# Monitoring of Biodiesel Transesterification Process Using Impedance Measurement

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A thesis submitted in partial fulfilment of the requirement of the
Liverpool John Moores University for the degree of
**Doctor of Philosophy**

September 2014

# Abstract

Alternative diesel fuels have been the subject of extensive investigation. Fatty acid methyl ester (FAME) based Biodiesel manufactured from vegetable oils or animal fats is an excellent candidate to replace common diesel fuel being renewable, non-toxic and often giving rise to reduced exhaust gas emissions. The transesterification process has been commonly and widely used to produce biodiesel from vegetable oil or animal fat. Vegetable oils or animal fats generally have viscosities higher than standard diesel oil. This means that it is necessary to reduce the viscosity by means of reacting vegetable oil with alcohol in the presence of a suitable catalyst. The target product for this reaction is methyl ester, with glycerol and potentially soap produced as by products with the process of transesterification. Methylester (Biodiesel) is produced by converting triglycerides to alkylesters. A batch transesterification process has two significant mechanisms, and exhibits a mass transfer controlled region that precedes a second order kinetically controlled region. In order to control the conversion process it is useful to employ process monitoring. In particular monitoring of the mass transfer processes that limits the initial reaction rates could prove to be beneficial in allowing for process optimization and control.

This thesis proposes the use of a new method of biodiesel process monitoring using low frequency (15kHz) impedance sensing which is able to provide information regarding the progress of mass transfer and chemical reaction during biodiesel production. An interdigitated (ID) sensor has been used to monitoring the biodiesel process The ID sensor is of simple construction and consists of two sets of interleaved electrodes (fingers). The two sets of electrodes are separated by a gap and when an AC excitation voltage is applied across the interleaved electrodes an oscillating electric field is developed. The response of the fluid surrounding the sensor to the applied excitation was then used to determine progress of the chemical reaction by evaluating the real and complex impedance. A significant and unambiguous change in the components of impedance has been shown to occur during mixing (mass transfer) and transesterification.

The impedance measurements gained during transesterification were then used for the development of a system model. A systematic approach was used to select mathematical models and system identification techniques were evaluated. The system identification investigation used real process measurement data in conjunction with the Matlab system identification toolbox.

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# Acknowledgements

In the name of God, the Most Gracious and the Most Merciful

I would like to express my deepest gratitude and sincerest thanks to my supervisors, Dr. David Allanson and Dr. Christian Matthews, for his patient, support and guidance. His experience and enthusiasm have to be invaluable throughout the period of research for this thesis.

I would like to thank all those members of staff at Liverpool John Moores University whose helpful comments and general enthusiasm for the project provided encouragement to the author.

Further thanks must also be extended to all colleagues from DGHE scholarships. Discussion with them has been a learning experience and brought balance perspective on knowledge and daily life.

I appreciate the financial support from DGHE scholarship and Budi Indarsih as administrator.

On final note, I would like to thank my family for their encouragement over recent years and especially that support from my wife and kids, who sacrificed many years on the absent of me, to complete this study.

## Nomenclature

| | | |
|---|---|---|
| $A$ | $m^2$ | Surface area |
| $d$ | m | Distance |
| $q$ | coulomb | Electric charge |
| $C$ | F | Capacitance |
| $C_0$ | F | Capacitance of empty cell in Farad |
| $E$ | J | Energy joule |
| $f$ | Hz | Frequency |
| $f_a$ | Hz | Alias frequency |
| $f_{in}$ | Hz | Input signal frequency |
| $f_s$ | S/s | Sample rate |
| $G$ | m | Gaps between fingers in ID sensor |
| $I$ | ampere | Electric current |
| $I_d$ | ampere | Electric current sensor |
| $K$ | | Dielectric constant |
| $l$ | m | length |
| $L$ | H | Inductor |
| $N$ | | integer greater than or equal to 0 |
| $R$ | ohm | Resistance |
| $R_{id}$ | ohm | Shunt resistor |
| $V$ | volt | Electric potential |
| $V_{exc}$ | volt | Electric potential excitation |
| $V_{id}$ | volt | Electric potential sensing |
| $t$ | s | time |
| $T$ | Celsius | Temperature |
| $u$ | | Proses input |
| $y$ | | Proses output |
| $Z$ | ohm | Impedance |
| $Z_r$ | ohm | Impedance real components |
| $Z_i$ | ohm | Impedance imaginary components |
| $X$ | ohm | Reactance |
| $X_L$ | ohm | Inductive reactance |
| $X_C$ | ohm | Capacitive reactance |
| $W$ | m | Width of electrode on ID sensor |
| $w$ | kJ/mole | Activation energy |

