell durability test

Over 80 hours of operation has been has been achieved on glycerol reformate. Waste glycerol has been tested and gives the same electrical performance as pure glycerol (over 10 hours of operation.) The longest run so far has reached 30 hours after which the cell was still functional (see Figure 4.12.) This was achieved with pure glycerol at S/C = 1.35 and a flow rate of 0.01302 ml/min(glycerol) and during this time 30 g of glycerol was reformed. Very little carbon deposition was observed inside the reformer (only 0.12 g) and the water trap contained only trace amounts of pyrolysis products 0.034 g.

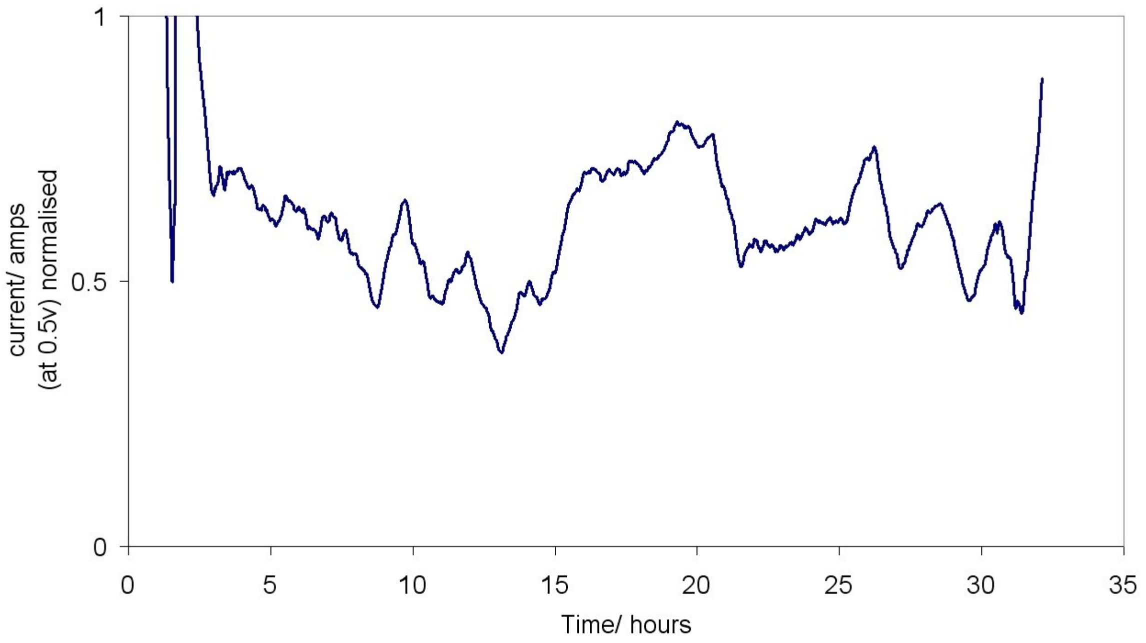


Figure 4.12: Fuel cell current degradation test running on pure glycerol. 0.013ml/min(glycerol), 800°C, 1.35 S/C.

4.4.8. Liquid pyrolysis product identification

High Performance Liquid Chromatography (HPLC) was used to analyse the water trap samples. However, there were too many peaks with concentrations which were too small to permit identification (40 components, most under 1mg see Figure 4.13). However, glycerol was identified by mass spectrometer and could be recognised by its residence time. Gas chromatographic analysis involved similar problems, although significant concentrations of several light components could be seen in the liquid and in the head space. Most of the water traps had a 'bad egg' smell which dissipated with time. No discolouration of the water trap samples was observed.

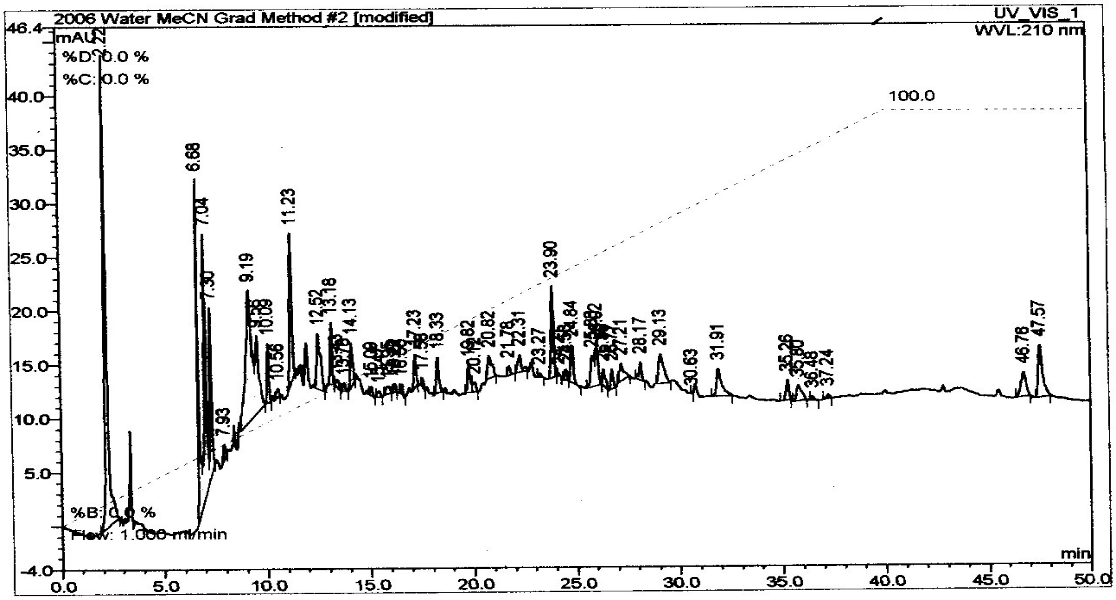


Figure 4.13: HPLC of water trap components. Too many peaks with concentrations which were too small for identification.

4.4.9. Process economics

This process could potentially take all the waste from a Biodiesel plant and convert it to useful energy. This would eliminate expensive disposal costs and generate money from the sale of the energy and ROC's. Next is an economic assessment of the process, with the bottom line showing its effect on the price of a litre of biodiesel. The reforming reaction takes place in the gas phase and energy is required to evaporate the reactants. In the past some biomass gasification systems had required more energy to convert the biomass than could be obtained from the product gas. However, these calculations show that the product energy should be more than sufficient to supply the process energy.

Basis for calculation: production of 1000 litres of biodiesel	
The yield of by-product from 1000 litres of biodiesel…………………….	200 litres
Amount of which is glycerol……………………………………………	100 litres
Amount of water Assuming 2x stoichiometric ratio (S/C=1.35)………..	100 litres
Process energy cost	
Energy to heat glycerol to boiling point………………………………….	48.7MJ
Energy to heat water to boiling point……………………………………	49.4MJ
Energy to vaporise glycerol …………………………………………………	121.8MJ
Energy to vaporise water ………………………………………………	344.6MJ
Energy to heat gas to reaction temperature at 800ºC…………………..	354MJ
Energy for endothermic reaction………………………………………..	173.5MJ
Energy cost total………………………………………………………..	**1092MJ**
Energy produced	
Hydrogen produced from 125kg glycerol………………………………..	18.05kg
Energy produced from calorific value of hydrogen………………………..	**2708MJ**
Net energy produced assuming 40% efficiency…………………………..	**646MJ**
Profit from sale of electricity …………………………………………….	0.448p/litre
Profit from sale of ROC's …………………………………………………	0.807p/litre
Saving on waste disposal cost…………………………………………….	0.6p/litre
Total additional profit per litre of biodiesel………………………………	**1.855p/litre**

Table 4.2: Economic calculation

From the results (section 4.2 and Figures 4.7 and 4.10) we can see that almost all the glycerol is converted to gas and only 0.5-2% is deposited as carbon.	
Power generated (in Figure 4.5) was …………………………………	0.35 Watts.
Glycerol flow rate to achieve this ………………………………...	1.8138×10^{-4} mol/min.
Hydrogen yield predicted using reaction equation 4.1 is ……………	1.2697×10^{-3} mol/min.
Calorific value of this hydrogen could generate energy of ………..	0.3809kJ/min.
40% of the energy produced is required to heat the reactants leaving ..	3.81watts.
Efficiency compared to experimental results (figure 4.5) was …… ….	**9.2% efficient.**

Table 4.3: Efficiency calculation. Additionally, further efficiency could be gained by using condensers to recycle the waste heat after the reaction.

4.5. Conclusions to Steam reforming

Steam reforming of glycerol and biodiesel by-products has been studied using Pt/Al_2O_3 catalysts over a range of conditions. A SOFC has been run on glycerol and biodiesel by-product for the first time. A thermodynamic analysis has been compared to the experimental results and several discrepancies were observed. At high temperatures almost 100% gas yield was reached and selectivities of up to 70% (dry basis) obtained. Steam reforming of glycerol is the dominant mechanism at temperatures above 700ºC, at flow rates under 0.6 mole/min per kg catalyst and at steam/carbon ratios of over 0.5. Optimum reformer performance was reached at 880ºC, a flow rate of 0.12 mols/min (glycerol) per kg catalyst and steam/carbon ratio of 2.5. The SOFC performance was irreversibly degraded thus indicating high carbon deposition at flow rates above 0.20

mols/min (glycerol) per kg catalyst, and steam/carbon ratios below 0.5. The SOFC would not operate at temperatures below 600 ºC because the zirconia did not allow oxygen movement and quickly degraded at very low steam/carbon ratios.

Under the same reaction conditions the yield of by-product glycerol was on average only 70% of the yield of pure glycerol. This is because the long chain fatty acid impurities are harder to reform and more likely to form carbon. In 30 hour experiments pure glycerol deposited 0.4% of feed as carbon whereas by-product glycerol deposited 2% of feed. Under the right conditions SOFCs can operate on reformed glycerol for a considerable length of time which indicates the reformate is of good quality and compatible with gas turbines or engine driven generation equipment. Steam reforming is a viable alternative use for by-product glycerol and could potentially take all the waste from a biodiesel plant and convert it to higher value product.

CHAPTER 5

KINETICS OF THE BIODIESEL REACTION IN A BATCH REACTOR; ATTAINING 96.5% ESTER

5.1. Introduction

In the EU, biodiesel is sold to the EN14214 standard (European Committee for Standardization, 2003) which stipulates 96.5% ester content. Typically, in the Green Biodiesel company, biodiesel made from recovered cooking oil only reaches 90% ester content or less (Table 5.3). This was a major problem because the product value was too low, it had to be blended with higher quality fuels and some whole sellers would not accept it. Commercial biodiesel is a relatively new industry and the theory behind the process was not well understood. In the literature there are conflicting theories (Boocock *et al*, 1996) and no numerical theories have been proposed that predict effects of variables on ester content. The green biodiesel company did not know how to improve their product quality so this author was tasked to investigate the problem. The problem described in this chapter is the theory and practice of reaching 96.5% ester content in a batch reactor.

The transesterification reaction is a cascade reaction where the triglyceride oil is stripped of fatty acid chains in stages until only glycerol remains (Figure 5.1.). Initially progress is fast with 85% conversion occurring in the first 5 minutes of the reaction but after this the rate drops to almost nothing making it difficult to reach 96.5% (Noureddini *et al*, 1997). In this chapter a range of experiments ware conducted to find out what was causing the low quality issue. The reaction kinetics of the batch reaction were evaluated and a numerical theory was developed to help understand the reaction and predict conversion. Mass spectrometry was also used to identify the impurities which affect purity and find their source.

OVERALL: Triglyceride + 3 Methanol → Glycerol + 3 Methyl Ester

Triglyceride + Methanol → Diglyceride + Methyl Ester

Diglyceride+ Methanol → Monoglyceride + Methyl Ester

Monoglyceride + Methanol → Glycerol + Methyl Ester

Figure 5.1 Stepwise reaction mechanism. (Adapted from Harvey et al., 2003)

5.1.2. Green biodiesel process

The Green Biodiesel process (Figure 5.2) starts with recovered cooking oil delivered to the factory in 33,000 litre tankers. This oil was delivered at 50 °C and stored in heated storage tanks to keep it from setting solid. Water and fatty acid was tested in the lab prior to accepting the tanker. Loads with higher than 2% water or 7% fatty acid were either rejected, or accepted at a discounted and blended down. No treatment was done to the oil to remove water or fatty acid prior to reaction. Methanol was delivered to the plant by tanker and stored at room temperature in flammable liquid storage tanks. Sodium hydroxide was delivered to the plant in sacks of solid pellets.

The methanol was measured out into a 500 litre mixing tank and mixed with sacks of sodium hydroxide which were manually loaded by an operator. There was no motor on top of the vessel because it would have been an ignition source, instead the methanol was pump mixed. Methanol was pumped out the conical bottom and pumped in at the tangent to the vessel to create a cyclone motion which mixed the NaOH. The Reynolds number was low. The sodium hydroxide reacted with the methanol to make methoxide and the temperature increased to 40 °C. The reactor for the transesterification reaction was a 2000 litre mixing vessel with a 10 KW motor driving duel anchor type paddle impeller s. The hot oil was loaded first and methoxide was pumped into the reactor and mixed to start the reaction. To aid mixing, the reactants were also circulated from bottom to top using a 5 KW pump. The Reynolds number of this mixing process was low, around 1000-2000, almost to the degree that the liquids would settle. The oil was usually mixed with 20% methoxide (by volume of oil) and mixed for 1 hour at just below the boiling point of methanol (~60 ºC). Usually 3.5 g of NaOH were used per litre of oil plus any extra needed to neutralise the fatty acids. Using this process it was impossible to reach the standard 96.5% ester content. When using lower quality oils the reaction process was often altered by adding 80% of the methoxide and reacting for 1 hour, followed by a second reaction with the remaining 20% methoxide, after separation of the glycerol containing layer. This alteration made it possible to use high fatty acid oils (up to 7%) but sacrificed yield (~75% yields). The impurities were removed in the first glycerol extraction but soap also emulsified biodiesel into the glycerol layer, reducing the yield.

This alteration gives the same ester content and it was still impossible to reach the standard 96.5%.

The whole operation was manually controlled by an operator pulling levers to open and close valves and turn on/off pumps. No advanced control was used. Since every tanker load of oil was different, operators were encouraged to "experiment" with the catalyst and methanol concentrations on each 2000 litre batch. Lab tests were used to guide dosage, and the volume of glycerol and other visual inspections were used to tell if a batch was successful. It was expected that after 3 batches the optimum concentration would be found, and the rest of the load could be reacted using the same conditions. The parameters of each batch were documented and recorded to help with shift handovers and track trends in plant performance.

After the reaction the products were pumped into one of many settling tanks. The settling process would be allowed to last between 8 to 24 hours. The waste glycerol would settle on the bottom and would be drained off and pumped into storage tanks waiting to be tankered away for disposal. The settled fuel would than be pumped into a wash tank and mixed with 10% water (by volume of oil) and mixed using compressed air jets for an hour. This would emulsify the fuel and water and transfer impurities into the water. The mixture would then be allowed to settle for 6-24 hours and the waste water would be pumped into storage tanks awaiting disposal by tanker. The washing-settle process was very ineffective and needed to be repeated 2 more times to remove enough impurities to get complete emulsion separation to give clear fuel. This used 30% water (by volume of oil) and lasted several days. After this process the fuel was clear but the water content was usually several times higher than the 500 ppm (parts per million) maximum specification, so further drying solutions were employed. Centrifugation and zeolite adsorbent were both tested but neither was found to be an acceptable solution. As a result the Green Biodiesel fuel constantly failed to meet ester content, water content and several other related quality parameters.

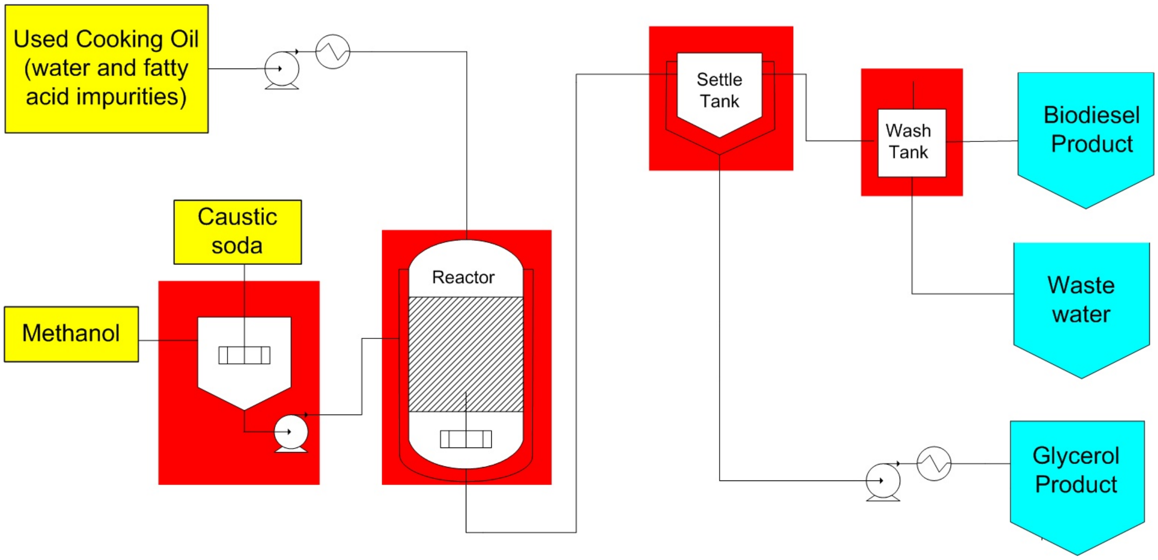


Figure 5.2 A flow diagram of the batch process used at Green Biodiesel. The reaction is a two stage process both stages occur in the same reactor. Washing is a three stage process all of which occur in the same wash tank. There are multiple reactors settle tanks and wash tanks to increase capacity.

5.2. Theory

There can be several reasons why a reaction does not reach completion. The thermodynamic equilibrium may limit conversion, feed impurities may contaminate the product and the rate of reaction may be too slow. These limitations are discussed below.

5.2.2. Thermodynamic conversion

Thermodynamics can tell us what degree of completion a reaction should reach at equilibrium. There are several complex reactions involved in transesterification but the process can be simplified down to three competing reversible reactions; esterification, hydrolysis and saponification. These reactions yield three competing products; fatty acid, ester and soap. The reactions are shown in Figures 5.3, 5.4 and 5.5. Minimisation of Gibbs free energy was used to calculate the equilibrium constants for these reactions, which are shown in the Figure legend. Component mass balances combined with these equilibrium constants can be solved to find ester content but certain assumptions and iterations are needed. The result is a maximum conversion for biodiesel transesterification reaction of 99.8% at 25ºC. This clearly shows that transesterification is a very thermodynamically favourable reaction with high equilibrium constant and potential for full conversion.

$$\mathrm{R\text{-}COO\text{-}R' + NaOH \leftrightarrow R\text{-}COO^{-}\,Na^{+} + R'OH}$$

Ester Sodium hydroxide Soap Methanol

Figure 5.3 Ester saponification to form soap (or soap esterification in reverse). Tri-glycerides, mono-glycerides, di-glycerides and fatty acids can also be saponified. $\Delta H_{298} = -22.9$kJ/mol. Equilibrium constant (298) $K_c = 5.118 \times 10^{-3}$.

$$R\text{-}COO\text{-}R' + H_2O \leftarrow \rightarrow R_3\text{-}COO\text{-}H + R'OH$$

Ester Water Fatty acid Methanol

Figure 5.4 Ester hydrolysis to form fatty acids (or esterification in reverse). Tri-glycerides, mono-glycerides and di-glycerides can also be hydrolysed. ΔH_{298} = 34.35kJ/mol. Equilibrium constant (298) $K_c = 8.1588 \times 10^{-6}$.

$$R_3\text{-}COO\text{-}H + NaOH \leftarrow \rightarrow R\text{-}COO^- Na^+ + H_2O$$

Fatty acid sodium hydroxide Soap Water

Figure 5.5 Fatty acid saponification to form soap (or soap hydrolysis in reverse). ΔH_{298} = -57.25kJ/mol. Equilibrium constant (298) K_c = 627.28 .

5.2.3. Feed Impurities

There are many possible impurities present in used cooking oils that could contaminate the final product. Even fresh cooking oils can contain impurities. Some typical vegetable oil impurities are listed in Table 5.1. In fresh cooking oil the most common impurities are plant serols, proteins and phospholipids. In the frying process the oil is exposed to high temperature for long periods of time, which allows complicated chemistry to occur. The main impurities created during frying are fatty acids and water which cause side the reactions during transesterification. Many other frying impurities have been identified in the literature and can be seen in Table 5.1 including dimers, cyclic compounds, polymers and leached food ingredients. Used cooking oil is of variable quality and it can be difficult to find out what is in each batch.

A badly designed process can introduce impurities into the product. These include: side reaction impurities (soap), by-product impurities (glycerol, water) and residual reactants (methanol, mono, di, tri-glycerides).

Impurity	**Source**	**Reference**
Plant sterols: Tocotrienol, Tocopherol	Fresh Cooking oil	Perkins and Erickson, 1996
Cholesterol	“	Perkins and Erickson, 1996
Phospholipids	“	Mittelbach, 1989
Glucosinolates	“	Mittelbach, 1989
Carolenoid, Carotenoids	“	Mittelbach, 1989
Phosphoglycerols	“	Mittelbach, 1989
Carotenes	“	Mittelbach, 1989
Chlorophyll	“	Mittelbach, 1989
Phorbol esters	“	Mittelbach, 1989
Toxalbumine	“	Mittelbach, 1989
Water	Used cooking oil	Freedman, 1984
Fatty acid	“	Freedman, 1984
Hydroperoxides	“	Mittelbach, 1989
Aldehydes	“	Perkins and Erickson, 1996
Proteins	“	Perkins and Erickson, 1996
Polymers	“	Perkins and Erickson, 1996
Dimers	“	Perkins and Erickson, 1996
Oxidised components	“	Perkins and Erickson, 1996

Table 5.1. Cooking oil impurities.