## Greek Symbol

| | | |
|---|---|---|
| $\varepsilon$ | F/m | Permittivity |
| $\varepsilon'$ | F/m | Permittivity of real component |
| $\varepsilon''$ | F/m | Permittivity of imaginary component |
| $\varepsilon_0$ | F/m | Permittivity of vacuum |
| $\omega$ | Hz | Frequency |
| $\rho$ | $kg/m^3$ | Material density |
| $\sigma$ | mho | Conductivity |
| $\sigma_0$ | mho | Conductivity at room temperature |
| $\theta$ | degree | Angle |
| $\lambda$ | m | Wave length |
| $\mu_0$ | H/m | Permeability of free space |

|  |  |  |
|---|---|---|
| $\tau_{DT}$ | s | time delay |

**Acronyms**

|  |  |
|---|---|
| ai0 | Analogue input 0 |
| ai1 | Analogue input 1 |
| ADC | Analog to digital converter |
| ASTM | American Society for Testing and Materials |
| ARB | arbitrary waveform generator |
| ARX | Auto regressive exogeneous |
| ARMAX | Auto regressive moving average with exogenous |
| BP | British Petroleum |
| DAC | Digital to analogue converter |
| DC | Direct current |
| DG | Diglycerids |
| DMM | Digital multimeter |
| ELVIS II | Educational Laboratory Virtual Instrumentation Suite II |
| FA | Fatty acids |
| FAME | Fatty acid methyl ester |
| FR | Flame retardant (glass-reinforced epoxy laminate) |
| FFA | Free fatty acid |
| FID | Flame-ionization detection |
| FTIR | Fourier transform infrared spectroscopy |
| GC | Gas Chromatography |
| GDP | gross domestic product |
| GHG | Greenhouse gas |
| GPC | Gel permeation chromatography |
| HPLC | High performance liquid chromatography |
| ID | Interdigital |
| LC-GC | Liquid chromatography with gas chromatography |
| LDR | Light dependent resistor |
| LPG | Long-period grating |
| OECD | Organization for Economic Cooperation and Development |
| MG | Monoglycerids |
| NI | National Instrument |
| NIR | Near infrared |
| NMR | Nuclear magnetic resonance |
| SE | Single ended |
| TLC | Thin layer chromatography |
| TG | Triglycerides |
| TAG | Triacylglycerols |
| TOE | Ton of oil equivalent, 1 toe = 41.868 GJ |
| WCO | Waste cooking oil |
| vi | virtual instrument |

# *Chapter 1*

# *Introduction*

## 1.1 Global warming

Human activity is known as one contribution to earth global warming which is caused by increased injection of greenhouse gases (GHG) into atmosphere. Human interference to the GHG including the daily activity such as land use change, emission of light-absorbing gas, emission of particulate matter with different size distribution and injection of chemical pollutants into the atmosphere at various levels (Sørensen, 2011).

Global atmospheric concentrations of carbon dioxide, methane and nitrous oxide have increased markedly as a result of human activities since 1750 and now far exceed pre industrial values determined from ice cores spanning may thousands of years. The global increases in carbon dioxide concentration are due primarily to fuel use and land use change, while those of methane and nitrous oxide are primarily due to agriculture (IPCC, 2007).

Even though there are hotly debated by some communities, global warming caused by human activities is now accepted in the scientific community. More evident have been found in academic literature about sea level rising (Levermann, *et al.*, 2013) or melt down on Antarctic ice (Chen *et al*., 2013). It is clear that carbon emission from utilizing fossil fuel for energy can contribute to increase world temperature caused multiple effects for daily life like rising sea level levels, extreme weather, unexpected climate changing, catastrophe etc. The effect of increasing earth temperature certainly endanger life on earth. It has been projected that global warming, it will adversely affected to human supply which are crucial to sustain life. Water supply, food supply, human health, human settlement are some factors which are sensitive to climate change.

To reduce impact of global warming many effort has been done by researchers around the world, especially in field of energy resources to find replacement for current energy resources which are believed as contributor of GHG. Renewable energy is one of the alternative energy which is promising to environmental friendly with its carbon neutral concept. Biofuel from vegetable oil is one attractive alternative to provide clean energy and sustainable supply.

## 1.2 Energy security

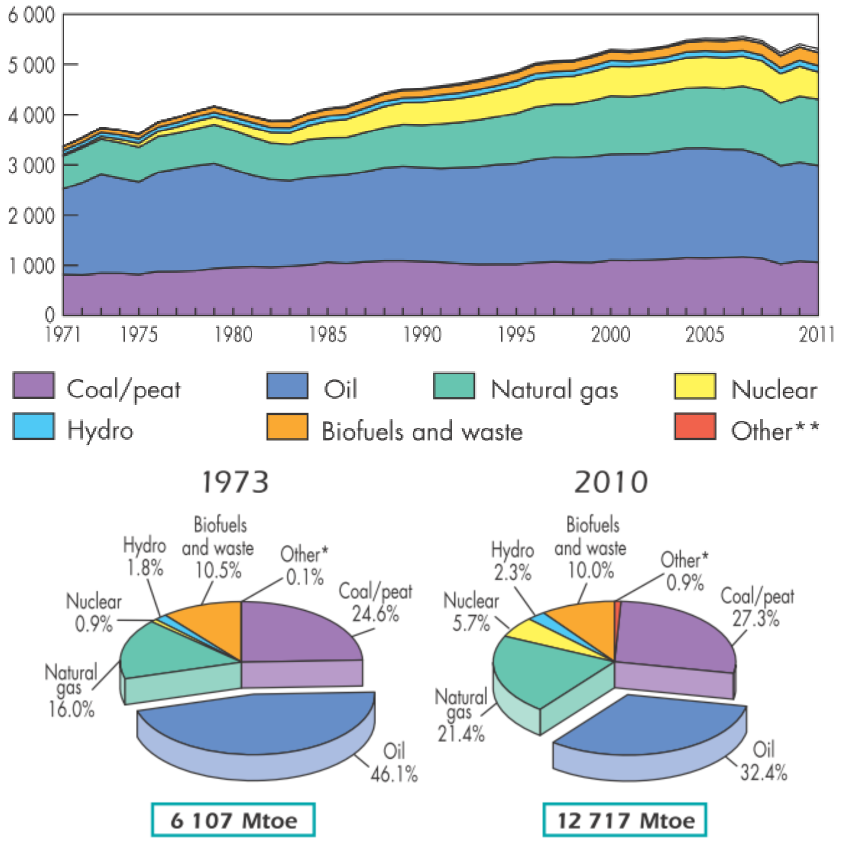
Definition of energy (E) may be derived from another concept of work (W). Work is defined as the use of a force (F) to move something, the force is the intensity with which we try to displace and object (by push, pull, lift, kick, throw, etc). The amount of work to do depend on how much force is applied and what distance (d) is being covered. Energy is found in different forms such as motion, heat, light and sound. There are many forms of energy, but they all can be put in two categories, kinetic and potential. Gravitational energies, chemical, nuclear and stored mechanical are potential forms of energy; motions, thermal, sound and electrical are kinetic.

Energy is main key on industrialized societies, it used to sustain and improve prosperity. Production of energy is interrelated with population, energy consumption, gross domestic product (GDP) and production of pollution for the world. It can be found in different forms and it comes from many different sources. Historically, massive utilization of energy started around 17th centuries when Great Britain started industrial era. Development in economic mean growing in energy demands, exploring natural energy resources such as coal, wood, hydro fuel, fossil fuel and nuclear energy. Utilizing fossil energy in the last decade is rise significantly and it has several issue concerning about climate changing and energy security.

Fossil fuel has been intensively used in the past few decades caused pollution for environment increasing amount of carbon dioxide ($CO_2$), it generate to steady increase of global temperatures. International energy agency reported on Figure 1.1, there has been significant increasing in energy demand in past 40 years.

Increasing public awareness on the serious damage of the environment led to the Kyoto Protocol in 1997, requiring some industrialized countries reduce their emissions of greenhouse gases. New evident shows by some scientist proved that surprisingly rapid loss of arctic ice caused by climate changes. Earlier prediction may have underestimate about emission reduction needed to avoid environmental damage.