5.2.4. Reaction rate

Most authors (Noureddini *et al* 1997, Boocock *et al* 1996, Dube *et al* 2007, Ma *et al* 1999 and Freedman *et al* 1984) agree that the transesterification reaction is initially mass transfer limited because the oil and methanol reactants are immiscible. Therefore, conversion could be modelled using a droplet size equation (Equation 5.1) and a reactor design equation (Equation 5.2). Ma *et al*, (1999) concluded that for the biodiesel reaction Misek's equation (Equation 5.1) could be used to predict droplet diameter. The Misek's equation was selected for use in this work because it was the mentioned in a respected biodiesel paper, it had simple parameters which were all known for the system of interest and it seemed to fit with results later on. The Rate equation of mass transfer limitation (Equation 5.2) was selected because it illustrates how surface area can be included in a reaction rate equation for mass transfer limited reactions. It was published in a well respected book and it is a physical equation, not empirical. This equation was simplified into equations 5.4 and 5.5, for ease of use in this work to include only one concentration and surface area term as is relevant for the fast reaction at surface model.

The droplets start off as methanol in a viscous oil phase and, through reaction, are changed to viscous mostly glycerol droplets in a biodiesel phase. The glycerol phase is often solid at room temperature which highlights the mass transfer problems. At reaction temperatures there are no solids present in the reactor. The reaction itself takes place in a thin film around the droplets because the reaction is very fast but limited by mass transfer. This was demonstrated by Boocock *et al*, (1996) who used co-solvents to achieve a single phase reaction that achieved very fast reaction times by removing the mass transfer limitation. In the two phase reaction, if mixing is insufficient then the droplets will reach localised equilibrium which will slow down the reaction. Without surface renewal caused by shearing of the droplets the process will be very slow. This is what causes the problem in our system which does not have the high Reynolds number turbulent flows and therefore conversion and speed of reaction is low.

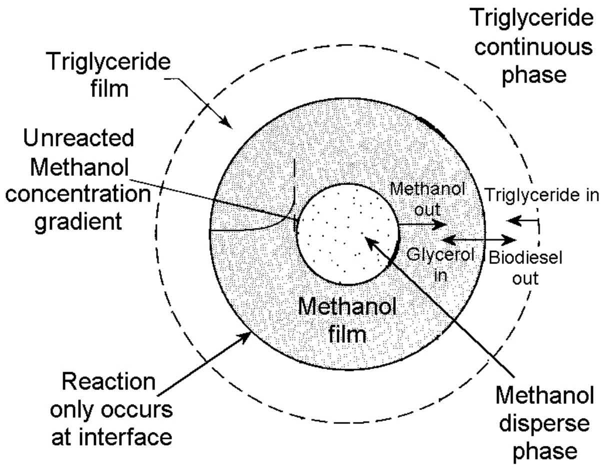


Figure 5.6 Mass transfer limited model. Reaction only occurs in thin film surrounding the droplet. Adapted from (Levenspiel., 1999).

$$d_o = \frac{16.3\left(H/D\right)^{0.46}\sigma e^{(0.087D)}}{n^2 d^2 \rho_c}$$ **Equation 5.1**

Misek's equation describes droplet diameter d_o. Impeller speed n, tank height H, tank diameter D, impeller diameter d, density of continuous phase ρ_c, surface tension σ. (Ma et al., 1999)

$$-r_a'''' = \frac{1}{\left(\frac{H_A}{K_{Al}aE} + \frac{H_A}{KC_B f_l}\right)} \times C_A$$

Equation 5.2

Rate equation of mass transfer limitation. This equation consists of two terms: liquid film resistance and liquid bulk resistance respectively from left to right. This is then simplified when one term is found to be dominant. The equation is from page 529 of Levenspiel (1999) but it has been adapted for use in liquid/liquid reaction. Ha is the henerys law constant, K_{al} is the rate constant per surface area, a is the area, E is the enhancement factor, f_l is the volume fraction that is liquid, k is the rate constant for reaction in the bulk, -ra'''' is the reaction rate in the whole reactor.

5.3. Previous results

In the biodiesel reaction, conversion tends to stabilise at about 90% and further mixing seems to have no effect (see Figure 4). Some researchers have interpreted this as a transition, from mass transfer to rate limitation, but others maintain that the reaction is only limited by mass transfer and some have completely different theories to what limits the reaction. Hence there is disagreement in the literature over what controls the reaction and limits conversion.

Freedman (1986) studied the kinetics of the biodiesel reaction and proposed both pseudo-first order kinetics and second order kinetic mechanisms depending on reaction conditions. A special shunt mechanism was offered to explain why intermediate concentrations deviated from the standard second order reactant profile. Rate constants were calculated by plotting Arhennius graphs (Lnk vs 1/T). Noureddini and Zhu (1997) studied the kinetics of the transesterification of soy oil. They concluded that the reaction was only mass transfer limited in the initial slow region after which a single phase was formed and the reaction rate increased. The reaction was said to be rate limited from then on, by a second order kinetic. They stated that the matching reaction rate curves from different impeller speeds proved that the reaction was rate imitated. They plotted Arhennius graphs and calculated rate constants for the reaction.

Boocock *et al*., (1996) noticed that transesterification using butanol at 30 ºC was 15 times faster than using methanol at 40 ºC. They concluded that this was because the methanol transesterification was a two phase system compared to the single phase butanolysis reaction. These realisations led them to develop a co-solvent system that used THF in 1.25 times the volume of methanol to form a single phase. The process dramatically increased the initial rate of reaction although there was still difficulty reaching the desired conversion. In their 1998 paper Boocock *et al* tested the kinetics of their new THF co-solvent method and tried to reach full conversion. They found the THF diluted and slowed the reaction and they could not get full conversion with one methanol injection because the amount of THF needed to achieve a single phase diluted the reaction too much. They explained the absence of mono and di-glycerides without recourse to Freedman's shunt mechanism. They reasoned that, the reaction takes place in the methanol where the hydroxyl groups of the created intermediates would be more soluble causing them to react further.

Ma *et al*., (1999) looked at the effect of mixing in beef tallow methyl-ester including droplet size observations. A difference was noted between adding the methanol while mixing compared to before mixing. Drop size verses impeller speed correlations were proposed for the beginning of the reaction. It was concluded that after reaction initiation a stable emulsion was created and the effect of stirrer speed was insignificant on conversion in the range 110 - 330rpm. Zheng (2006) concluded that no significant difference in the yield of biodiesel was found within the Reynolds number range of 6000 – 12,000 (100 - 600rpm). Darnoko and Cheryan., (2000) studied the effects of temperature on the reaction kinetics of the biodiesel reaction. They observed that higher temperatures did not reduce time for maximum conversion. They plotted Arhennius graphs (Lnk vs 1/T graphs) and calculated rate constants and activation energies for all the component reactions. Olivera *et al*., (2007) studied the effect of agitation intensity on alkali catalysed methanolysis of sunflower oil. They found droplet size distribution became smaller and narrower during reaction or with increased impeller speed. They observed the drop size to stay constant then reduce then level out which corresponded to the slow fast slow parts of the biodiesel reaction. They put the slowing of the reaction down to the nearing of a state of equilibrium.

It is evident from this discussion of previous work that the question of mass transfer in the biodiesel reaction has not been fully answered. Therefore, experiments were designed to show the phase separation in a small reactor, and theory was proposed to explain these new observations (Slinn and Kendall 2008).

5.4. Experimental

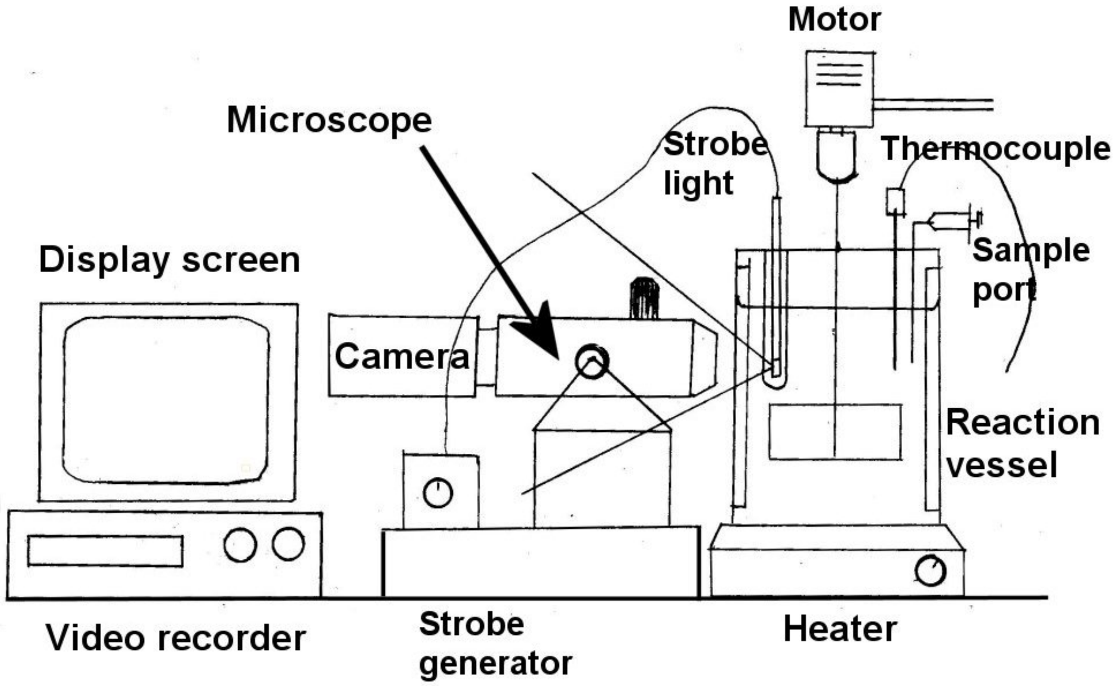


Figure 5.7 Equipment diagram. Equipment developed by Pacek *et al* (1998).

For experiments where droplet size measurements were important reactions were done in a 2 litre closed glass vessel and filmed using a camera-microscope-strobe light arrangement as shown in Figure 5.7. Samples taken from the reactor were chilled with ice water and quenched with acidic ion-exchange resin to stop the reaction then centrifuged to remove the glycerol. For experiments where multiple data points were needed whilst ensuring that temperature and mixing conditions remained constant, sealed centrifuge tubes were used in a large culture shaker. Reacted biodiesel samples were washed three times by shake mixing with water in centrifuge tubes followed by centrifugation to separate. For biodiesel distillation a single stage vacuum distillation apparatus was used with pressures set around 0.3 mbar and temperatures set between 132 ºC-170 ºC inside a fume cupboard.

The EN14214 standard test uses an internal standard gas chromatography method (European Committee for Standardization, 2003). It is based on the fact that only ester elutes from the chromatography column between the specified residence times (10 - 25 minutes) whereas the mono, di and triglyceride components will stick to the column. The test uses methylheptadecanoate, a 17 carbon chain ester which does not naturally occur in nature, as an internal standard with which to compare the areas of the ester peaks. Two drops of sample are weighed, then doped with a known weight of methylheptadecanoate in heptane and then injected into the gas chromatography (G.C.), where the peak areas are recorded. The area of the internal standard peak was related back to its weight in the sample. This provided a ratio which could be used to calculate the weight of ester from the total ester peak areas. This calculated weight of ester was then divided by the actual sample weight, to provide a percentage ester content for the sample (see Equation 5.4). This work used a HP5890 series II gas chromatograph with a HP1 column, split injection and flame ionisation detector (FID). In repeatability trials this method was accurate to within ±1% ester which is the basis for the error bars on the graphs in this thesis. A typical G.C. trace is given in Equation 5.3.

$$Ester\% = \frac{Area\ of\ Methylester\ peaks}{Area\ of\ internal\ standard\ peak} \times \frac{Weight\ of\ internal\ standard}{Weight\ of\ sample} \times 100$$ **Equation 5.3**

Used to calculate ester content in EN14214.

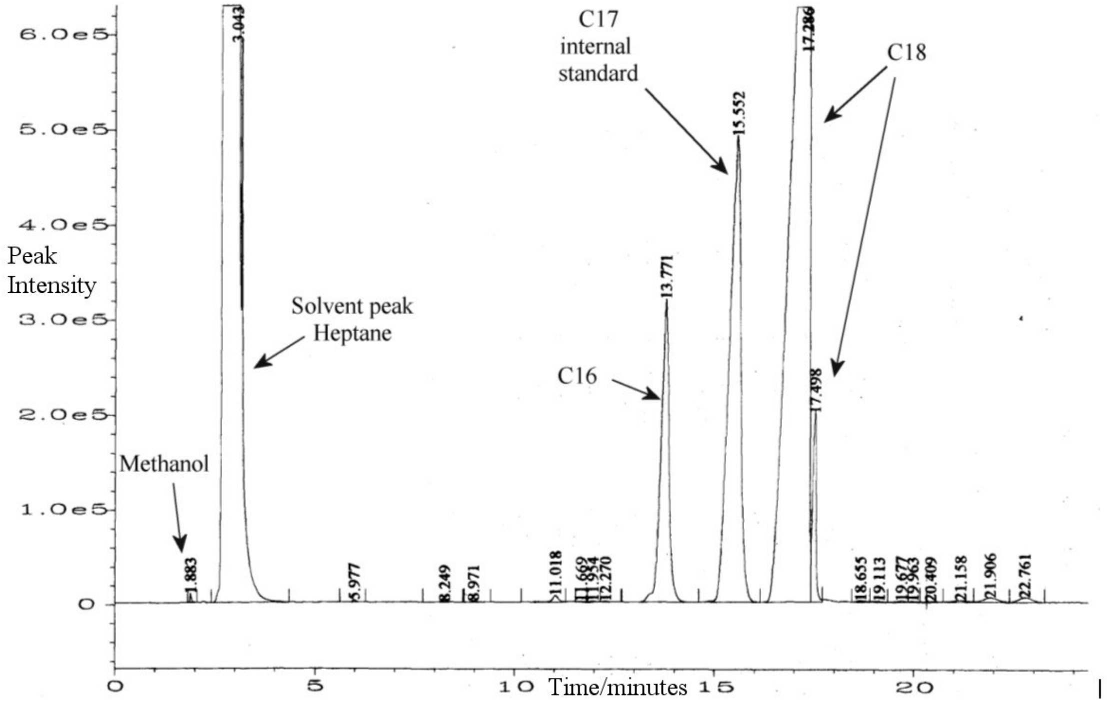


Figure 5.8 Typical gas chromatograph used to calculate ester content in EN14214.

This simple method eliminates the error incurred by varying injection volumes. However several assumptions have to be made this method; that all methylesters are detected equally in the flame ionization detector, that all methylesters are detected linearly with concentration in the flame ionization detector and that everything between the 10 - 25 minute residence time is methylester. The problem with this method is that not all the sample passes through the column and the heavy components stay stuck to the column until they eventually degrade enough to become volatile. There are arguably better methods than this official standard. One method uses a high temperature column through which all the sample components can pass including the mono, di and triglycerides. This method doesn’t involve an internal standard, but instead assumes that the peaks make up everything in the sample and that the ester peak area can be divided by the total peak area of the sample to give the ester content. This method can be used at the same time to give the mono, di and triglycerides content.

5.4.2. Materials

The methanol used was supplied by sigma Aldrich >99% purity, CAS number 67-56-1, other names: Methyl alcohol, wood alcohol, monohydroxymethane. The vegetable oil (rapeseed oil) used was supplied by KTC ltd and was edible food grade quality >99.9%, CAS number 8001-22-7, also called tri-glyceride, tri-glycerol, triaclyglycerol. The caustic soda (sodium hydroxide, NaOH) was supplied by sigma Aldrich and was 97% pure, CAS number 1310-73-2. The ethanol was supplied by sigma Aldrich, >99.5% purity, CAS number 64-17-5, also known as ethyl-alcohol. The heptane, supplied by sigma Aldrich, was chromatography grade, purity >99.5%, CAS number 142-82-5. The methlyheptadecanoate was chromatography grade, 99.7% pure. Other synonyms used are: Methyl margarate, Heptadecanoic acid methyl ester, C17-methylester. It was supplied by sigma Aldrich, CAS number 1731-92-6.

5.5. Results

5.5.2. Proofing the mass transfer mechanism

In order to improve the reaction conversion we must first understand the governing dynamics of the biodiesel reaction. From the thermodynamic calculations it was clear that thermodynamics do not limit the reaction. Therefore there must be a kinetic rate or mass transfer limitation. The conversion problem is illustrated well by Figure 5.9 where the data points never reach the 96.5% standard.

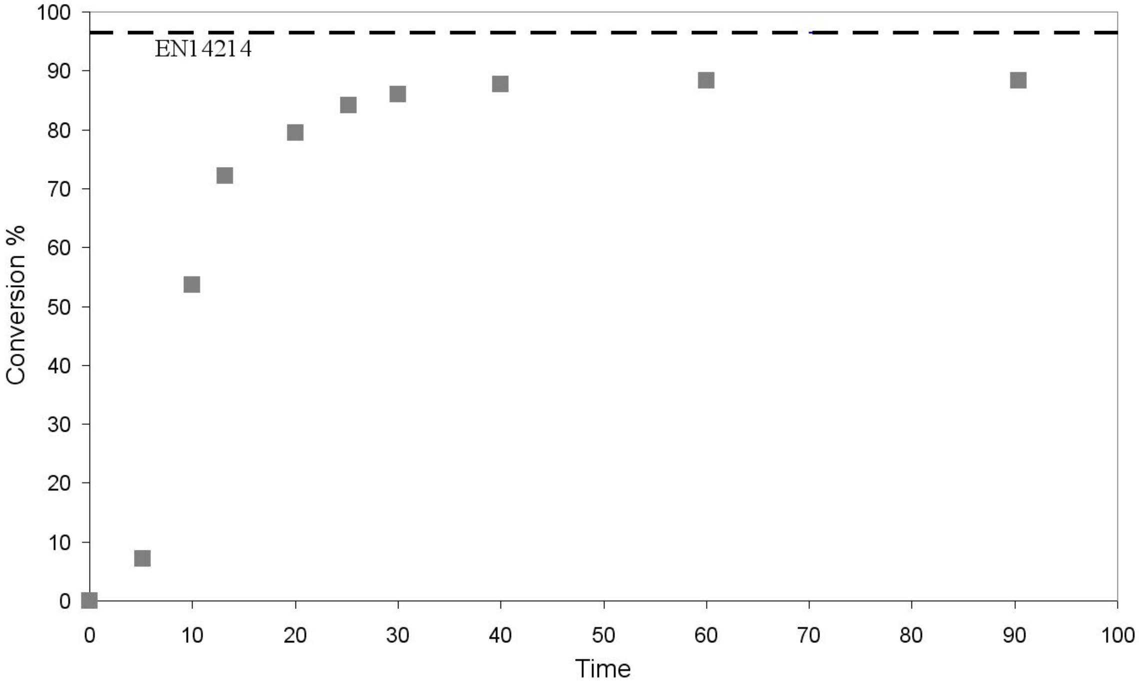


Figure 5.9 Progression of the biodiesel reaction over time. Shows typical biodiesel reaction stopping short of 96.5% standard. Reaction conditions 55°C, 6:1 mole ratio, 200rpm.

This graph is not original and has been published before by many authors (Darnoko, Boocock, Freedman, Noureddini and Olivera). The problem is that no single reaction mechanism has explained the sudden change in reaction rate and there is substantial disagreement in the literature over its cause. First or second order reaction models do not level out to the same degree as shown in the graph.

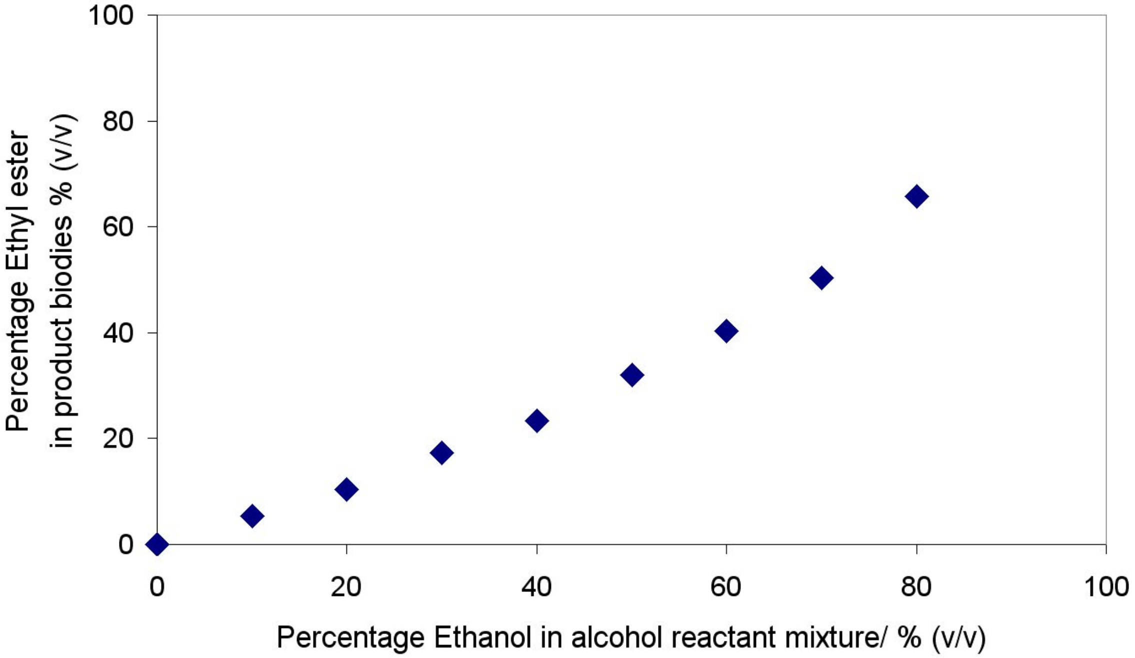


Figure 5.10 Product ratio of reactions involving different ratios of ethanol to methanol reactant. Indicates mass transfer limitation. Reaction conditions 55°C, 2:1 volume ratio, 200rpm.

Subsequent experiments involved using both ethanol as well as methanol for the alcohol reactant. This work showed an interesting correlation as shown in Figure 5.10. Ethylester is the product of the reaction involving ethanol and oil just like methylester is the product of reaction involving methanol and oil. This graph shows that the ratio of ethyl to methyl ester is equal to the ratio of concentrations of ethanol to methanol which would only be the case if the reaction was mass transfer limited. If the reaction were kinetic limited the product ratio would correlate to the relative rates of reaction of methanol and ethanol with oil. This graph indicates that the reaction is for the most part mass transfer limited; however, it does not explain what causes the sudden level out in conversion. There could still be a change in mechanism as suggested by Noureddini and Zhu (1997) which would not be shown on this graph.