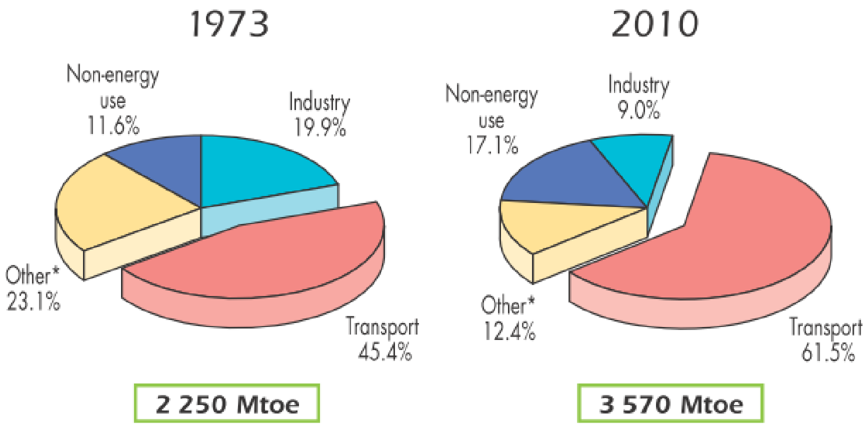
At present, most of energy used comes from fossil fuels such as petroleum, coal and natural gas. While fossil fuels are still being created today by underground heat and pressure, the fuels are being consumed more rapidly than they are being created. Therefore, fossil fuels are considered non-renewable as they are not replaced as soon as we use them.



*Other includes geothermal, solar, wind, heat etc.

**Figure 1.1** World total primary energy supply from 1971 to 2010 by fuel (Mtoe)(IEA, 2012)

It can be seen from figure 1.1 that there are consistently increase on energy demand in the past 40 years. Natural gas, Nuclear, coal, hydro and other have have significant increase in utilization, while Oil and biofuels have slightly decrease.



*Includes agriculture, commercial and public services, residential and non-specified other

**Figure 1.2** World oil consumption from 1971 to 2010 by sector (Mtoe)(IEA, 2012)

Figure 1.2 shown that oil utilization has mainly used for transportation purposes, and it has increased significantly. Transport sector is one of important infrastructure on economic development, an efficient transportation system can provide economic and social opportunities and benefits which have result in positive multipliers effect like as increasing quality of life, better accessing to the market, employment and additional investment. It can be seen that transportation sector is highly dependent on fossil oils and a distraction to oil supply will have multiple effects to economics even to country stability in some developing countries. Unfortunately, oil supply will not last forever, because of oil cannot be replaced right away and it predicted to deplete soon.

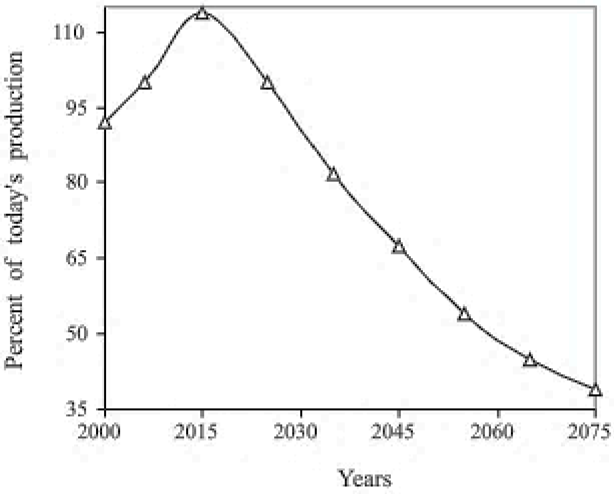


**Figure 1.3** Global oil production scenario based on current production (Demirbas, 2008).

Peak oil exploration in figure 1.3 has been predicted with various simulation tools and argument some authors however there is no clear consensus when the world oil production reach the peak. It can be divided in two prediction, late peak prediction and late peak prediction. Late peak prediction has estimation that peak will occur after 2015 while early peak prediction have pessimistic prediction that peak occurred 2005-2018 (Chapman, 2013). Figure 1.3 is reflecting a pessimistic estimation that a peak of oil production will occur in around year 2015. In spite of inconsistency in date of oil production reach a peak production, all has agreed that there will be decrease in oil production.

Primary energy consumption in developed and developing countries currently relies on fossil fuels. Most petroleum nowadays comes from the same sources, it makes the economic situation in non-producer countries highly influenced by stability producers country. Petroleum is primarily used for transport which is basic economy sector in many countries, consequently petroleum supply and prices reliability and stability are affected, and this is especially so in the developing countries.

Increasing population and global industrialization made significant to energy consumption, whereas current oil reservoirs are very limited and feared depleted very fast at the current rate of consumption. BP reported that world proved oil reserves at the end of 2012 is 1668.9 barrels, it can be safe the oil production to provide petroleum demand for the next 52.9 years (BP, 2013). However, there will be uncertainty about the future of oil deposits, many possibilities with different scenarios. The petroleum deposits can be discovered every year by leading petroleum companies with intensive survey and research. The worst scenario might be happening are no one petroleum reservoirs will be found and the worlds will prepare for the next fifty years.

## 1.3 Carbon neutral energy supply

The fundamental of life is basically relying on of photosynthesis process. The process of photosynthesis primarily converts carbon dioxide and water to biomass. At the end of photosynthesis product there are some purposes to full fill human need, energy, food and valuable stuff. Energy from biomass especially wood became the major source energy since long time ago and still provide around 30 % of world energy consumption. Even the use of biomass remains the dominant contribution to the energy supply of many developing countries; it can contribute around 70-90% of energy demand (Nelson, 2011).

Figure 1.4 depicted of biomass formed form of carbon dioxide when it get reaction with oxygen through the process of burned either by combustion or respiration (food) it will gain some amount of $CO_2$ fixed in it. As the result the concentration carbon dioxide on the atmosphere is remain constant compare to the utilization of fossil fuel, At this point the ideas about carbon neutral is appear. It is makes the biomass conversion to bio-fuel is attractive option to substitute fossil fuel.

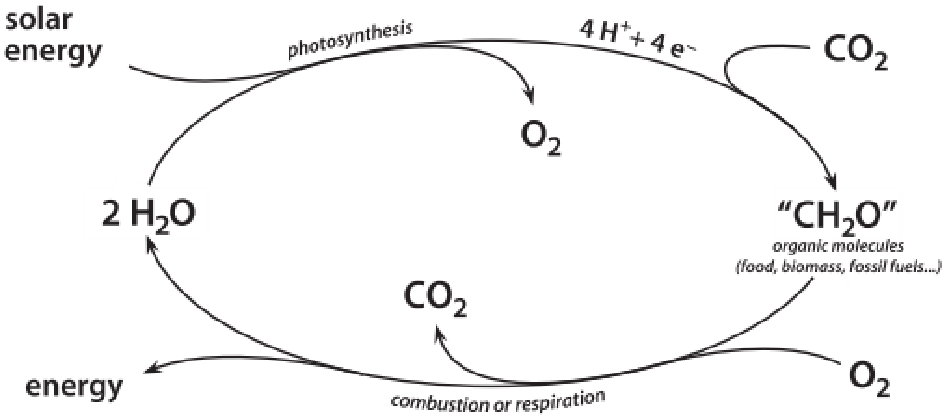


**Figure 1.4** Natural photosynthesis, combustion and respiration process (Armaroli & Balzani, 2011).

Generally the products of bioenergy to produce heat for households and industries, biofuels (in the form of gaseous, liquid or solid) and electricity. Different with fossil fuel, biofuel can be generated from biomass, using viable technology to obtain energy. Biofuels can be classified based on their form. Biogas and syngas (from biomass gasification) can be classified on gaseous biofuels, liquid biofuels including biodiesel, bioethanol, vegetable oil etc and solid biofuels such as briquettes from biomass, sawdust, charcoal and woods.

A concept of carbon neutral energy come if the source of the fuel or if they are made from carbon recovered from biomass of captured from ambient air using industrial process. Photosynthesis uses energy from sun to recycle carbon dioxide to form new plant life. The plant can use as energy resources as biomass or converted its seeds in to fuel.

## 1.4 Alternative Energy from renewable energy

Renewable energy are often called as alternative energy which are potential as source of energy with carbon neutral or zero emission of air pollutants and greenhouse gases. Renewable energy can be converted into useful form of energy by converting natural resources into energy. This energy is using sun energy which is has direct and direct effects of the earth such as solar radiation, biomass, wind, water. Compare with fossil fuel, the availability renewable energy sources are more distributed.

### 1.4.1 Wind Energy

Wind energy has been used for centuries to pump water or mill agriculture crops. Nowadays wind turbine has been used to produce electricity in large scale. The design can be very efficient and can reduce the cost of electricity production. Wind energy is clean and available in many areas including offshore. Often the wind are blowing strong across the sea it make perfect location for generate electricity. Large scale wind turbine can generate 500kW until 6 MW electricity. Wind energy gaining popularity since the awareness of renewable energy. From ecological aspects wind energy have some benefits including ;

- In operational wind turbines are not emits any pollutants compare with other source energy such as liquid or biomass. $CO_2$ as the major parts of pollutant is produced when fuel or biomass are burned.
- Wind turbine has no residue left behind when its operational as Nuclear plants.
- There are other utilities for land occupied by wind farms, such as agriculture

- When the wind turbine is decommissioning, the cost of cheaper compare with the other power plants especially compare with nuclear power plant.