Since the reaction is at some point mass transfer limited the next step was to look more closely at droplet sizes through out the reaction. This is difficult work as the droplets are very small and diffract light well. However using the technique of real-time optical microscopy it was possible, at lower impeller speeds, to measure droplet size vs. time in several reactions. The results are shown in Figure 5.11 and the screen shots in Figure 5.12. This shows the droplet size initially reducing and then increasing.

Only one other group has taken this approach (Olivera *et al.*, 2007) but they used lower temperatures in order to make the droplets visible to the technique via increased viscosity. They reported a reduction of droplet size, but noticed no subsequent increase in size because they were not using actual reaction conditions. Evaporation is an important factor because most biodiesel manufacturers operate open non pressurised reactors.

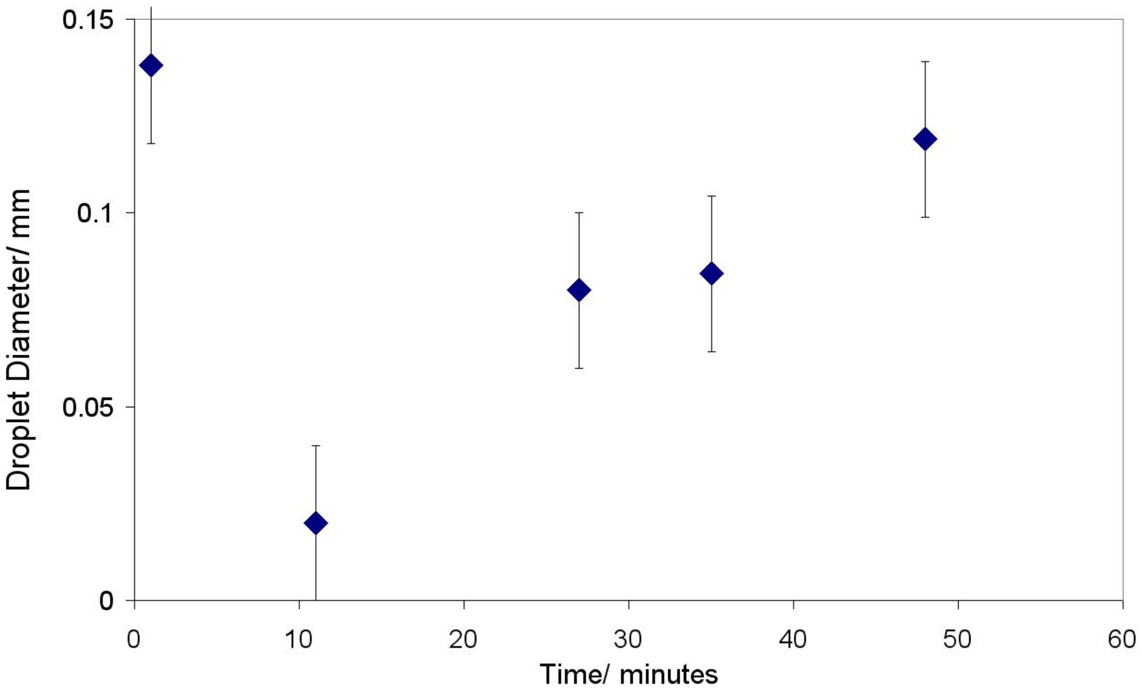
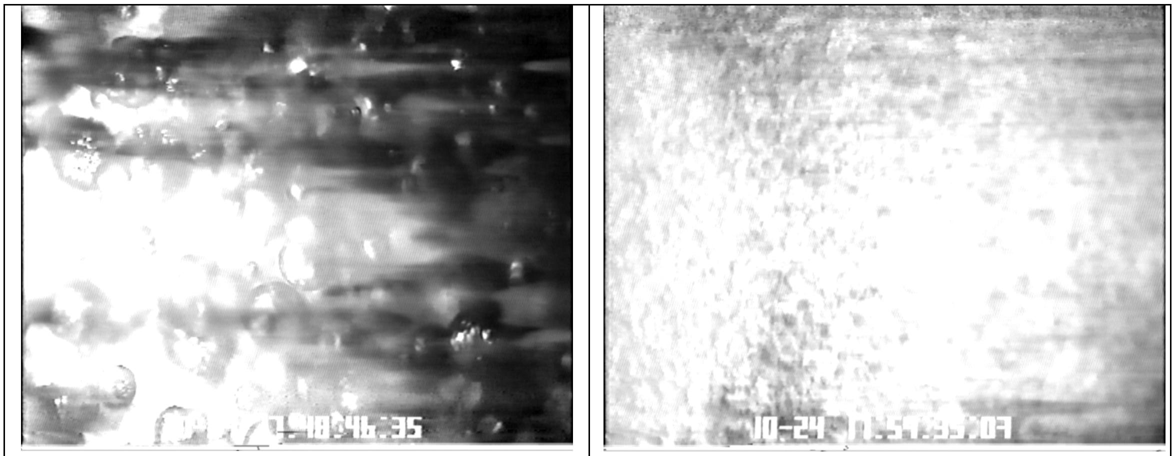
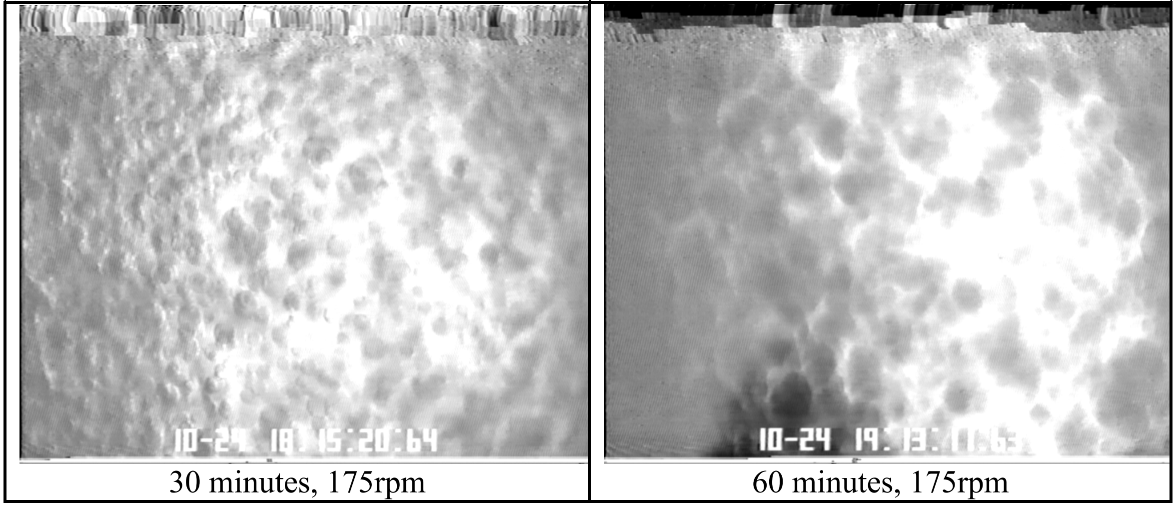


Figure 5.11 Changes in average droplet size over the course of the biodiesel reaction. Each data point is an average of 300 measurements. Detection limit 0.02mm. Reaction conditions 55°C, 6:1 mole ratio, 200rpm.



30seconds, 175rpm

15 minutes, 175rpm



30 minutes, 175rpm

60 minutes, 175rpm

Figure 5.12 Images of biodiesel reaction droplet sizes through progression of reaction. Width of all images the same = 2.38mm

In the reaction soap, together with mono and di-glycerides are formed which are very surface active. These would reduce interfacial tension so it makes sense that the droplet size would reduce as these intermediates are created. It also makes sense that the droplet size would increase again as they are consumed or trapped inside viscous glycerol droplets. Other droplet size results showed that droplet size was highly sensitive to methanol concentration. Droplet size seemed to increase with decreasing methanol concentration and decrease with added methanol. This was probably because of viscosity variation. Because the reaction takes a long time and is nearly at methanol's boiling point, it is likely that some methanol will evaporate which would therefore reduce droplet size. It was realised that this size variation could be pivotal to explaining the slow-fast-slow nature of the biodiesel reaction, and why it does not reach completion. The next step was to incorporate this mass transfer limitation into a kinetic model which could be used to make predictions that could be tested.

5.5.3. Finding order of reaction and rate constants

The real time droplet size data was used to calculate surface area and plotted against the real time ester content to derive the reaction kinetics order of reaction. The reaction rate equation governing mass transfer limitation can be simplified for the biodiesel reaction to Equation 5.4 for first order or Equation 5.5 for second order. This form of rate equation allows the total interfacial area (a) to be included in the rate equation which is important for mass transfer limited reactions. In reality the rate would be dependant on both methanol and oil concentration, but simplifications have to be made to make the maths solvable. Equation 5.4 is a fair assumption if methanol is in a large excess and Equation 5.5 is a fair assumption if the concentrations of reactants are stoichiometric. However our reaction is in between these simplifications so a fudge factor of 2 is required for the concentration term. Concentration is doubled for the modelling equation, this is listed in Table 5.2 fit parameters.

$$r_a = kaC_a$$

Equation 5.4

For First order (A → products)

$$r_a = kaC_a^{\;2}$$

Equation 5.5

For Second order (2A → products) or (A + B → products when $C_{ao} = C_{bo}$)

Curve fitting was used to determine the reaction order by seeing which hypothesis best fit the data points. Figure 5.13 shows a reaction rate vs. time plot with real data points set against different order of reaction predictions. Real time droplet size data was used in some of the lines to see if that helped the fit. A visual closeness of fit, trial and error method was used to find the rate constant for the curves to match the data points as closely as possible. The hypothesis which fit the closest and was solvable was second order with changing interfacial area during reaction. The R^2 value for this fit was 0.92. The two theory lines which do not involve drop size were clearly the worst fit to the real data which is further proof that mass transfer is pivotal to the reaction mechanism.

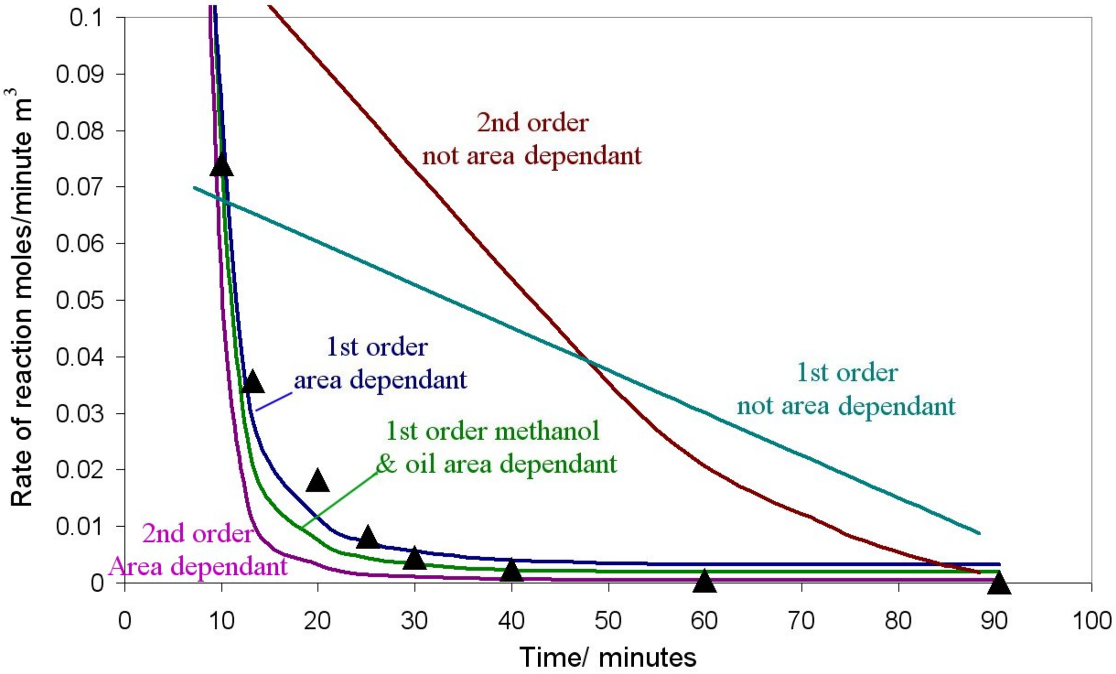


Figure 5.13 Curve fitting of different reaction rate hypotheses to reaction rate vs time data. Showing that area dependant 2nd order is best fit to experimental data. Reaction conditions 55°C, 6:1 mole ratio, 200rpm. Data points are experimental results.

5.5.4. Modelling reaction conversion

To model the reaction, we must use a reactor design equation and know the interfacial-area (a) for the system of interest. Interfacial-area depends on droplet size which depends on interfacial tension which changes through out the reaction as components are formed and lost. To find how the degree of conversion effects the interfacial tension during reaction Misek's equation of droplet size was used, first mentioned in Ma *et al*, 1999. This equation was used to calculate interfacial tension from the measured droplet sizes through out reaction. This interfacial tension was plotted against the conversion to develop an empirical function which could be used for prediction of interfacial tension under different reaction conditions Figure 5.14. This empirical function is also listed in the fit parameters in Table 5.2. This was developed using trial and error comparing to data points and quadratic function was the simplest function that best fit the results.

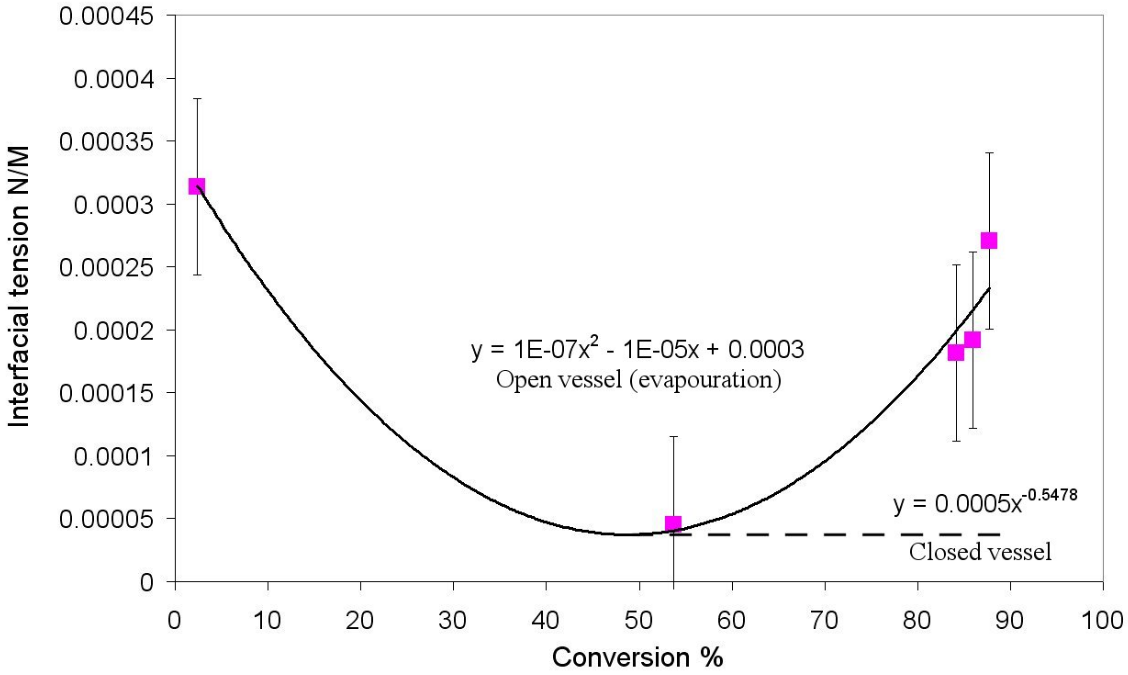


Figure 5.14 Interfacial tension vs ester content relationship. Showing how interfacial tension changes during reaction. Reaction conditions 55°C, 6:1 mole ratio, 200rpm. Data points are experimental results line is theory line for comparison.

This method does not give an accurate measure of interfacial tension because it is based on indirect measurements. This is necessary though because it is a fast reaction which is changing as it is being measured and an online measurement is needed to see the changes with time. Pendent-drop method was used to confirm ball-park measurement accuracy, on samples of reaction mixture. The error bars are large, plus or minus a quarter of full scale movement of the variable. Figure 5.14 shows a quadratic function of conversion was the best continuous function to fit the interfacial tension data. The R^2 value of this fit was 0.81, although this may be because of the lack of data points. If a completely sealed reactor is used then evaporation would not be a factor and a different function would be needed also shown on the Figure 5.14. Because of the changing interfacial tension observed it is necessary to relate interfacial tension to conversion and use an iterative formula when trying to model the conversion.

$$X_a = \left(1 - \left(\frac{1}{1 + \left(k \times at \times C_{ao}\right)}\right)\right)$$

Equation 5.6

Modified equation for conversion of second order reaction in a batch reactor. Area term added. Modified from (Levenspiel., 1999)

To model biodiesel conversion the second order batch reactor design equation (Equation 5.6) can be modified and used. This equation was selected because it was the simplest equation that could represent our reaction system -second order, batch reactor. It is a physical equation, not empirical and it was found in a respected book. The equation was then modified to include an area term to reflect the changing interfacial-area, which is mass transfer limiting. It is limited because it is designed to predict conversion from initial set of parameters that are not supposed to change in reaction, therefore our model needs to be integrated over the reaction to compensate for the changes at each time step during the reaction. Misek's equation can be used to find this area and the empirical equation for σ (in table 5.2) can be used to estimate interfacial tension used in the Misek equation. The result of adding these formulae together is the equation shown in equation 5.7 which can be used to predict biodiesel conversion in reactions.

The conversion used in the empirical equation for σ (table 5.2) is always taken from the previous time step, therefore making equation 5.7 iterative. At each time step the product of interfacial-area and time (a.t from equation 5.6) is calculated by summing the interfacial areas of all previous time steps (using Simons rule) hence the sigma sign in equation 5.7.

$$X_a = 1 - \left(\frac{1}{1 + KC_{ao} \times \sum \left[\left(V_{meoh} \times 3\right) / \left(\frac{V_{reactor} \times 1000}{2 \times 10} \times \left(\left(\frac{16.3\left(H / D\right)^{0.46} e^{(0.087D)}}{n^2 d^2 \rho_c} \right) \sigma \right) \right) \right]} \right)$$

Equation 5.7. Proposed biodiesel conversion equation for two phase biodiesel reaction in a batch reactor. Where σ is the equation from table 5.2.

Fit parameters	Value used
K	0.3
σ	$0.0000001c_a^{\ 2} - 0.00001c_a + 0.0003$
C_{ao}	$2C_{ao}$

Table 5.2 Parameters used to fit equation model to data. K value was arrived upon from figure 5.13 and visual least squares method, σ

Figure 5.15 shows the resulting theory lines calculated using this method and shows other methods that are less successful (i.e. assuming first order or not accounting for interfacial-area change). The second order theory that accounts for changing interfacial tension based on conversion is the best fit to the real data and provides the correct slow-fast-slow curve for conversion.

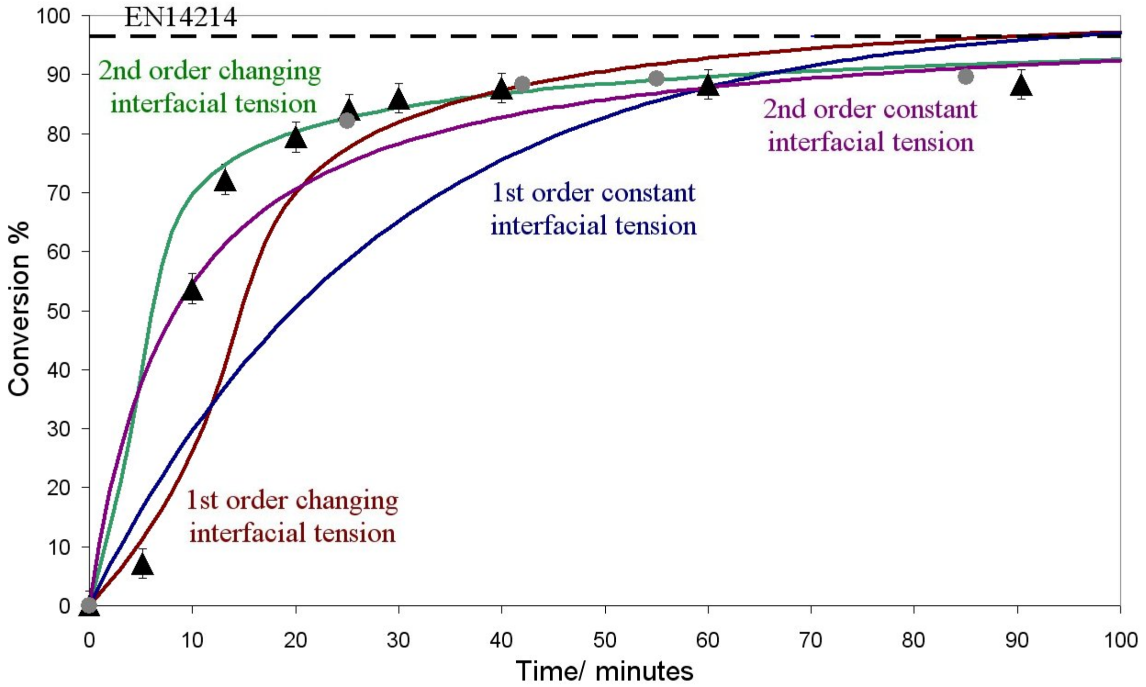


Figure 5.15 Ester content vs. time graph showing goodness of fit to reaction rate hypotheses. Showing 2nd order changing interfacial tension is the best fit to experimental data. Reaction conditions 55°C, 6:1 mole ratio, 200rpm. Data points are experimental results from two data sets, lines are theory lines for comparison.

One point worth noting is that the model is simplified to the form (oil) → (ester) and does not show mono and di-glycerides concentration which is negligible most of the time. Mono and di-glycerides are more soluable in the methanol reactant and tend to react preferentially (Boocock *et al*, 1996). One time where these concentrations may not be negligible is at the beginning of the reaction where the theory line shows a sharper increase than the real data points. This may be because the reaction has to first produce mono and di- glycerides to lower the interfacial-tension and boost reaction where as the theory assumes that conversion is straight to ester.