Despite all advantages of wind turbine there are some drawbacks of wind turbine utilities,

- Wind can be difficult to predict, it makes hard to make continuous supply of electricity.
- Sound pollution may produce by wind turbine, therefore the wind turbines are not suitable to be built near residential areas.
- Large scale of wind turbine can be a threat to the bird and become potential conflicts for birds' population.

### 1.4.2 Solar energy

Solar energy is one of indigenous form of energy which can be utilising in some ways. Solar energy can be directly converted into heat or electricity. A photovoltaic is widely used to generate electric current from direct sun light. In photovoltaic operation light is absorbed and an electron acquires kinetic energy to move it to another energy level within the materials. Primary material for photovoltaic cells are semiconductors. Although photovoltaic is concerned to be expensive, there are some applications which they are cost effective, especially stand-alone systems in remote area, where they are far from utility grid. Photovoltaic and wind has main advantage over conventional thermal system plants which they are not require water.

### 1.4.3 Water power

Water energy may be the oldest source of energy used by human, used to rotate mail stone to grind grain. Water energy provides mechanical energy to drive turbine generated electricity. The energy in water can be in the form of potential energy from a height difference like in a dam or kinetic energy due to water flow in rivers. Large scale of hydropower is main contributor to electric supply in the world. The world installed capacity is has increased 2% per year from 462 GW in 1980 to around 850 GW in 2009. However the hydroelectric percentage of electric power has decreased from 21% in 1980 and16% in 2010.

Small scale of water turbine is micro hydro which has capacity below 100kW. Micro hydro does not need dams and a reservoir as water is diverted then conducted in a penstock to a lower elevation and turn water turbin to generate electricity. Micro hydro has benefit over the other renewables energy as follows:

- It is efficient energy source, with small amount of flow can generate electricity.
- Compare with small scale PV or Wind turbine micro hydro will provide continuous supply electricity.
- Less impact to the surrounding ecology because no reservoir needed.
- Low cost investment is suitable for remote locations.

The disadvantages of micro hydro as follows :

- The water supply is dependent on season, there is low power in summer times in some places.
- Each site has different characteristic such as stream size (flow rate and head) and distance from power to the load.

### 1.4.4 Waste

Waste can turn into a useable form of energy, including electricity, heat and fuel for transportation (i.e. diesel fuel). Waste conversion can turn into useful energy in some ways the most well-known process is incineration. Waste usually comes from a mixture of different stuff. Residual waste which is the waste left over by recycle process. Some part of the residual waste contains from things made from hydrocarbon like plastics, this type of waste can be considered as non-renewable. The other part of waste is renewable which is part of things that were recently growing such as wood, paper, food etc. Renewable waste can be processed either burn or by anaerobic digestion to produce biogas.

### 1.4.5 Biofuels

The term biofuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. A variety of fuels can be produced from biomass resources including liquid fuels, such as ethanol, methanol, biodiesel, Fischer-Tropsch diesel, and gaseous fuels, such as hydrogen and methane. Liquid biofuels are primarily used to fuel vehicles, but can also fuel engines or fuel cells for electricity generation. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries (Demirbas, 2008). Compared to fossil fuels, biodiesel have some advantages, a. Biofuels are easily available from common biomass sources, b. They represent a close carbon dioxide-cycle in combustion, (c) biofuels have considerable environmentally friendly potential, (d) there are many benefits to the environment, economy and consumers in using biofuels and (e) they are biodegradable and contribute to sustainability. The benefits include greenhouse gas reductions that include reduced carbon dioxide emissions, which will contribute to domestic and international targets, the diversification of the fuel sector, biodegradability, sustainability and an additional market for agricultural products. Biofuels help to protect and create jobs (Demirbas, 2008).

Ethanol is one of kind alcohols; ethyl alcohol [$C_2H_5OH$] has a clear and colourless liquid. Ethanol has oxygen content and a high octane rating therefore it clean burning fuel. Ethanol is most commonly used to increase the octane rating on combustion engine by blend with gasoline and it can increase the emission quality of gasoline engine. In some countries it is usual to using ethanol blended with gasoline, blend of 10% ethanol and 90% conventional gasoline fuel is to be named E10 blend or shortly E10. Ethanol can be produced by fermentation of sugars that are converted from many different starch plants. This has been a long history practiced throughout the world. Ethanol which is produced from corn, barley, potato, rice and wheat can be called grain ethanol while ethanol generated from cellulose biomass like trees and grasses is called bioethanol (Lee *et al.,* 2007). Producing ethanol from grain and cellulose is using biochemical process and different process with chemical ethanol. Ethanol from biomass is an attractive option because it is cheap, abundant and renewable resource includes various agriculture residues that can be converted to liquid fuel. Compare with the ethanol from different commercial raw materials such as corn, wheat or sugarcane has potential detractors because of competition with its use as a food source for human which can affect the sustainability of the production (Amores *et al.*, 2013).

Bio-oil can be obtained from agricultural residues or forestry via gasification through fischer-Tropsch synthesis reaction. Biomass feedstock especially wood biomass is attractive to use as fuel because it can avoid distraction on various food product prices. The process generally including biomass gasification for producing syngas (CO + $H_2O$), gas cleaning and Fischer-Tropsch synthesis reaction (Hanaoka *et al.*, 2010).

Biodiesel is alternate fuel for diesel engine, it is commonly produced by a chemical reaction via transesterification process. The feedstock comes from various resources of vegetable oils and animal fat such as tallow and yellow grease. The feedstock from vegetable oils can be from edible or non-edible oil and waste or cycle oil. Edible oil like rapeseed, soybean, palm, sunflower, peanut, groundnut may be consider as first generation source of biodiesel because they are first group of oils to be used for biodiesel production. However, using edible oils as source of biofuel has been lead to prolonged debated about food and fuels, because it will come with other consequences (Cotula, 2013). The other sources of biodiesel is algae and seaweeds, it become an attractive choices because it can avoid competition for arable land and would not distract food and feed supplies.

Biodiesel is offer an alternative environmental friendly fuel which has lower pollution impact over current diesel fuel. Moreover, biodiesel has sustainable source because it can obtain from renewable resource such as vegetable oils or animal fats. The major ingredients in vegetable oils or animal fat is triglycerides (TG). TG is esters of fatty acids (FA) with glycerol, there are several different FA can be found on the TG.

To generate biodiesel, vegetable oil or animal fat is processed using transesterfication process, a chemical reaction to reduce viscosity. The vegetable oil and animal fats on that process is reacted with alcohols (commonly methanol) with the presence of a catalyst (base or acid). Methanol as alcohols reactance in transesterification process is widely used, the main reason that methanol is less expensive compare the other alcohol variants.

The source of biodiesel can be from a great variety of feedstock, these feedstock source can come from common edible vegetable oil (soybean, rapeseed, palm oil, canola, coconut etc.), non-edible vegetable oil like jatropha curcas, animal fat such as beef tallow and waste oils from food (used frying oils from restaurant). The availability of the oils is dependently depending on geography and it is necessary to change production process since each oil has different quality.

In many countries, biodiesel is not replacing petro diesel 100% and commonly blend with petro diesel instead of pure biodiesel, because biodiesel is well miscible with petro diesel in all blend ratios. Blends of biodiesel usually denoted by abbreviation like B5 which represent blend of 5% biodiesel with ordinary diesel fuel, in addition pure vegetable oils and animal fats which blend with petrol diesel should not called to be ‘biodiesel’. Edible vegetable oil is most common biodiesel materials, however since cost is the main concern in biodiesel production, the use of non-edible vegetable oils like Jatropha Curcas has been studied.

Substitute of biodiesel as fuel in diesel engine has some benefits ;

- Petro diesel has higher emission when use as diesel fuel such as CO, particulate matter compare with biodiesel.
- Biodiesel feedstock comes from vegetable oil or animal fats and it is a source of renewable fuel.
- Biodiesel is not containing any sulphur and biodiesel emission is not containing any $SO_2$.
- For storage biodiesel safer than petrodiesel because biodiesel has higher flash point.

As replacement of petro diesel, biodiesel has a few drawbacks, :

- $NO_x$ emission slightly higher
- In cold climates biodiesel is less convenient due to higher freezing point.
- Long term storage is not recommended, because biodiesel is less stable.
- Using B100 biodiesel may harm plastic, natural rubber gaskets and hoses, therefore it is recommended for such application using better materials properties.

The disadvantages of biodiesel are significantly eliminated when biodiesel blended with petrol diesel fuel.

## 1.5 Biodiesel process

Vegetable oil is not suitable if directly used in most diesel engines due to high viscosity, to reduce the vegetable oils' viscosity commonly using trasesterification or alcoholysis. Transesterification process is a chemical conversion of long chain triglyceride oil molecule into its corresponding fatty ester, the reaction also yield glycerol as by product. The widely used transesterification process is batch reaction, and the chemical reaction takes a place when the oil is mixed with alcohol + catalyst. Catalyst, temperature and stirrer speed in trasesterification process will improve both reaction rate and yield.