This model is not absolutely accurate, there are ways to improve upon it, but it is a good theory for how a better model could be developed. The model has an R^2 value of 0.79. The theory is only applicable within the limitations of the study i.e. in a non-pressurized, two phase, batch reactor. Also the results themselves are very difficult to interpret because gas chromatography is only accurate to within about 5% and some of the trends observed in these results had very minor differences, close to this error range. The fit parameter in table 5.2, although many, were needed and sensible. The model could be improved if it was made to be first order in methanol and oil but still second order overall. This would put the maths beyond this authors ability but would remove the need for the $2C_{ao}$ fit parameter. The goodness of fit could also be improved by a better droplet size expression than Misek's equation or a more accurate surface tension vs conversion correlation. The model is good at predicting the end result of the reaction.

This method shows that the reaction is always, both mass transfer limited and rate limited, and that there is no need to split the data into different zones which have different theories. This is a first which no-one else has observed. This theory can now be used to show how conversion depends on the various reaction variables and to predict how new reactor designs will behave.

5.5.5. Effect of mixing

Figure 5.16 shows the effect that different Reynolds numbers created by different impeller speeds have on the conversion. The second order mass transfer limited theory is a good fit to the results but evaporation of methanol has meant that the results are slightly lower than predicted. Strong mixing was required which mean that a sealed vessel couldn't be used in this experiment. The theory explains why Ma *et al*., 1999 observed that "impeller speed does not affect conversion." Impeller speed does affect conversion but there must be excessive mixing in order to see a difference within the experimental error of all the equipment. Note that the theory predicts 96.5% conversion after one hour at 4000 Re, which is very strong mixing beyond most commercial biodiesel reactors. For a low viscosity ratio fluid such as this, the shear rate required for breakage is so large that droplet breakage only occurs in the impeller region (Olivera *et al*., 2007). Therefore a new highly mixed reactor is needed. One limitation of the theory on this graph is that the Misek equation of droplet size does not take into account settling which will increase droplet coalescence at the lower Reynolds numbers. Therefore the theory will mistakenly show higher ester content than the data at the lower Reynolds numbers. The R^2 value is low (0.32). This low value shows the poor quality of the results therefore more data must be obtained before any proper conclusions can be made here.

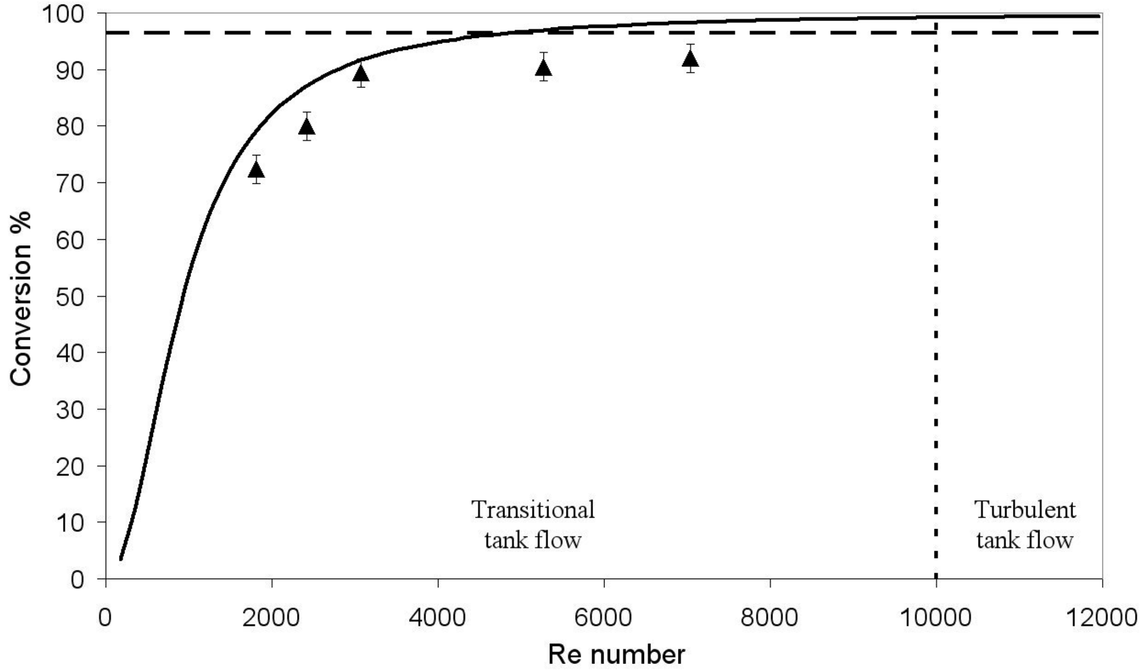


Figure 5.16 Effect of Reynolds number from changing speed on ester content. Reaction conditions 55°C, 6:1 mole ratio, 1 hour batch reaction. Data points are experimental results line is theory line for comparison.

5.5.6. Effect of temperature

Now the Arrhenius' equation can be used to calculate the dependence of rate upon temperature and make predictions of reaction rate at higher temperatures. Using Noureddini and Zhu's data (1997) for conversion vs time at different temperatures a graph can be drawn of Ln(k) vs. 1/T which exhibits a straight line. The gradient of this straight line is equal to –E/R where R is the ideal gas constant. Once the constants k_o and E have been calculated, rate constants at different temperatures can be generated. For the mass transfer limited second order theory Figure 5.17 shows how these new rate constants work at the different temperatures used in the Noureddini data. Noureddini himself noted that "the effects of temperature look a lot like the effects of impeller speed" this is because the terms that are affected are in the same place in the overall rate equation.

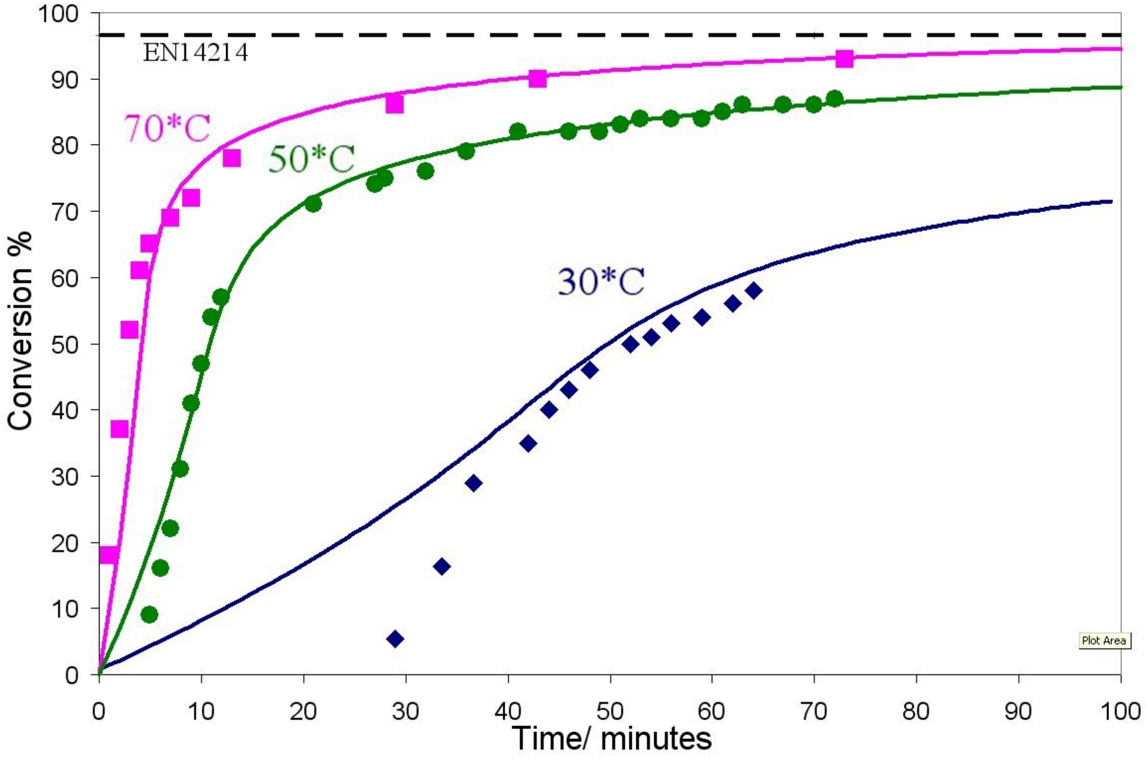


Figure 5.17 Reaction conversion vs. time curves at different temperatures. Reaction conditions 6:1 mole ratio, 3100Re. Data points are experimental results lines are theory lines for comparison.

Temperature affects viscosity which would affect Reynolds number, but this is not taken into account in the Misek equation for droplet size. Therefore there could be deviations from this theory that could be solved by using a better equation for droplet size which includes a viscosity term. However the theory clearly holds up even without this. The R^2 values for the curves are 0.82, 0.98 and 0.8 for the 70ºC, 50ºC and 30ºC lines respectively. The initial difference between theory and data points for the 30 ºC data maybe due to mono and di-glyceride formation and settling. Often at insufficient impeller speeds or poor vessel configurations the methanol reactant can stay floating on top of the oil and the impeller will only suck down a few droplets at a time until the reaction has progressed to the extent that the viscosity and interfacial tension is lowered enough to fully disperse the methanol reactant. This has the effect of artificially delaying the start of reaction.

5.5.7. Effect of methanol ratio

Increasing methanol ratio is the easiest way to increase conversion but also the most expensive for commercial producers. The reason it is so effective is because there is more oil than methanol, so increasing the methanol fraction directly increases the interfacial area of the two phases (up to 50% v/v). The theory shows a fit to the experimental results as shown in Figure 5.18. However the R^2 value of -0.44 shows that the fit is poor, worse than the mean of the results. This is because there is too much scatter in the results and more data is needed before meaningful conclusions can be made. Most commercial producers will not increase methanol ratio above 0.2 volume ratio because it is not economical, therefore this is not a viable way of reaching standard. Because the reaction takes an hour to complete, evaporation of methanol is an important factor. A sealed or pressurised vessel would be an advantage because it would help prevent evaporation over the course of reaction. It could also allow the use of higher reaction temperatures.

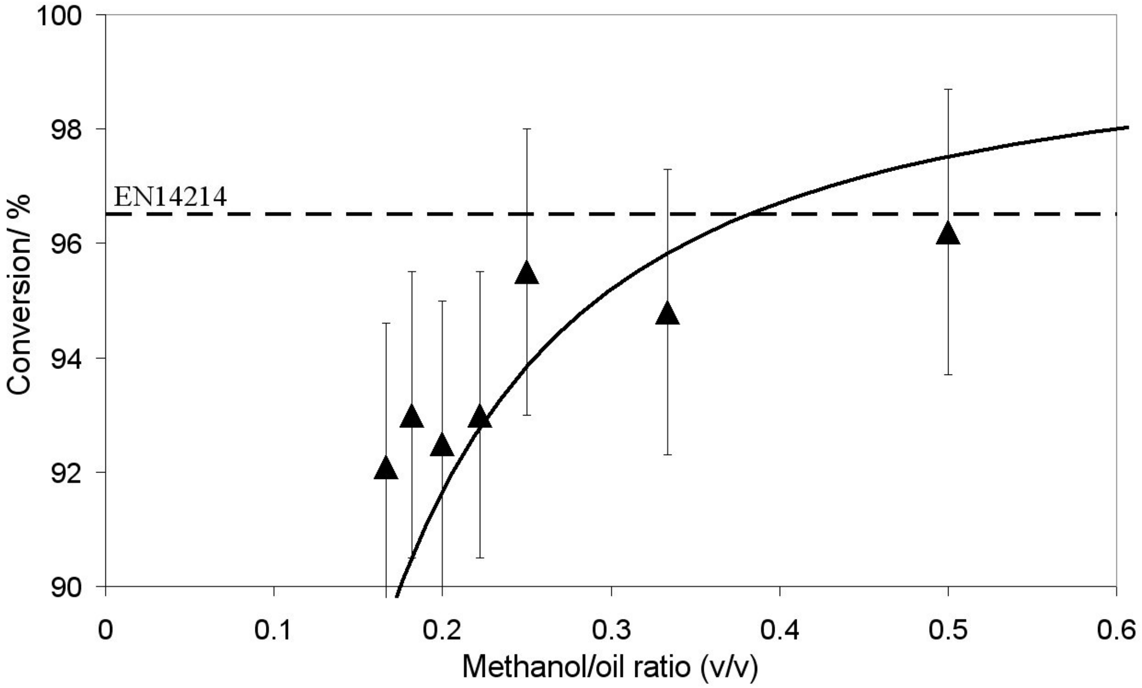


Figure 5.18 Effect of methanol ratio on reaction conversion. Reaction conditions 55°C, 1 hour reaction, 175rpm. Data points are experimental results line is theory line for comparison.

5.5.8. Effect of NaOH concentration

Another way to increase conversion is by using more NaOH catalyst. Boocock et al (1996) stated that the reaction is dependant on the methoxide and oil concentration (not methanol) therefore increasing the NaOH will push the methoxide forming reaction and result in increased conversion. The results of increasing NaOH ratio are shown in Figure 5.19. The theory had to be changed to take into account methoxide concentration. The theory line shown in Figure 5.19 was adapted to this new data set and a new equilibrium constant was selected. The method was to assume that reaction was first order in both methoxide and oil (2nd order overall) and to assume that the methoxide concentration was proportional to NaOH. The theory matches the data in that it shows an increase in conversion with increasing NaOH concentration. However the data shows a maximum point followed by a fall in ester content. The reason for the drop is increased back reaction in the washing process which may be a thermodynamic limitation. The R2 value of the fit, not including the final point, is 0.53. Because of the high degree of error and small differences in the results it is difficult to draw any strong conclusions. In addition to the drop in conversion a reduction in yield was also noted with higher NaOH concentrations. This has been noted by other authors and is put down to the NaOH forming soap surfactants which emulsify the product biodiesel into the glycerol layer. This clearly shows that there is an optimum NaOH ratio above which there is no further benefit to increasing the NaOH concentration. The methanol ratio used in these results was 0.5 volume ratio, much higher than usual, which is why the results are very high for this batch reactor.

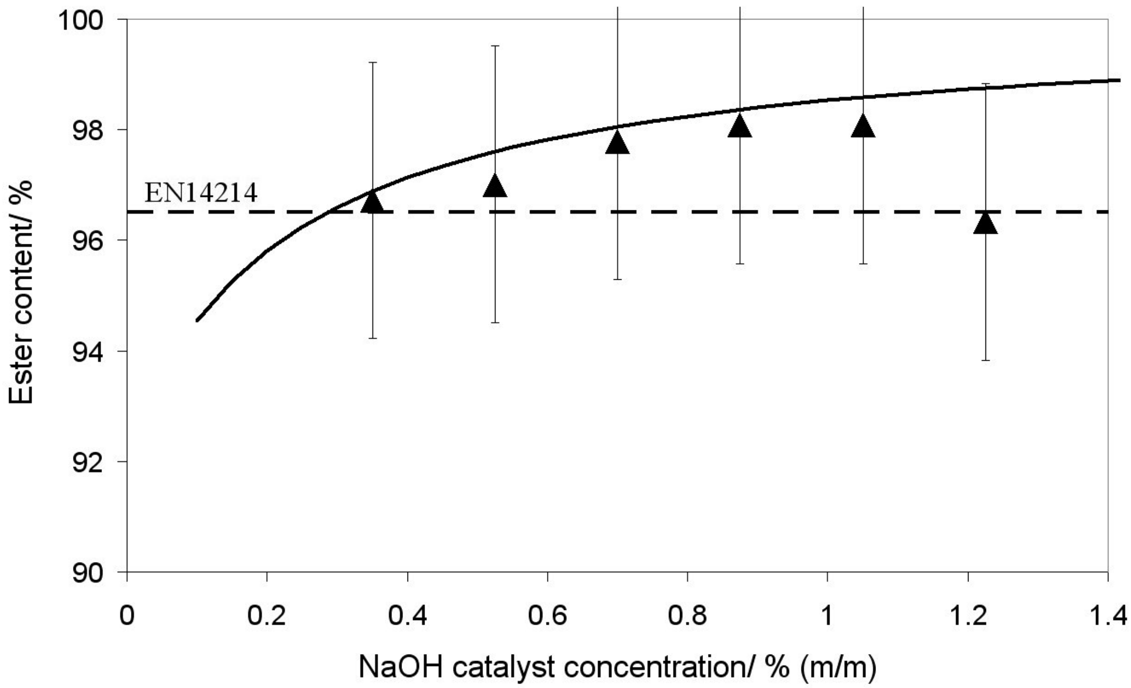


Figure 5.19 Effect of NaOH concentration on reaction conversion. Data points are experimental results line is theory line for comparison.

5.5.9. Waste oil Impurity results

Next waste oils were tested to see if impurities would affect the ester content. The G.C. analysis of several failed Green Biodiesel samples is shown in Table 5.2. The Table shows the magnitude of the problem where the average ester content was only 87.9%. The Table shows that there are two problems preventing the samples reaching the standard. When the ester, mono, di and tri-glyceride contents are all added together the total does not reach 100%. This indicates that there is some impurity(s) which are not esterifiable. The average total esterifiable matter of the samples was 93.4%. This leaves an average 6.6% of unesterifiable impurities. The average sample also contained 5.3% of unconverted but esterifiable material due to incomplete reaction. Both of these problems (incomplete reaction and impurities) cause biodiesel to fail EN14214 and are of equal importance for the purpose of reaching the standard from used cooking oil.

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Averages
Ester content	85.2	88.1	86.2	90.8	85.1	89.1	84.6	87.0	89.0	91.4	93.2	91.7	81.9	84.3	87.2	88.3	89.0	90.0	87.9
Monoglyceride content	0.21	0.27	0.34	0.22	0.39	0.35	0.82	0.71	0.48	0.48	0.29	0.55	1.46	1.18	0.88	0.85	0.72	0.60	0.60
Diglyceride content	0.05	0.39	0.84	0.27	1.10	0.83	1.54	1.46	1.11	0.83	0.37	1.11	2.71	2.58	1.82	1.55	1.26	1.14	1.16
Triglyceride content	0.04	0.87	2.51	1.04	3.14	2.27	4.37	3.84	3.31	2.15	1.03	3.29	7.68	8.31	5.82	5.20	5.07	4.42	3.58
Free Glycerol	0.38	0.28	0.06	0.04	0.01	0.01	0.29	0.24	0.01	0.20	0.20	0.01	0.30	0.29	0.22	0.24	0.21	0.19	0.18
Total Glycerol	0.45	0.50	0.53	0.24	0.59	0.45	1.17	1.03	0.62	0.67	0.43	0.64	1.86	1.83	1.31	1.21	1.10	0.97	0.87
Total Esterifible	85.5	89.6	89.9	92.3	89.7	92.6	91.3	93.0	93.9	94.9	94.9	96.7	93.8	96.4	95.7	95.9	96.1	96.2	93.4
Unconverted	0.3	1.5	3.7	1.5	4.6	3.5	6.7	6.0	4.9	3.5	1.7	5.0	11.9	12.1	8.5	7.6	7.1	6.2	5.3
Unconvertable	14.5	10.4	10.1	7.7	10.3	7.5	8.7	7.0	6.1	5.1	5.1	3.3	6.3	3.6	4.3	4.1	3.9	3.8	6.6

Table 5.3. Typical compositional analysis of used cooking oil methylesters.

Since the problem of unesterifiable impurities usually only occurs in used cooking oils it can be assumed that the impurity is created from what happens during the frying process. In the literature there are many impurities that are present in cooking oils (see Table 5.1) but only a few which are created during the frying process. Dimers, cyclics, polymers, leached food ingredients and oxidised molecules could all be responsible for this unesterifiable impurity.

Vacuum distillation was used to separate the ester and concentrate the impurity for further analysis. The impurities came off in the residue fraction which meant that they were higher boiling molecules. An electro spray mass spectrogram (MS) was then taken of the distillate residue (see Figure 5.20). Gas chromatography mass spectroscopy (GCMS) was not used because the components of interest were too heavy to work in GC. However this meant that the mass spec trace was a mess of different compounds many of which overlap one another. The electro spray method does not fragment the components because of the way the ions are created. However it does create adjuncts of the compounds with sodium [M+Na] and potassium [M+K] ions (Holcapek *et al*, 1999). The spectrograph shows peaks at masses which coincide with the ions of mono, di and tri-glycerides of different fatty acids. There are also peaks which coincide with the masses of dimer molecules of different fatty acid combinations. Several of these dimer peaks do not coincide with masses of other familiar compounds and so the peak can only be explained by the presence of a dimer. However there are also several other peaks which could not be accounted for by masses of any known or familiar compounds.

Dimers are chemically very similar to methyl-ester, they are created in the high temperature process of frying where the double bonds in two fatty acid chains have reacted to form a cross link. They are most commonly two methyl-esters joined together but can be any combination of joined ester, mono, di or tri-glycerides. Chemically dimer fatty acid chains are less likely to be esterified than non-dimerised fatty acid chains because the cross link makes esterification of the head groups difficult. The only way to separate the 6.6% average of unesterifiable impurities is by distillation of the biodiesel product which is unattractive economically.

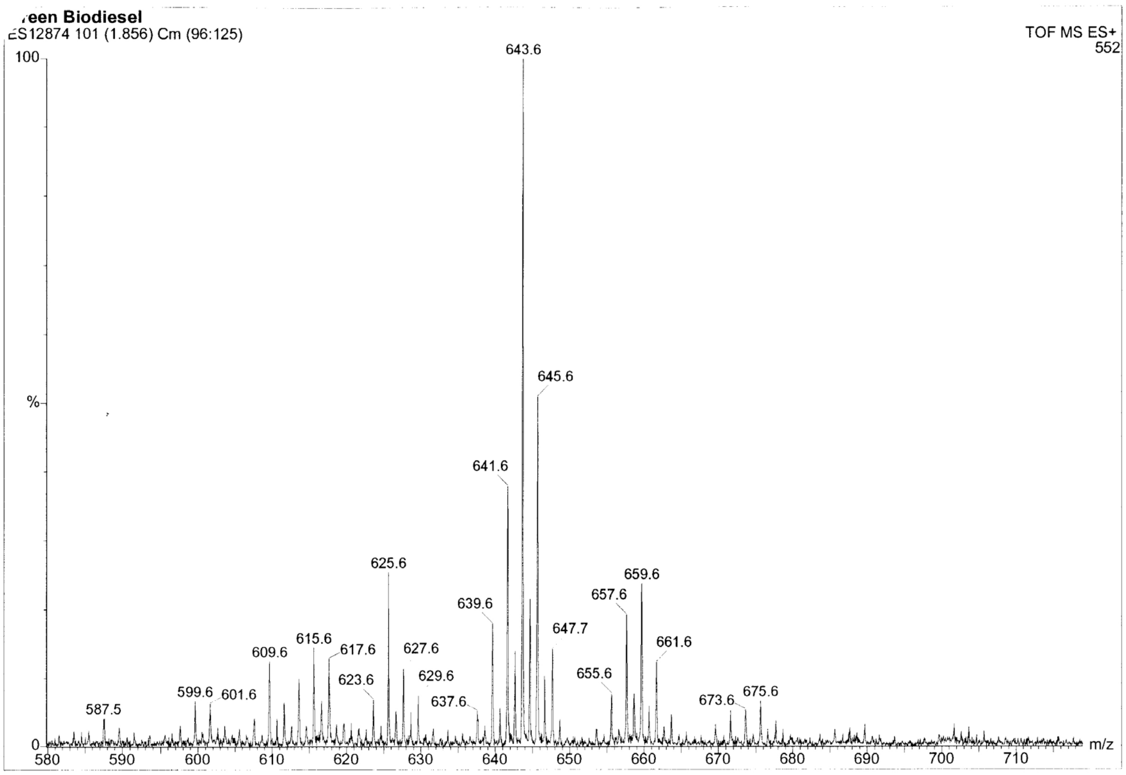


Figure 5.20 Mass spec data showing presence of dimers.

5.6. Discussion of possible solutions to the phase separation problem

5.6.2. Single phase

A single phase reaction would allow reaction to occur across the whole reactor volume instead of limiting it to the interfacial area of the droplets. Therefore a single phase process could overcome the mass transfer limitation and massively increase conversion. A single phase can be achieved by using solvents to solvate the methanol and oil into one phase. Biodiesel is a solvent which will do this and the effect can be helped by using less polar alcohol reactants such as ethanol and propanol that are more solvable in oil.

In this research single phase reactions were tested but the conversion (92.5% average) did not significantly improve upon the standard biodiesel reaction (90% average) and used more reactants. This is a surprising and counterintuitive result which differs from Boocock's results (1996). The problem seemed to be the dilution of the NaOH catalyst across the biodiesel phase. From early experiments on flame colorimetery (photometry), according to method used by Black's (1970) this author knew that the NaOH catalyst stayed with the methanol. With a two phase reaction the methanol and catalyst are trapped together inside the droplets which creates a high local concentration of reactants and acts like power house for the reaction. Boocock's work used THF, a much stronger solvent and therefore required less volume which diluted the reaction less. When biodiesel was used as the solvent the concentration needed to reach a single phase was about 5 x the methanol volume compared to Boocock's 1.25. Because of these problems the work with single phase reactions was abandoned.

5.6.3. Co-surfactants and co-solvents

It may be possible to reduce droplet size by adding a co-surfactant or co-solvent to reduce interfacial tension. Various experiments were done with co-solvents and surfactants and some positive results were found. A 20% mixture of ethanol in methanol was found to give a 2% increase in conversion over just methanol of the same volume. The effect was only slight but has been confirmed by multiple data sets. The ethanol would also slightly increase the solubility of the oil in the alcohol reactant, thus helping mass transfer to the droplets. This process uses careful phase control to achieve the result; it is a balance between single phase and two phase reactions. Optical microscopy showed very small droplet sizes below 20 micron. Tensiometer readings confirmed interfacial tension was slightly lower than with normal reactants. However it was noted in the results for NaOH concentration that there is a limit to the gains which can be made by adding surface active chemicals to the reaction. The down stream clean up is made less efficient and yield of biodiesel is sacrificed to the glycerol waste.

5.6.4. Optimisation of mixing

Of all the different variables the most promising is the mixing intensity. Figure 5.16 predicts that 96.5% ester is possible through increased mixing alone. Increasing the mixing will make the reaction progress faster and limit the evaporation of methanol ensuring smaller droplets at the tail end of reaction. Increasing the mixing energy is the cheapest and most effective way of increasing reaction conversion and product quality. However in most industrial biodiesel reactors the tank and impeller sizes are such that it would be impossible to achieve sufficient turbulence. Therefore we must reduce the reactor size. The only way to reduce the reactor size yet still maintain high throughput is to use a flow reactor.

For a low viscosity ratio fluids such as the biodiesel reaction, the shear rate required for breakage is so large that droplet breakage only occurs in the impeller region (Olivera et al., 2007). Therefore the reaction only occurs in the impeller region. This means that, in addition to strong mixing, we need a reactor where the mixing region covers the entire reactor so as to prevent dead zones. Therefore a new continuous flow reactor is needed which has strong mixing throughout. In a batch reactor the reaction may have a long residence time but if properly mixed in a flow reactor the residence time could be greatly reduced. It is a fast reaction but only seems slow because the wrong reaction conditions were being used. This shorter residence time could lead to shorter required reactor lengths.

Plug flow reactors are not unusual in the petrochemical industry. In large scale chemical plant almost all reactions are done in flow reactors. In refineries all the catalytic reactions are done in plug flow reactors. Reactions such as fluidic catalytic cracking, hydrotreating, hydrodesulphurisation and reforming are all done in plug flow reactors. Biodiesel should be done in a similar way.

5.7. Conclusions

The biodiesel reaction was studied using optical microscopy to measure droplet size during reaction. The droplet size was observed to initially decrease and then increase which correlated with the creation of surface active intermediary's and then the consumption and evaporation of methanol. This observation was seen to explain the slow-fast-slow nature which limits the biodiesel reaction. For the first time both mass transfer and reaction rate were show to be liming conversion throughout the reaction. For the first time a numerical theory was developed which seemed to fit the data under the limitations of the study (non-pressurized, two phase, batch reactor). Predictions were made about ester content against different variables which were tested and found to agree with the theory. With waste cooking oil, feed impurities were found to be as important as reaction mechanism for determining ester content. Mass spectroscopy identified these waste oil impurities as dimers which can only be removed by distillation. Increasing the mixing intensity was identified as the best way of increasing conversion. A new continuous reactor was needed with stronger mixing throughout its volume. This reactor will be described in the next chapter.

CHAPTER 6

BIODIESEL CONTINUOUS REACTORS

6.1. Introduction

A plug flow reactor is like a string of individual batch reactors set up along a pipe, so one might expect that the same residence time is needed in a plug flow reactor as in a batch system. Therefore a simple pipe reactor would need to be extremely long to give both the necessary residence time and maintain turbulent flow to prevent back-mixing. However by packing the pipe with mixing elements turbulent flow can be achieved at much lower flow rates, thus reducing the length of reactor. Since the reaction is mass transfer limited the greater mixing that this offers may actually reduce the residence time needed, compared to the poor mixing achieved in a batch reactor, a double benefit.

This Chapter looks at two different continuous reactor designs that use different strategies to reach 96.5% conversion. One reactor uses long residence times whilst the other reactor uses strong mixing. Both have the potential to reach 96.5% conversion so a process and economic comparison is needed.

6.2. Theory

6.2.2. Conversion dependence on flow properties

To understand what is happening inside the reactor, the reaction and reactor must first be studied separately. Chapter 4 dealt with the reaction kinetics which was found to be second order and dependant on interfacial area. Now this Chapter examines reactor design and performance. Real reactors are never completely mixed flow (Equation 6.2) or completely plug flow (Equation 6.1), always a mixture of both flow properties (Equation 6.3). Equation 6.1 is the equation for conversion of a second order reaction in an ideal plug flow reactor. Equation 6.2 is the equation for conversion of a second order reaction in a single ideal mixed flow reactor. Equation 6.3 is the equation for conversion of a second order reaction in a series of ideal mixed flow reactors. These three equations are all derived from first principles (non-empirical) and are limited because their parameters are not supposed to change during reaction.

$$X_a = 1 - \left(\frac{1}{1 + C_{a0} K t} \right)$$

Equation 6.1

Ideal plug flow second order reaction conversion.

$$X_a = 1 - \left(\frac{-1 + \sqrt{1 + C_{a0} 4 K t}}{2 C_{a0} K t} \right)$$

Equation 6.2

Ideal mixed flow second order reaction conversion.

$$C_n = \frac{1}{4kt_i}\left(-2+2\sqrt{\left.\begin{matrix}\vdots \\ -1\ldots+2\sqrt{-1+2\sqrt{1+4C_{ao}kt_i}}\end{matrix}\right\}N_t} \right)$$

Equation 6.3

Tanks in series second order reaction conversion (Levenspiel, 1999).

6.2.3. Residence time distribution (RTD)

A residence time distribution will reveal the flow regime inside the reactor. The RTD is a simple stimulus response experiment used to find the residence times of fluid elements through the reactor. Once reactor flow properties and reaction kinetics are known then predictions of reactor conversion can be made using either of equations 6.1, 6.2 or 6.3. These predictions are shown later in the theory lines that accompany the results. The best stimulus response experiment is the pulse method, where a pulse of non-reactive tracer is injected into the flow and its concentration measured against time after the reactor. The shape of the exit tracer curve shows the residence time distribution which reveals what happens inside the reactor. An ideal pulse is a square peak but in reality the pulse is more irregular. With irregular peeks the tracer concentration must be measured in real-time both before and after the reactor and then the peak differences when superimposed gives an RTD curve which tells what happens inside the reactor. To find out what is occurring inside the reactor a model has to be applied to the input output tracer peaks. The simplest model is the tanks in series model where the flow through the reactor is approximated to several tanks in series, the more tanks N the closer the reactor is to plug flow. Equation 6.4 shows the number of tanks calculation where σ is the peak variance and $\bar{t}$ is the peak mean average residence time. This can be used to find out which flow equation is the correct assumption or to calculate the number of tanks N for use in the tanks in series flow model.

$$N = \frac{\left(\Delta \bar{t}\right)^2}{\Delta\left(\varphi^2\right)}$$ **Equation 6.4**

Number of tanks calculation (Levenspiel, 1999).

Another more accurate but more complicated method is to use Laplace transforms to subtract the input tracer curve from the output tracer curve to find the true reactor RTD. It can then be easily judged which model best fits the reactor RTD curve -tanks in series, convection model or compartment model. For this system the tanks in series model was chosen because it is a good approximation and is simple to use.

6.2.4. Power of mixing in stirred tanks

To compare the reactors there must be some fair basis for comparison. Pressure drop or stirrer speed can’t be compared because the reactor configurations are too different. The pipe reactor has no stirrer but a high pressure drop where as the 7 tanks reactor has a strong stirrer and negligible pressure drop. The fairest way to compare reactors is mixing energy used per volume of fluid.

Mixing power used in a stirred tank can be expressed as Equation 6.5. The power number is $P_{o,}$ impeller power is P_w, impeller speed is N and impeller diameter is D. For fully baffled vessels, P_o can be correlated with Reynolds number using Figure 6.1.

$$P_o = \frac{P_w}{\rho n^3 d^5}$$ **Equation 6.5**

Definition of power number.

In a stirred tank there is a Reynolds number power number relationship (see Figure 6.1) which can be used with this equation 6.5 to calculate the mixing power if the stirrer speed, impeller diameter and Reynolds number are known. This relationship can be used to estimate the rate of mixing in the 7 tank continuous reactor. The flow in a stirred tank is laminar at Reynolds number <10, transitional<100,000 and fully turbulent above 100,000 (Harnby *et al.*, 1985). In our reactor Figure 6.1 shows that the power number P_o is approximately 4.2 over the whole range of Re numbers used.

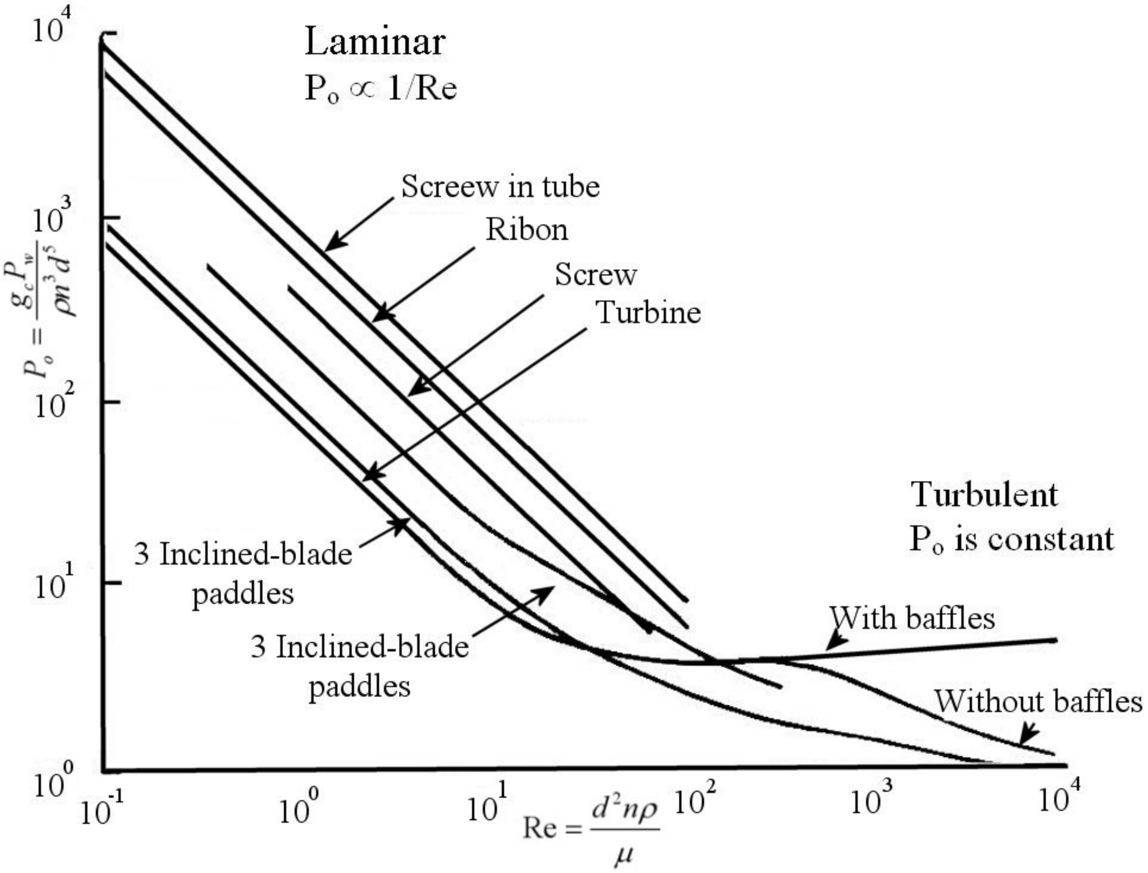


Figure 6.1. Reynolds number power number relationship for various impellers. Adapted from Harnby *et al.*, 1985.

6.2.5. Power of mixing in pipes

Mixing power used in a pipe reactor is simply the product of pressure drop (ΔP) and flow rate Q (Equation 6.6).

$$P_w = Q \times \Delta P$$ **Equation 6.6**

Power in a static mixer

The mixing in a static mixer is generated hydraulically and is dependent on flow rate. The energy dissipation in static mixers can be described reasonably well by the friction factor concept used for flow in pipes. This can be combined with Darcy's friction factor law to yield equation 6.7 which describes the energy dissipation as a function of other detailed parameters in a static mixer. This shows that the pipe diameter is a very influential factor which will be important in scale up of a biodiesel pipe reactor. In a static mixer the equation for Reynolds number is the same as for in a regular pipe, but the boundaries for laminar and turbulent flow are different, for example a Reynolds number in a Kenics mixer is laminar<100 transitional<1000 and turbulent at 1000 and above.

$$\Phi = \left(\frac{4}{\pi}\right)^3 \frac{f_D Q^3}{2d^7\theta}$$

Equation 6.7

Design equation for a static mixer. Where Φ is energy dissipation, f_D is Darcy's friction factor, Q is flow rate, d is pipe diameter and θ is mixer voidage.

$$\varepsilon = \frac{\Delta P V}{\rho L}$$

Equation 6.8

Energy dissipation rate in a pipe equation. Where ε is energy dissipation rate, ΔP is pressure drop, L is length of pipe and V is velocity.

6.2.6. Droplet size theory

Droplet break-up occurs when the cohesive forces are smaller than local shear forces exerted by the surrounding fluid. This interaction can be characterized by the Weber number equation 6.9, which is defined by the ratio of fluid inertial to superficial forces.

$$We = \frac{\tau}{\sigma / d_0}$$

Equation 6.9

Definition of Weber number. Where τ is the shear stress, and d_0 is droplet diameter.

Turbulent motion can be considered to be a superposition of different sized velocity fluctuations. Kolmogorov (Harnby *et al., 1985*) argued that, for large Reynolds numbers, the smaller eddies are independent of bulk flow and mixer geometry. The largest eddies are the size of the mixer and hold the most energy which gets cascaded down to numerous smaller eddies which hold less energy. Eventually the energy is dissipated as heat in the smallest eddies by viscous forces. These smallest eddies are said to be of the Kolmogorov length scale. The Reynolds number is the balance between inertial and viscous forces and at the Kolmogorov length scale Re=1 (Harnby *et al*., 1985). From dimensional reasoning, the Kolmogorov length scale is defined in Equation 6.10. where ν is the kinematic viscosity and ε is the energy dissipation rate.

$$L_k = \left(\frac{\nu^3}{\varepsilon} \right)^{1/4}$$ **Equation 6.10**

Kolmogoroff's length scale.

6.3. Previous results

6.3.2. Droplet size equations

Prince and Blanch (1990) used a droplet column to investigate droplet collisions arising from turbulence, buoyancy and laminar shear flows. They assume the predominant cause of collisions in turbulent systems are turbulent eddies and used Kolmogoroff's theory to estimate the collision rates and contact times. Eddies of the inertial sub-range are considered to be responsible for the random motion of droplets, as those smaller than the droplet length contain insufficient energy to affect droplet motion, whilst those much larger will transport groups of droplets with little relative motion.

Alves *et al* (2002) investigated local bubble size in a dual turbine stirred tank and used a similar relationship to that developed by Hinze for liquid-liquid dispersions see equation 6.10. Hinze's equation can be used to predicted droplet size assuming $D_{32} \alpha d_{max}$. Where ε is the impeller power per unit mass, σ is the interfacial tension d_{max} is the maximum stable droplet size and D_{32} is the droplet sauter mean diameter. This equation was used to make the theory line for the pipe reactor graphs in this thesis. Alves *et al* concluded that the bubble size in stirred tanks could be correlated using the following equation

(Equation 6.12). Where β is –0.14 to –0.24, Pg is aerated turbine power, V is liquid volume, C” is a constant and the equation is only valid for non-coalescing liquids. However the same equation has been proven to work for liquids-liquid solutions with some coalescence by Pacek *et al* (1998).

$$d_{\max} \propto \left(\frac{\sigma}{\rho}\right)^{3/5} \varepsilon^{-2/5}$$ **Equation 6.11**

Hinze equation (1955) bubble size in turbulent flow.

$$D_{32} = c''\left(\frac{p_g}{v}\right)^{\beta}$$ **Equation 6.12**

Alves equation (2002) bubble size in stirred tanks.

Calabrese, *et al* (1986) tested many theories for the influence of viscosity and surface tension on droplet size in their paper on drop size in turbulent stirred tanks. The most relevant of which are equations 6.13 and 6.14. Where We is the Weber number, A is the interfacial area, Re is the Reynolds number, μ_d is the viscosity of the dispersed phase, μ_c is the viscosity of the continuous phase.

$$\frac{D_{32}}{L} = A\ We^{-3/5}$$ **Equation 6.13**

Influence of viscosity and surface tension on droplet size in turbulent stirred tanks (Calabrese *et al,* 1986).

$$\frac{D_{32}}{L} = 2.1\left(\frac{\mu_d}{\mu_c}\right)^{3/8} \mathrm{Re}^{-3/4}$$ **Equation 6.14**

Influence of viscosity and surface tension on droplet size in turbulent stirred tanks (Calabrese *et al,* 1986).

Song and Han (2005) used computer modelling (CFD), dimensional analysis and graphical analysis to develop a pressure drop correlation for Kenics static mixers which covered both laminar and turbulent conditions. They found that the aspect ratio, AR (length of mixing element/diameter) was of particular importance to the friction factor and hence the pressure drop, especially at high Reynolds numbers. Their results showed that above Reynolds numbers of 100 lower AR ratio elements gave higher friction factors and pressure drops. They produced a correlation for the friction factor which covered all Reynolds numbers but has different constants for laminar, transitional and turbulent regions (as shown in Table 6.1.) Where C_f is the friction factor, AR is the aspect ratio, K is a constant from the table, Re is Reynolds number and n is number of mixer elements.

$$C_f AR^{2.04} = K\left(\mathrm{Re}\, AR^{2.15}\right)^n$$ **Equation 6.15**

Song and Han's equation of friction factor in Kenics static mixers (2005)

$\mathrm{Re}/AR^{2.15}$=	0-100	100-1000	1000-∞
K=	320	32	2.66
n=	-0.86	-0.36	0

Table 6.1. Constants for Song and Han's equation of friction factor in Kenics static mixers (2005)

6.3.3. Biodiesel continuous reactor background

Dubé *et al* (2007) took advantage of the solution properties of methanol/triglyceride/methylester system to create a membrane reactor. Large excess methanol volumes were used to wash the reacted biodiesel and glycerol through a membrane leaving the insoluble triglyceride behind for further reaction. The main problem was that large volumes of methanol were needed, several litres to react just 100g of oil and over a process time of 6 hours making it far from commercial.

Leevijit *et al* (2007) recently used a multi-tank reactor design similar to the one used in this thesis. He claimed to be able to reach 99% conversion with a 12 minute residence time. The reactor volume was 2.2 litres and the operating conditions for optimum conversion and yield were 17.3 litres/hour, 0.6 Watts/m^3, 6 minutes residence time, 200 rpm impeller speed. Their results show an optimum stirrer speed above which the reaction was slowed by increased mixing speed, but no scientific explanation was offered for this observation and the decrease was within experimental error for the measurement technique. A non standard thin layer chromatography method was used to measure ester content which is not that stated in EN14214 specification.

Harvey *et al.*, (2003) used an oscillatory plug flow reactor with 8 theoretical tanks in series to produce biodiesel that meet the standards for mono, di and tri-glycerides. However there was little in house testing of fuel and no graphs of ester content published. The residence times were between 10 – 30 minutes and optimisation is on going.

Noureddini *et al* (1998) identified mixing as a key concern that has not been fully addressed. He tested both high shear and static mixer continuous reactors. His results showed that the variation in mixing between 0-1000 rpm gave a difference of about 10 % conversion. He used a 2 litre reactor with flow rates of 18 litres/hour. As with the Leevijit results the conversion was found to decline after an optimum impeller speed but at the much higher speed of 2000 rpm and by a significant amount. Only a confused scientific explanation was offered for this observation. No sample neutralisation or quenching method was mentioned to stop reaction and so samples could have reacted further outside the reactor. The static mixer was proved to give higher conversion than the high shear mixer.

It is clear from this discussion that the question of how a continuous flow reactor should be set up has not been fully answered. Therefore, experiments were designed to distinguish two types of reactor; one made from continuous pipe containing static mixers; the other from a series of stirred tanks.

6.4. Experimental

6.4.2. RTD measurement method

The two reactors studied in this Chapter are shown in Figures 6.2. and Figure 6.3. One is a pipe reactor 5.4 m long, 10 mm internal diameter, 300 ml void volume and filled with 3.5 m of evenly spaced Kenics static mixer elements. The other is made up of 7 tanks stacked on top of each other with a central impeller running down the middle. The tanks are 140 mm internal diameter and 70 mm high with a liquid volume of 2.9 litres. The reactants move from tank to tank by an over flowing weir mechanism flowing from top to bottom which prevents back mixing. Both reactors were installed with taps along the reactor length so that samples could be extracted mid reactor to see the progress of the reaction through out its length.

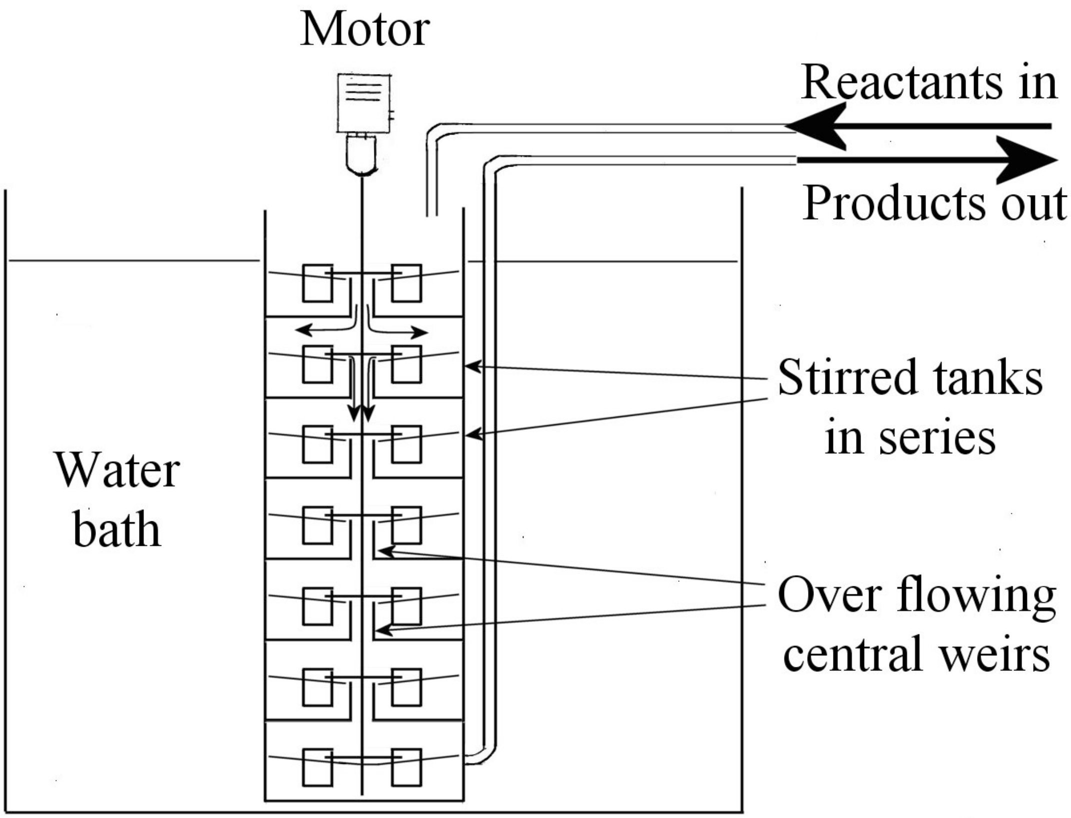


Figure 6.2. Tanks in series reactor equipment diagram.

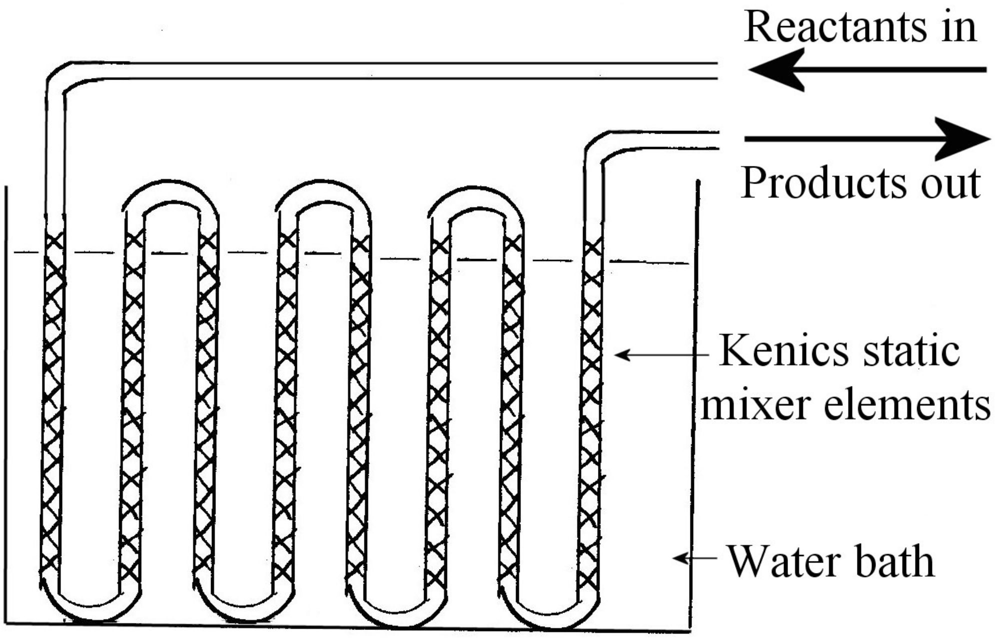


Figure 6.3. Pipe reactor equipment diagram.

The experimental set-up used for the RTD measurements is shown in Figure 6.4. Nitric acid was manually injected into the pipe before a small static mixer and several diameters before the input conductivity meter. Mains water was pumped at a constant flow rate through the reactor and past two conductivity meters. The length of empty straight pipe upstream of the reactor test section was always greater than 50 diameters.

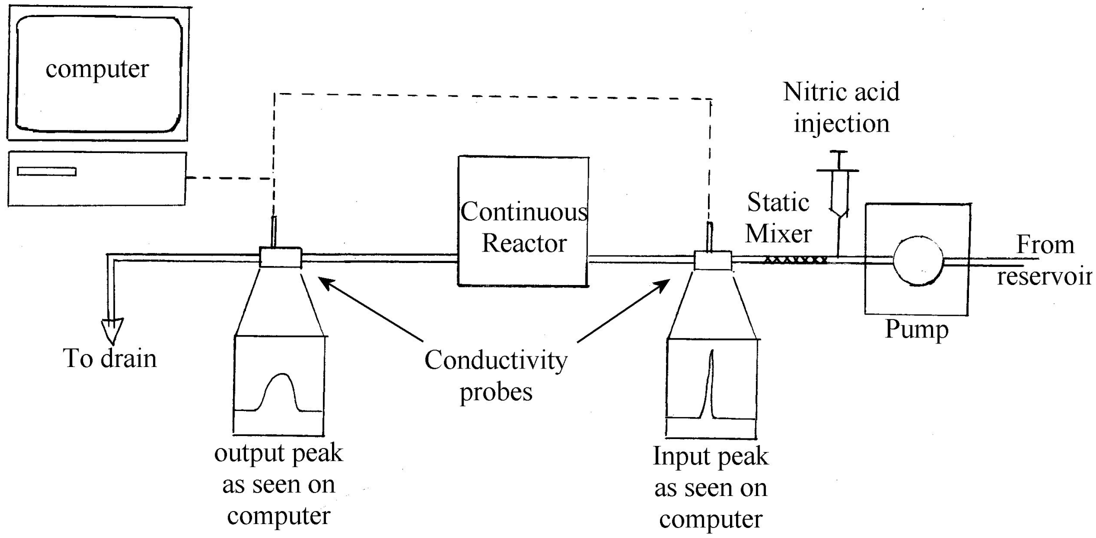


Figure 6.4. Residence time distribution experimental setup.

The conductivity probes consisted of two platinum wires coated with black, amorphous platinum, between which the conductivity was measured. The volume of the measurement coil was of the order of 0.1 ml. The conductivity probes gave a response which was linearly related to concentration. To check the quality of the inlet pulse, and thereby allow correction of the outlet response curves, a probe was positioned before the mixer. The RTD tracer method was performed at a variety of different flow rates and impeller speeds, to see what effect this had on the results. The RTD method used is described in the theory section of this Chapter. The data acquisition card was supplied by Texas instruments and software was custom made at the University of Birmingham using Lab View software. The software took 20 conductivity measurements per second, logged and displayed them on screen for both conductivity meters.

6.4.3. Biodiesel continuous reactor operation method

The purpose of the experiments was to test the ester content of the biodiesel produced by different continuous reactor configurations, flow rates and mixing intensities. Two continuous reactor configurations were tested, a pipe reactor and a tanks in series reactor. The sodium methoxide reactant was prepared before the experiment, the oil was heated to 70 ºC and then temperature equalised with the water bath prior to use. The reactants were pumped by peristaltic pumps and initially mixed by injection nozzle followed by a short static mixer section before the reactor. In the reactor the temperature was automatically controlled by a hot water bath thermostat. Temperature was measured by both K-type thermocouples and checked using an infra-red thermometer. The pressure drop in the reactor was measured by a pressure gauge. Flow rate was set by calibration of the peristaltic pump revolutions with flow rate measurements and the pump revolutions were closely monitored during experiment to account for load variations. For each reactor steady state was obtained by waiting for 5 reactor volumes to flow through before samples were taken. The flow rates ranged from one reactor volume per hour (similar to batch) down to one volume per 5 minutes.

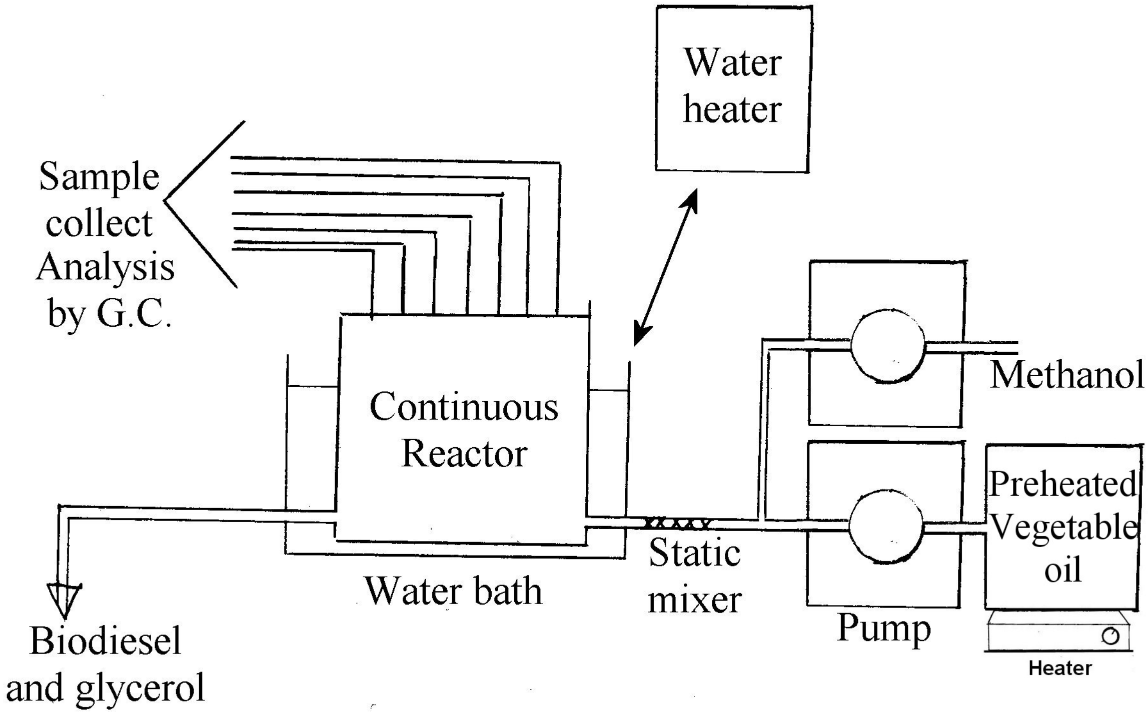


Figure 6.5. Continuous reactor test rig.

Samples taken from the reactors were chilled with ice water and quenched with acidic ion-exchange resin to stop the reaction then centrifuged to remove the glycerol. Reacted biodiesel samples were washed three times by shake mixing with water in centrifuge tubes followed by centrifugation to separate. The test for ester content used in the EN14214 standard uses an internal standard gas chromatography method which was described in Chapter 5.5.1.

6.5. Results

6.5.2. Modeling reaction conversion

A theory can be developed for modelling pipe reactors in the same way that the successful theory was developed for the batch reactor. A droplet size equation and a design equation for conversion can be put together and integrated to account for changing interfacial-tension along the reactor length. For the pipe reactor, the design equation 6.1 was selected and modified to include a surface area term. The Misek equation that was used in chapter 5 batch theory equation, refered to tank size dimension and so cannot be used for coutinuous pipe reactor theory. Instead Hinze equation 6.11 can be used because it refers to only interfacial-tension and energy dissipation rate. The Hinze equation can supply the droplet size and thus surface area term for the design equation. Interfacial tension for the Hinze equation must be calculated using the empirical correlation developed in chapter 5 in Table 5.2 and Figure 5.14. In the case of the pipe mixer the enclosed pipe, high pressure and fast reaction ensure that no methanol evaporates so the no evaporation correlation on Figure 5.14 is selected. The energy dissipation rate (ε) for the Hinze equation can be calculated using equation 6.8 which is generic for all pipe flow. When all these equations are put together the result is equation 6.16 which can be used to predict conversion in a pipe reactor.

This model assumes that there is no back mixing, no evaporation and it assumes that the surface tension follows the correlation described in Figure 5.14. The second order plug flow reactor design equation was selected because it was the simplest equation that could represent our reaction system -second order, plug flow reactor. It is a physical equation, not empirical and it was found in a respected book (Levenspiel, 1999). It is limited because the equation was designed to predict conversion from an initial set of parameters that are not supposed to change in reaction, therefore our model needs to be integrated over the reaction to compensate for the changes at each time step during the reaction. The fit parameters are shown in table 6.2. The model could be improved if it was made to be first order in methanol and oil but still second order overall. This would put the maths beyond this author's ability but would remove the need for the $2C_{ao}$ fit parameter. The goodness of fit could also be improved by a better or a more accurate surface tension vs conversion correlation. The model is used in graphs 6.10 – 6.14 to predict the theory lines for comparison with results.

$$X_a = 1 - \left(\frac{1}{1 + C_{ao} k \times \sum \left[6 \times \frac{V_{meoh}}{V_{reactor}} \Big/ \left(\frac{1000}{10} \times \left(\frac{\Delta P v}{\rho_c L} \right)^{-0.4} \left(\frac{\left(0.0005 C_a{}^{-0.5478}\right)}{\rho_c} \right)^{0.6} \right) \right]} \right)$$

Equation 6.16. Proposed biodiesel conversion equation, for two phase biodiesel reaction in a continuous pipe reactor. where ΔP is pressure drop, L is reactor length and v is velocity. It is clear that the equation is made from connecting Hinze equation 6.11 with ideal plug flow reactor equation 6.1 and energy dissipation rate equation 6.8. This is the theory used in the theory lines of Figures 6.10 and 6.11.

Fit parameters	Value used
K	0.3
σ	$0.0005C_a^{-0.5478}$
C_{ao}	$2C_{ao}$

Table 6.2 Parameters used to fit equation model to data. K value was arrived upon from figure 5.13 and visual least squares method, σ

The same thing can be done for a continuous tanks-in-series reactor as it was for batch reactors in chapter 5 and above for pipe reactors. A droplet size equation and a design equation for conversion can be put together and iterated to account for changing properties during reaction. For tanks in series the design equation to use is Equation 6.3 which is for ideal mixed flow in a tank reactor. The droplet size equation to use could be either the Misek's equation or Hinze Equation 6.11. In the end Misek's equation was selected because it was simpler and did not require a separate equation to find the energy dissipation rate. To integrate the tanks in series reactor model the tanks can be calculated individually, one after the other, and the results of one tank feed into the calculation for the next. Just like in reality how the concentration of the tank before cascades in to the next tank. This replaces the need to use Simons rule to integrate an equation over time or length, because discrete reactor elements (tanks) can be calculated with changing parameters through out the reactor. this removes that limitation.

This model assumes that there is no back mixing and it assumes that the surface tension follows the correlation described in Figure 5.14 and shown in table 6.3. The second order mixed flow reactor design equation was selected because it was the simplest equation that could represent our reaction system -second order, mixed flow reactor. It is a physical equation, not empirical and it was found in a respected book (Levenspiel, 1999). The fit parameters are shown in table 6.3. The model could be improved if it was made to be first order in methanol and oil but still second order overall. This would put the maths beyond this author's ability but would remove the need for the $2C_{ao}$ fit parameter. The goodness of fit could also be improved by a better or a more accurate surface tension vs conversion correlation. The model is used in graph 6.7 to predict the theory lines for comparison with results. An ideal plug flow theory line is also shown on figure 6.7 for comparison and this uses the equation described in Equation 6.16.

$$X_i = 1 - \left[\frac{-1 + \sqrt{1 + C_{i-1} 4 \left(\dfrac{6V_{meth}}{\left(\dfrac{16.3 \left(\dfrac{H}{D} \right)^{0.46} \sigma e^{(0.087D)}}{n^2 d^2 \rho_c} \right) V_{reactor}} \right) k\tau_i}}{2C_{i-1} \left(\dfrac{6V_{meth}}{\left(\dfrac{16.3 \left(\dfrac{H}{D} \right)^{0.46} \sigma e^{(0.087D)}}{n^2 d^2 \rho_c} \right) V_{reactor}} \right) k\tau_i} \right]$$

Equation 6.17 Proposed biodiesel conversion equation, for two phase biodiesel reaction in a continuous tanks-in-series reactor. Where σ is from the developed empirical equation from table 5.2. This equation is iterative and uses concentration from previous reactor stage C_{i-1}. T_i is time in stage i, X_i is the conversion at stage i. It is clear that the equation is made from connecting misek equation 5.1 with ideal mixed flow reactor equation 6.2. This is the theory used in the theory lines of Figure 6.7.

Fit parameters	Value used
K	0.3
σ	$0.0000001c_a^{\ 2} - 0.00001c_a + 0.0003$
C_{ao}	$2C_{ao}$

Table 6.3 Parameters used to fit equation model to data. K value was arrived upon from figure 5.13 and visual least squares method, σ

6.5.3. Tanks in series reactor

The first reactor to be tested was the tanks in series reactor. Before the reactor was used to make biodiesel it was tested with RTD method to check its flow characteristics. This allowed problems with the reactor to be diagnosed early before use with more complicated biodiesel. Originally the reactor was slightly different but was re-designed because of problems. The reactor was originally completely full and the flow between tanks was achieved through small holes in the plates separating the tanks instead of weirs, however this design meant that reactants could diffuse between tanks. The RTD tests for this reactor indicated serious back mixing at the intended flow rates and the reactor had to be altered. The redesigned reactor as shown in Figure 6.2 uses overflowing weirs to eliminate the back mixing problem. Figure 6.6 shows the tracer curves before and after the overflowing weir reactor. Using equation 6.4 to calculate the theoretical number of tanks in series gives 5.8 tanks which is closer to plug flow. Several RTD's were done at different flow rates and impeller speeds to see how this affected the RTD. The results showed no significant change in number of theoretical tanks with impeller speed or flow rate, 0.1 tanks difference when impeller speed was doubled therefore the is no significant back mixing and the mixing is not flow rate dependant.

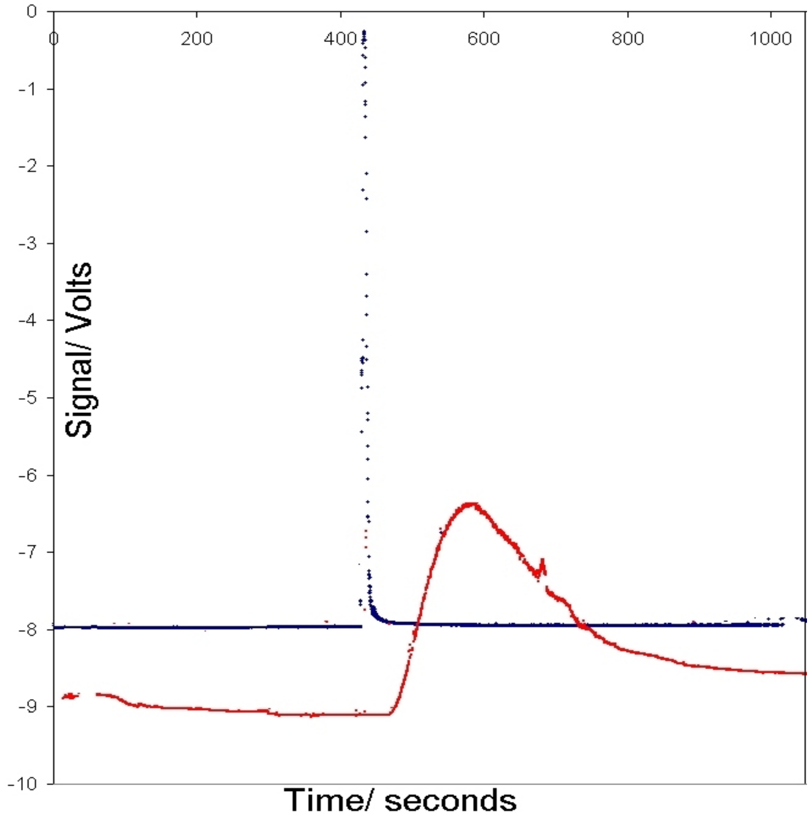


Figure 6.6. Tracer curves for re-designed 7 tanks in series reactor. Blue dots are input signal and red dots are output signal. 3 litres/hour, 10ml of nitric acid tracer 200rpm impeller speed.

The results from the biodiesel reaction in this reactor are shown in Figure 6.7, which shows conversion vs. no of stages. The maximum impeller speed the motor could deliver was 200 rpm. It was realised that with the same mixing as in the batch reactor the same or better residence time would be needed. Therefore reaction conditions were set to be the same as in the batch reactor. The theory lines for both ideal plug flow (Equation 6.1) and for stirred tanks in series (Equation 6.3 or 6.2) are included on the graph and the reaction conditions are written below. It is assumed for the theory lines that there is no back mixing because of the results from the RTD experiments. It is assumed for the theory lines that there is evaporation similar to in a batch reactor, because the residence time and temperature is the same as in a batch reactor and the vessel was open to atmosphere. The results roughly fit the tanks in series theory prediction and never reach 96.5% conversion. The R^2 value of the fit is 0.76, which, despite the irregular final data point, is fairly high. The high R^2 value was because the differences in data points, due to low conversions, was much higher than the error in the results. The theory predicts that the reactor will reach 96.5% conversion if the impeller speed is increased to 400 rpm or the residence time increased to 3.5 hours or the number of tanks is increased to 20. Work with this reactor was stopped because the results were deemed to be worse than that of the batch reactor and the design limited the experimental variables that could be tested. These results seem to conflict with the results of Leevijit *et al*., 2007 who claimed to reach 96.5% conversion using residence times of only 12 minutes at only 100 rpm with six series stirred tanks in series. This casts doubt on the accuracy of the Leevijit results and it may be down to their non standard ester measurement technique.

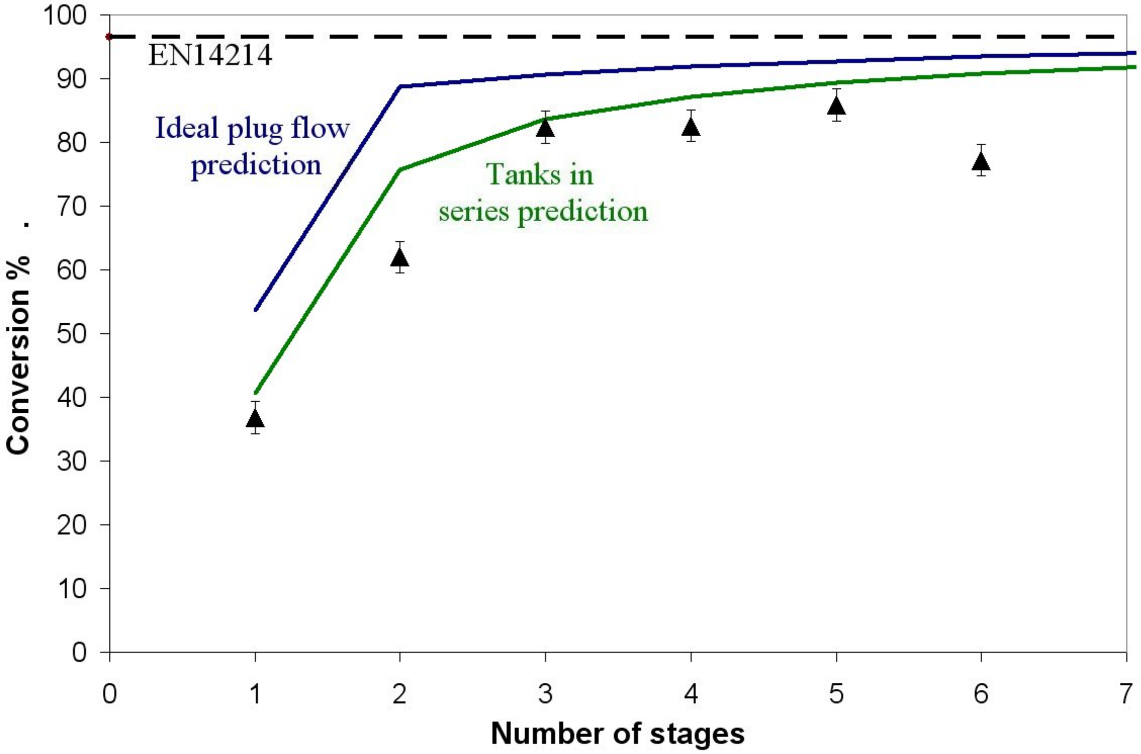


Figure 6.7. Effect of number of tanks in stirred tanks in series reactor. 3 litres/hour, 200rpm impeller speed, 55°C, 1:4 methanol:oil volume ratio. Data points are experimental results lines are theory for comparison developed from chapter 6.5.2.

6.5.4. Pipe reactor results

The static mixer pipe reactor was tested with RTD and the results are shown in Figure 5.8 which shows the tracer curves before and after the pipe reactor. For this reactor the tanks in series approximation (Equation 6.4) shows 67.8 theoretical tanks in series, a good approximation to plug flow. Various different flow rates were tested with RTD but the flow was always a good approximation to plug flow so equation 6.1 can be safely used for graph theory lines.

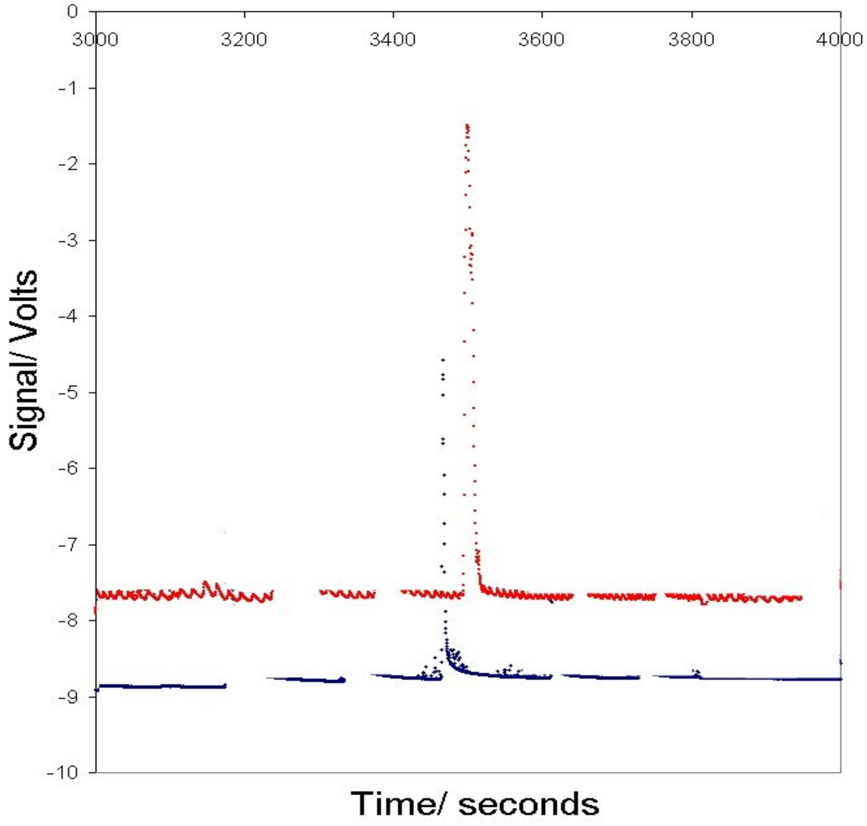


Figure 6.8. Tracer curve for the pipe reactor same scale as for 7 tank reactor. Blue dots are input signal and red dots are output signal. 17.8 litres/hour, 1ml nitric acid tracer.

Initial results with the pipe reactor were promising and the residence time needed seemed small. Evaporation of methanol would not be a factor because at these faster reaction times the reaction would consume methanol many times faster than evaporation. Therefore the power law correlation devised in Chapter 5 Figure 5.14 for the no evaporation assumption was used in the theory lines for this reactor. The relationship between pressure drop and flow rate in the pipe reactor was measured and the results are plotted in Figure 6.9. The results can be seen to follow the Bernoulli equation. these results were used in the theory lines for the pipe reactor. The pressure drop was assumed to be a linear correlation to the reactor length for the theory lines.

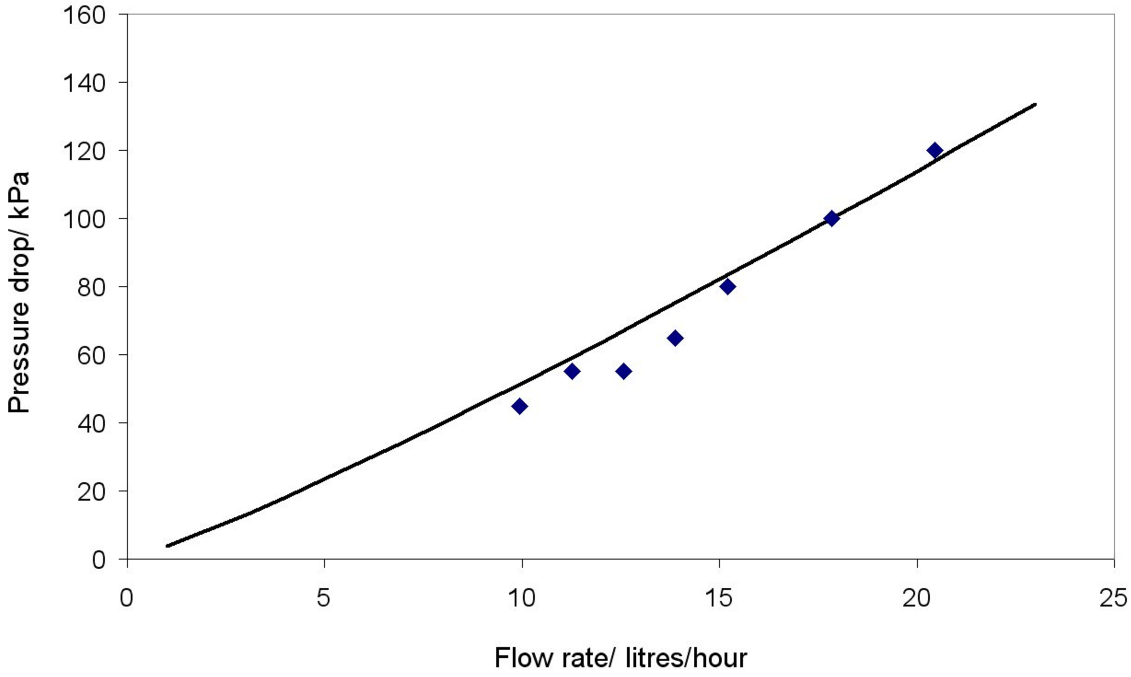


Figure 6.9. Pressure drop vs. flow rate correlation for the pipe reactor.

The effect of flow rate in the pipe reactor is shown in Figure 6.10. The results exceed a conversion of 96.5% conversion over a range of flow rates, a result which few authors have managed to achieve. The results over this flow rate range can be compared with the theory line to show that the theory developed in Chapter 5 using low intensity batch reactors can be modified for use in the strongly mixed pipe reactor geometry. If the theory is valid for both of these different geometries then it this is further proof of its validity. The R^2 value of the fit is 0.92, this is very good considering the small differences between results. Theory lines predicting biodiesel reaction conversion have not been published before. In the pipe reactor the flow rate will affect the reaction conversion in two ways, it will reduce residence time but it will increase mixing intensity. These two effects on conversion work against each other but residence time seems to be the limiting factor because it goes down. No optimum mixing speed was identified and decreases in ester content were solely due to reduction in residence times. The second order changing interfacial tension theory is closest to the actual results. Theory predicts that this reactor will no longer produce to 96.5% standard when the flow rate is increased to 40 litres per hour and the result would seem to agree with that. The theory may not be accurate at very low flow rates because gravitational settling and agglomeration would lead to phase separation which the theory does not take into account. At zero flow rate the conversion should also be zero but soon after this, the conversion should increase to where the theory lines are set.

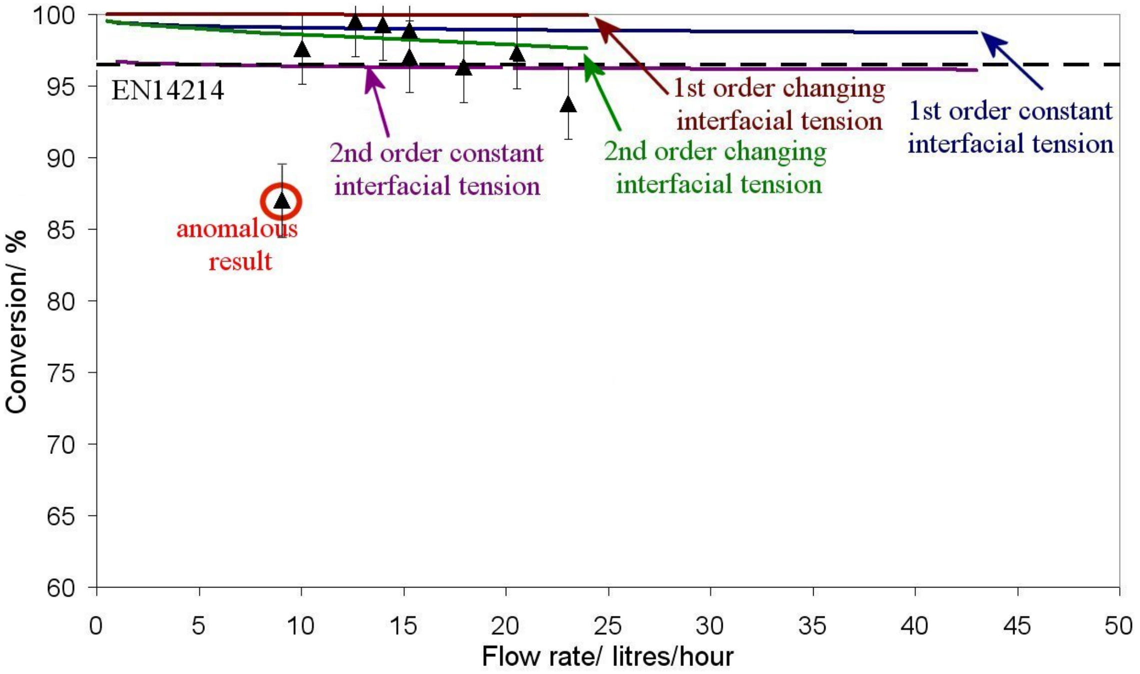


Figure 6.10. Effect of flow rate on conversion in pipe reactor. temperature 55 °C, 1:4 methanol:oil volume ratio, 5.4m reactor length. Data points are experimental results lines are theory for comparison developed from chapter 6.5.2.

The results for pipe reactor length vs. conversion are shown in Figure 6.11. These results show just how effective the static mixers are at mixing and converting the reactants. The 96.5% conversion is reached within the first metre of the reactor. The remaining length of reactor is not seen to increasing the conversion much further and only serves to increase the pressure drop. The results show this reactor could be optimised by reducing its length and hence reducing the pressure drop. The results roughly agree with the theory which shows that the standard should be meet with a 2 metre reactor length. Discrepancies between results and theory could be because of the difficulties involved in extracting samples mid reactor which give extra time for reaction, even if only a few seconds and experimental error. The second order changing interfacial tension theory is again the closest to the actual results. The R^2 value of the fit was -8.9 which means that a straight horizontal line through the results would be a better fit. However the second order changing interfacial tension theory is the very close to a straight horizontal line in the region of the data points, closer than other the theories, so the R^2 value is deceptive. Also with the high conversions obtained leading to small differences between results well within the 5% G.C. error.

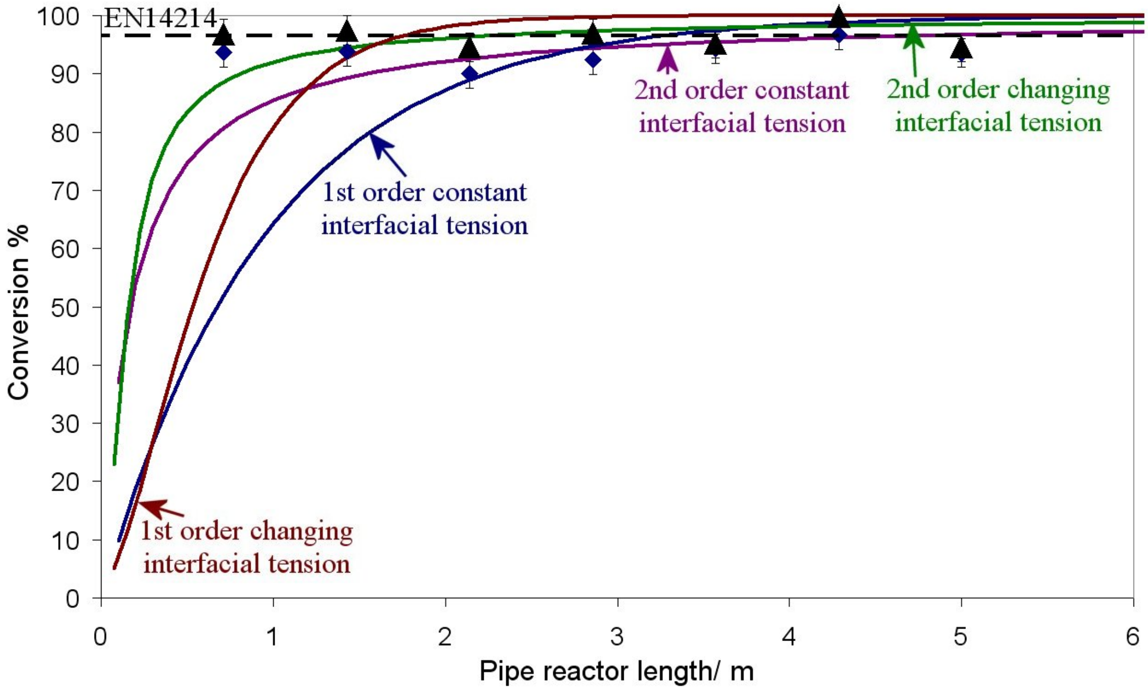


Figure 6.11. Effect of reactor length on conversion in pipe reactor. 17.9litres/hour flow rate, 55 °C, 1:4 methanol:oil volume ratio. Data points are experimental results lines are theory for comparison developed from chapter 6.5.2. Black triangles are washed samples blue diamonds are same samples before wash.

The effect of temperature on the conversion in the pipe reactor is shown in Figure 6.12. The results roughly agree with theory. The theory predicts that around temperatures of 40 °C are needed in the reactor to reach the standard 96.5% conversion. The actual results showed the correct trend but the conversions were slightly higher than predicted. This may be due to experimental or measurement error. These results show that temperature is not as important as other variables such as flow rate or reactor length and that the reaction could be done at room temperature with a longer reactor.

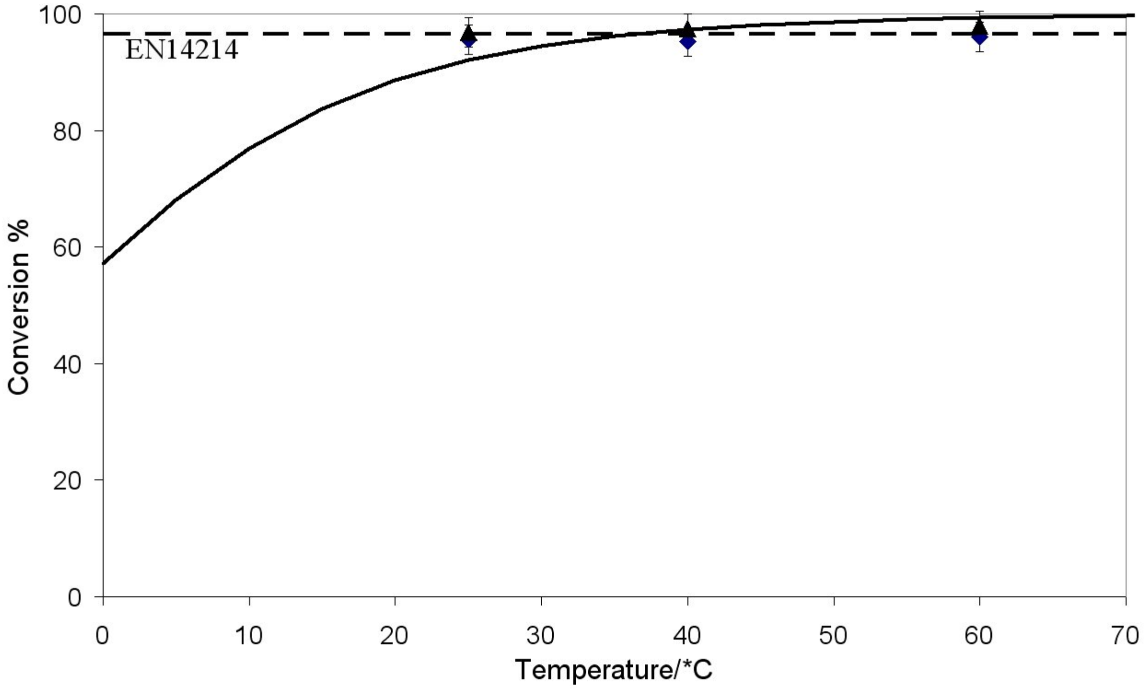


Figure 6.12. Effect of temperature on conversion in pipe reactor. 17.9litres/hour flow rate, 5.4m length, 1:4 methanol:oil volume ratio. Data points are experimental results line is theory for comparison developed from chapter 6.5.2. Black triangles are washed samples blue diamonds are same samples before wash.

The effect of methanol concentration on the biodiesel conversion is shown in Figure 6.13. The results predict how much methanol is needed to reach the standard 96.5% conversion under the stated reaction conditions. Since methanol is an expensive raw material most biodiesel producers would like to minimise its use. The industrial standard methanol ratio is 0.2 volume ratio. With the strong mixing of the pipe reactor it was conceivable that less methanol might be necessary. When this graph is compared to the batch reactor graph (Figure 5.18) this is shown to be true, although 0.2 volume ratio is still needed to reach the 96.5% standard even with the enhanced mixing. Without the enhanced mixing it was not possible to reach the standard unless 0.4 volume ratio was used. This graph, with its enhanced mixing, is probably close to the limit set by the thermodynamic equilibrium. This graph confirms that the industrial standard is very close to the optimum ratio. Some industrial biodiesel producers have inadequate reactors and compensate by using extra methanol to increase interfacial area, with this reactor it is not necessary. The theory lines shown assume plug flow and no evaporation of methanol.

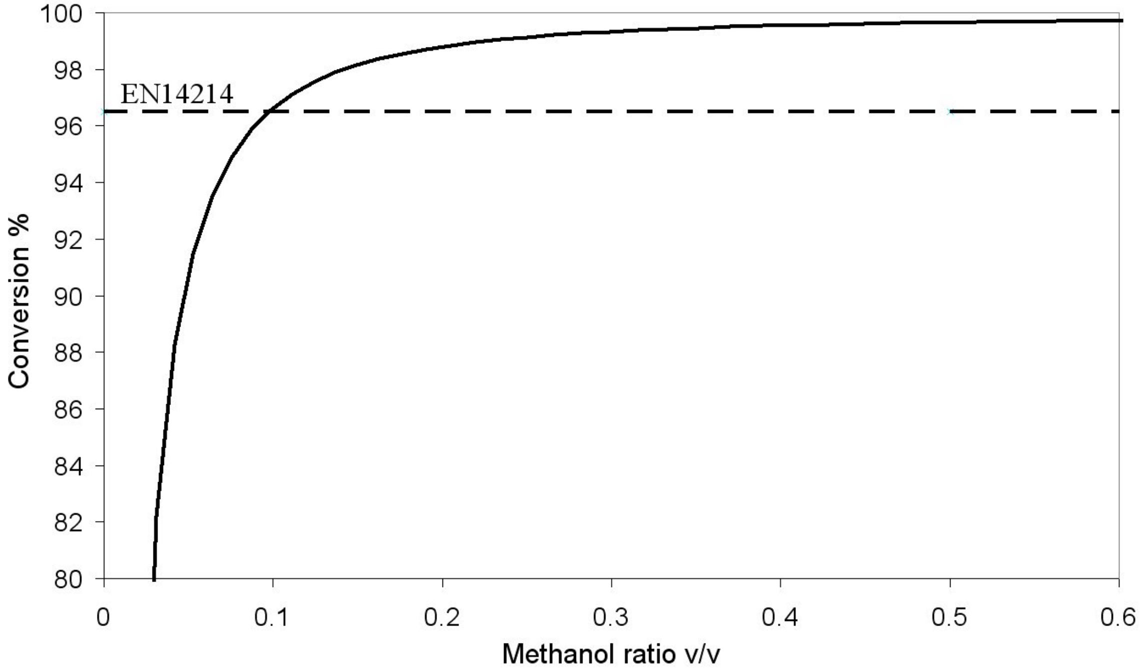


Figure 6.13. Effect of methanol ratio on conversion in pipe reactor. 17.9litres/hour flow rate, 5.4m length, 55 °C. Line is theory prediction of results.

The effect of NaOH concentration on the biodiesel conversion is shown in Figure 6.14. The results show how much NaOH is needed to reach the standard 96.5% conversion under the stated reaction conditions. Since excess NaOH reduces yield by emulsifying the product biodiesel into the waste glycerol, most biodiesel producers would like to minimise its use. In industry between 0.35% -1% (m/m) NaOH is used. With the strong mixing of the pipe reactor it was conceivable that less NaOH might be necessary. This graph shows that this is not the case, the same amount of NaOH is needed but with the pipe reactor it is now possible to reach the standard using this amount. The data shows a maximum point followed by a fall in ester content with the washed sample results but not with the unwashed results. The reason for the drop is increased back reaction in the washing process which may be a thermodynamic limitation. The maximum is in the same place as compared to the results from the batch reactor graph Figure 5.19 which would confirm that this is a thermodynamic limitation. Any other comparisons between the two graphs are difficult because of the high methanol ratio used in the batch reactor results.

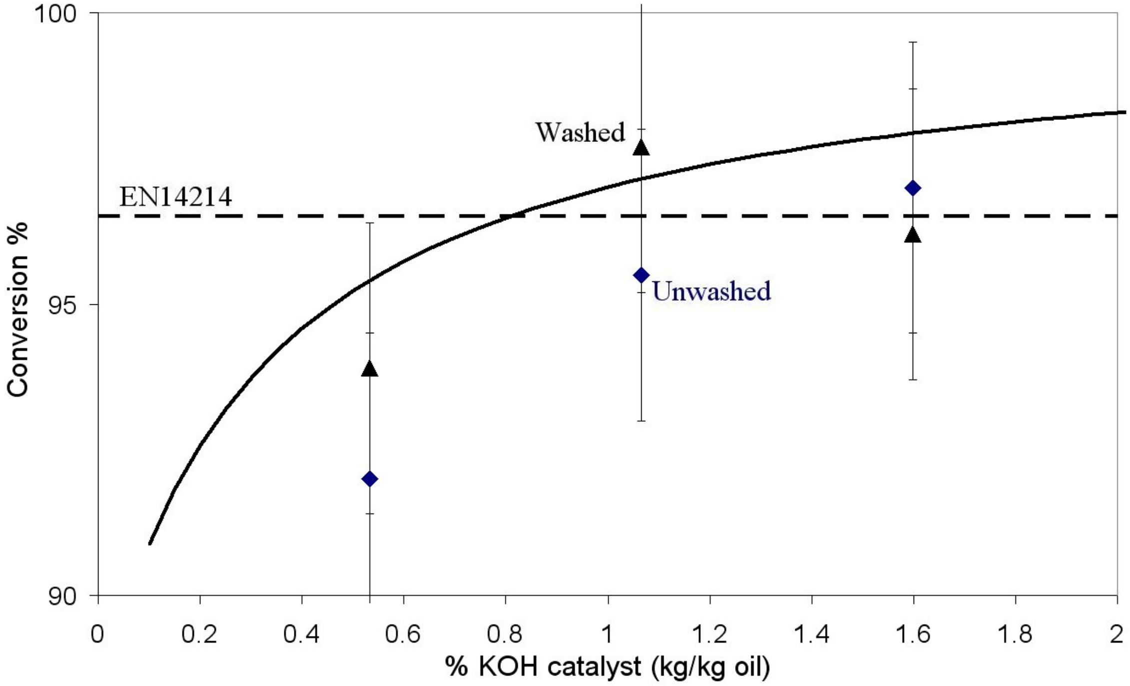


Figure 6.14. Effect of catalyst concentration on conversion in pipe reactor. 17.9litres/hour flow rate, 55°C, 1:4 methanol:oil volume ratio, 5.4m length. Data points are experimental results line is theory for comparison. Black triangles are washed samples blue diamonds are same samples before wash. High catalyst concentration causes side reaction in washing stage which was unpredicted by the theory.

The energy used per litre of biodiesel produced is plotted in Figure 6.15 vs. the conversion in the two reactors. The graph clearly shows that the pipe reactor is far superior in conversion attained, but also in the minimum energy that is used. In the pipe reactor the mixing occurs across the whole of the reactor diameter and nothing can by-pass the mixing elements. In the tanks in series reactor, as in the batch reactor before it, mixing only occurs in the impeller region. This has the effect of back mixing in a batch reactor, the well mixed parts of the vessel will mix with parts of the vessel that are less well mixed, and hence less well reacted, to ensure that higher conversion is not possible. This also has the effect that a lot more total mixing is required in order to meet the conversion required. This combined with the less ideal flow characteristics of the tanks in series reactor mean that the tanks in series reactor requires a lot more mixing for the same degree of conversion.

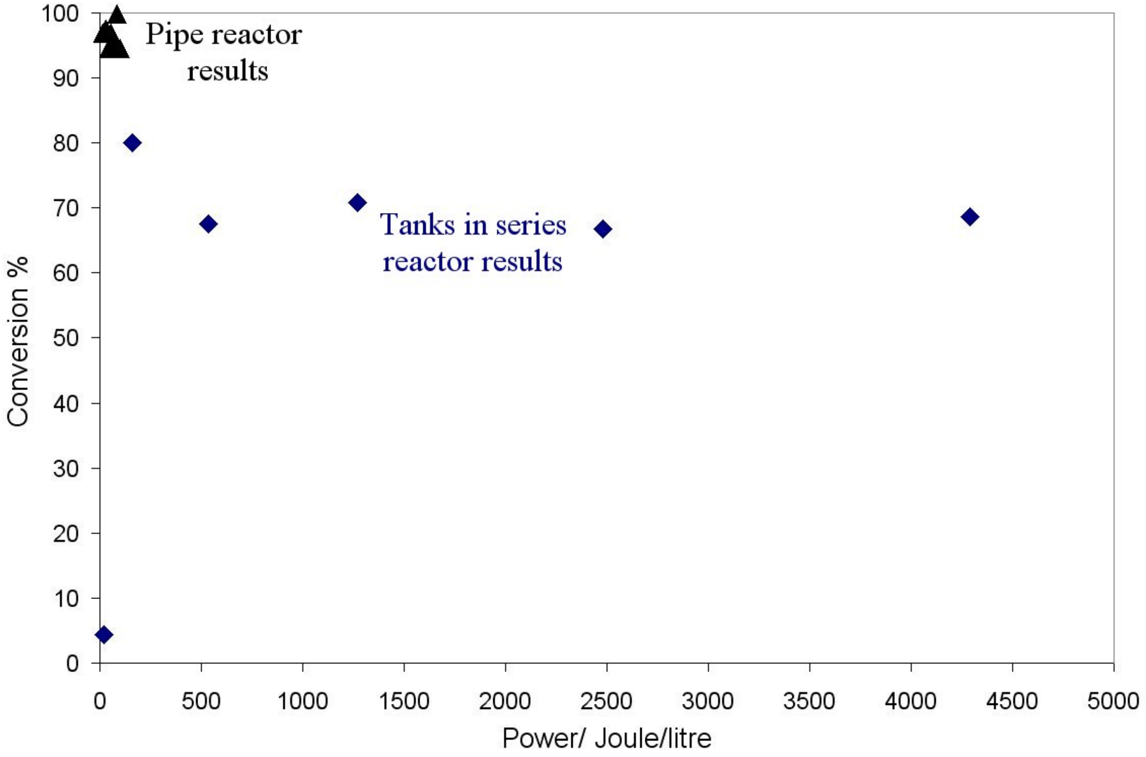


Figure 6.15. Energy used per litre of biodiesel produced vs. conversion in each reactor. 55°C, 1:4 methanol:oil volume ratio, other conditions differ due to different reactor configurations.

6.6. Discussion

Any biodiesel reactor has to either have long residence times or strong mixing but those which have long residence times must also eliminate the evaporation of methanol by using sealed or pressurised reactors. High temperature also slightly helps in pressurised reactors but it will cause problems if the methanol is free to evaporate in open to atmosphere reactors. Evaporation in a pipe reactor still occurs but is much less of a problem because of the high pressure and fast speed of reaction. In the pipe reactor the evaporating gases had the effect of pushing the flow faster and reducing residence time.

The pipe reactor tested used strong mixing in the form of static mixers to achieve the desired conversion quickly before evaporation could take place. The tanks in series reactor was designed to work using long residence times but the initial linked tanks design allowed back-mixing which contaminated the products with the reactants. Theory suggests that the initial linked tanks design could work if flow rate were increased enough that back mixing became insignificant and mixing were increased to allow the reaction to reach completion in such a limited residence time. However the mixing and flow rate required to reach conversion were beyond the means available for a reactor of this diameter and a thinner and longer reactor with more stages would be needed. Thus the ideal linked tanks reactor would be a pipe reactor. The overflowing weirs reactor was an improvement because it eliminated back mixing and made flow rate independent from the number of theoretical tanks in series. This meant that a long residence time could be used with out back mixing problems and in theory the quality standard could be meet in this reactor with sufficient mixing and residence time assuming that evaporation of methanol could be minimised. Overall the best design was easily the static mixer pipe reactor because less mixing energy was used per litre of fluid reacted and because its control and manufacture is so much easier. Using the pipe reactor in conjunction with an input/output heat exchanger could result in considerable energy cost savings compared to the batch reactor. However there could be problems with scale up due to the nature of static mixers where as the over-flowing weirs tanks in series reactor would be easily scaleable

6.7. Conclusion

This Chapter looked at two different continuous reactor designs that use different strategies to reach 96.5% conversion. The tanks in series reactor used long residence time, and the pipe reactor used strong mixing. The strongly mixed pipe reactor produced biodiesel better than 96.5% quality. The tanks in series reactor failed to reach this standard by a wide margin. The theory developed in Chapter 5, was proven to work well in predicting the conversions in reactors of vastly different designs. Using this theory the operating conditions necessary for reaching 96.5% conversion was predicted for both reactors. Evaporation and back mixing were identified as important factors in long residence time reactors. It was concluded that strongly mixed pipe reactor was superior to the tanks in series design. This was because pipe reactor gave a better conversion, it required less energy per unit of biodiesel produced, was closer to the ideal plug flow model and was simpler to control. This new pipe reactor could help gain a better selling price for the biodiesel product by increasing the fuel quality. Significant savings could also be made on the energy bills because heat transfer could be easily implemented making the fuel better for the environment.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1. Conclusions

1. It is possible to produce significant improvements in biodiesel processing by the methods described in this thesis;
    a. By reforming the by-product glycerol with the waste water to hydrogen to add value.
    b. By enhancing the mass transfer to increase the purity of product ester.
    c. By moving from a batch to a continuous esterification reactor.

2. The scientific conclusions.

    Steam reforming conclusions

    a. Thermodynamic calculations can be used to predict steam reforming conversion but there are some discrepancies.
    b. A SOFC will run on glycerol and biodiesel by-product.
    c. Catalyst life is reduced with by-product glycerol because of the longer carbon chains in the contamination.
    d. At high temperatures almost 100% gas yield was reached and selectivities of up to 70% (dry basis) obtained

Reaction kinetic conclusions

a. Observations of droplet size were seen to explain the slow-fast-slow nature which limits the biodiesel reaction. Droplet size was reduced then increased, first by formation of surface active intermediaries then followed by consumption of methanol by reaction and evaporation.
b. Both mass transfer and reaction rate were show to be liming conversion throughout the reaction.
c. A numerical theory was developed which seemed to roughly fit the data in the non-pressurized, two phase, batch reactor studied.
d. With waste cooking oil, dimer -feed impurities were found to be as important as reaction mechanism for determining ester content. This often made it impossible to reach 96.5% using used cooking oil.

Continuous reactor conclusions

a. The theory developed in Chapter 5, was adapted for a continuous reactor and proven to work in predicting the conversion for the continuous reactor.
b. Two strategies can be used to reach 96.5% conversion: long residence time or strong mixing.
c. Evaporation is a problem for long residence time reactors and back mixing is a problem for continuous reactors. Both problems can prevent the biodiesel from reaching the EN14214 standard.

3. The economic benefits
    a. Possible 4p/litre additional profit if on site steam reforming of waste products is employed as opposed to paying for tanker waste disposal services.
    b. Possible extra profit of 2p/litre because increased purity of biodiesel will generate a better selling price.
    c. Possible 1p/litre energy saving because continuous process makes heat exchange possible. This makes the fuel greener which could in future be taken into account with RTFO subsidies or carbon credits.
    d. Safe guarding the essential tax break by ensuring quality standards are meet. The tax break is only given to biodiesel, which is defined by law as fuel which meets the EN14214 standard.
    e. Removing liability and risk from potential law suits arising from poor quality fuel harming vehicles.

7.2. Recommended future work

This work is part of a bigger picture of biodiesel research. Other areas which need further work are as follows.

1. The separation and purification stages need to be tested and optimized. There are many options for biodiesel purification and they need to be selected, ordered and tested to guarantee biodiesel passes all quality tests present in EN14214.

2. Scale up of continuous reactor. Scale up from 17 litres/hour to 1000 litres/hour is needed to reach industrial scale demonstration. Issues involved would be:
    a. Scale up of static mixer elements
    b. Scale up of separation technology

3. Crop production methods and yields need to be optimised to biofuel production instead of food production. How the biomass is produced is as important as how it is converted if biodiesel is ever to be developed for wide spread use to combat climate change. As the chemical conversion process are optimised so must the bio-oil production process. This should involve bioreactors or genetically engineered energy crops.

4. A heterogeneous catalyst should be developed for use in continuous reactor. A break through in biodiesel heterogeneous catalysis would eliminate the need for many of the downstream purification processes currently needed.

5. Discussion with larger petrochemical industries about the methanolysis process versus other options such as hydrotreating of vegetable oils and blending with fossil fuel oils.

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Appendix

There have been several journal publications in connection with this work. These articles are printed here in chronological order. The titles include Formulating liquid ethers for microtubular SOFC's, Steam reforming of biodiesel by-product to make renewable hydrogen and Developing the reaction kinetics for a biodiesel reactor. The later paper has been reviewed and accepted for publication in Bioresource Technology but the author is awaiting proofs. The other papers are already published. The first paper was based on research done by the author and data collected which was later not used in the thesis. The other two papers are based on chapters of this thesis.

This author's involvement for the first paper was only that of some limited data collection and experimentation involving diesel engines. Kevin Kendall was the main author who wrote the paper and John Precce was also involved in experimentation and data collection with fuel cells.

For the steam reforming paper this author did all the work and was the main author. The other named authors were only used to check formatting, grammar (Christian Mallon) and checking mathematics (James Andrews).

For the Biodiesel kinetics paper this author did all the work and was the main author. The other named author, Kevin Kendall, helped with structure and formatting.

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Short communication

Formulating liquid ethers for microtubular SOFCs

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Abstract

One of the key problems of applying solid oxide fuel cells (SOFCs) in transportation is that conventional fuels like kerosene and diesel do not operate directly in SOFCs without prereforming to hydrogen and carbon monoxide which can be handled by the nickel cermet anode. SOFCs can internally reform certain hydrocarbon molecules such as methanol and methane. However, other liquid fuels usable in petrol or diesel internal combustion engines (ICEs) have not easily been reformable directly on the anode. This paper describes a search for liquid fuels which can be mixed with petrol or diesel and also injected directly into an SOFC without destroying the nickel anode. When fuel molecules such as octane are injected onto the conventional nickel/yttria stabilised zirconia (Ni/YSZ) SOFC fuel electrode, the anode rapidly becomes blocked by carbon deposition and the cell power drops to near zero in minutes. This degeneration of the anode can be inhibited by injection of air or water into the anode or by some upstream reforming just before entry to the SOFC. Some smaller molecules such as methane, methanol and methanoic acid produce a slight tendency to carbon deposition but not sufficient to prevent long term operation. In this project we have investigated a large number of molecules and now found that some liquid ethers do not significantly damage the anode when directly injected. These molecules and formulations with other components have been evaluated in this study. The theory put forward in this paper is that carbon–carbon bonds in the fuel are the main reason for anode damage. By testing a number of fuels without such bonds, particularly liquid ethers such as methyl formate and dimethoxy methane, it has been shown that SOFCs can run without substantial carbon formation. The proposal is that conventional fuels can be doped with these molecules to allow hybrid operation of an ICE/SOFC device.

Keywords: Microtubular SOFC; Ether fuels; Carbon deposition on anode; Hybrid ICE/SOFC

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Steam reforming of biodiesel by-product to make renewable hydrogen

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Abstract

The aim of this paper was to investigate the viability of steam reforming the combined glycerol and water by-product streams of a biodiesel plant. A platinum alumina catalyst was used to optimise the operating conditions for glycerol steam reforming and mass spectroscopy was chosen to measure reformer gas yield. The problem is that glycerol steam reforming is relatively untested even with pure glycerol and the by-product quality may be too poor. The strategy was therefore to optimise the process using pure glycerol and compare the performance with by-product glycerol. To test catalyst degradation caused by carbon deposition, a Solid Oxide fuel cell (SOFC) was used as a separate reformer and electrical performance was measured to indicate carbon deposition. This is the first time a SOFC has been run on glycerol. The results showed that thermodynamic theory can be used to predict reformer performance. At high temperatures high gas yield can be reached (almost 100%) and selectivities of 70% (dry basis) obtained. The optimum conditions for glycerol reforming were 860 °C temperature (maximum tested), 0.12 mols/min glycerol flow per kg of catalyst and 2.5 steam/carbon ratio. Reforming catalysts lasted for several days of continuous operation with minimal degradation, 0.4% of feed deposited. By-product glycerol performed slightly worse with a lower yield and more carbon deposition, 2% of feed. The results show that glycerol steam reforming is a viable alternative use for glycerol and potentially a better option than purification.

Keywords: Biodiesel; Glycerol; Reforming; Hydrogen; Fuel cell

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DEVELOPING THE REACTION KINETICS FOR A BIODIESEL REACTOR

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Abstract

The aim of this paper was to investigate the kinetics of the biodiesel reaction in order to find out how best to reach 96.5% methyl ester. The purity of the biodiesel product was examined using gas chromatography to the EN14214 FAME standard and real-time optical microscopy was used to observe the reaction. The problem was the reaction doesn't reach completion and the mechanism is not understood. It was observed that droplet size had a major influence on reaction end point and that the reaction was mass-transfer limited. This observation was confirmed by developing a mass-transfer based reaction model using the data from the batch reactor which agreed with results from other researchers. The model predicted better conversion with more mixing intensity. The results show that significant improvements could be made to the conventional FAME process.

Key words: Biodiesel, reactor, reaction, transesterification, theory.