The studies on the transesterification process indicate there are two important stages during batch transesterification process. At the beginning of the reaction a mass transferred control region has dominated the process followed by a kinetic controlled region (Noureddini, *et al.*, 1997). Reducing mass transfer region will increase overall chemical reaction, by shortening the overall chemical process.

Vegetable oil and methoxide (methanol + catalyst) is immiscible and mass transfer resistant exists between the two fluids. The transesterification reaction has initial mass transfer control region in heterogeneous regime and followed chemical reaction controlled region in pseudo homogenous regime. Chemical reaction is very slow due to the small active specific catalyst surface in early reaction time, as soon as methylester formed, it is become a mutual solvent because methylester is soluble in both vegetable oils or methanol, therefore the system contains just one layer where the chemical reaction control the kinetics (Vicente, *et al.*, 2005). Stamenkovic reported a research of transesterfication chemical reaction after mass transfer by measuring the drop size of disperse methanol during the process. The drop size of methanol reduced rapidly with the progress of chemical reaction and the rate of drop size reduction increased as the reaction temperature increased, and the agitation rate is remaining constant. It is related to the formation of the emulsifying agents stabilizing the emulsion of methanol drops into the oil, which formed faster at higher temperature. Also, the emulsifying agent is causing the increase in the specific interfacial area. Therefore, when the two immiscible phases (triglyceride and methanol) are mixed and the reaction was started, the agitation is no longer needed (Stamenkovic, *et al.*, 2008).

Frascari has verified the ideas to stop or reduce agitation speed by identify optimal agitation speed which lead to a significantly reduction of the mixing energy. It is possible to reduce the agitation energy up to 200 times lower compare with common liquid to liquid transesterification process. Also the research reveals the fact that complete halt of agitation after 1-2 minute mixing led to a further decrease of mixing energy without any increase of reaction time. A 250 rpm mechanical agitation transesterification process for 1 minute can yield 99% oil conversion with specific energy consumption of 3.6 $J/kg_{biodiesel}$ (Frascari *et al.*, 2009).

For a large application of biodiesel transisterification process, continuous process is commonly used. However, batch reactor proses is widely used as this process is economically interesting for biodiesel for biodiesel ranging between 4000 to 7000 ton/year (Sakai *et al.,* 2009).

## 1.6 Material and Method

In order to undertake an investigation into the possibility of using impedance measurement as a means of monitoring the transesterification reaction a small scale (<100ml) batch reaction was established in the laboratory. Methanol (99.9%) and KOH (85%) (Supplied by Atom Scientific Ltd) and food grade sunflower oil were used as the reactants.

### 1.6.1 Transesterification

All experiments were conducted in a 100mL borosilicate flask, mechanical agitation was provided by magnetic stirrer and the temperature controlled by use of a hot plate. 60mL of sunflower triglyceride was decanted into the flask and the methoxide was injected at a controlled rate into the bottom of the flask. Transesterification reactions were undertaken at one temperature, 40 ° C, the methanol to sunflower ratio was 6:1 and 1% KOH was used utilized as the catalyst. The methanol to oil ratio used was twice the stoichiometric ratio as this ratio is normally used in industrial process so as to ensure high conversion efficiency.

### 1.6.2 Sensor and Data Acquisition

In order to investigate the potential of using ID sensors to monitor transesterification reactions a simple sensor was fabricated, The electrode pattern was created on a printed circuit board using a FR4 substrate. The copper plate thickness was 35µm; the width of the track forming the ID fingers was 1.6mm and the surface finished by Ormecon (partial chemical tin for ultra-flat pads). The original layout was created by Proteus 7 PCB design software and a number of sensors were produced from a single PCB sheet. The resulting sensor had a 1.5cm$^2$ effective area and 0.4 mm gap width between digits. A precision shunt resistor (40.2K 0.1% tolerance) was used to sense the circuit current. Data Acquition was accomplished using a National Instrument ELVIS II and associated National Instrument LabVIEW software.

### 1.6.3 System Identification

Capacitance data reading from the transesterification process was then processed by the Matlab System Identification toolbox. Although state estimation of the transesterification process can be determined using graphical estimation techniques, back box identification was selected because the techniques required little prior knowledge of the system physics (model structure and associated parameters) as they are determined during system identification process. Figure 1.5 shows the flowchart conducted, impedance measurement from biodiesel process will be used as input for System Identification.

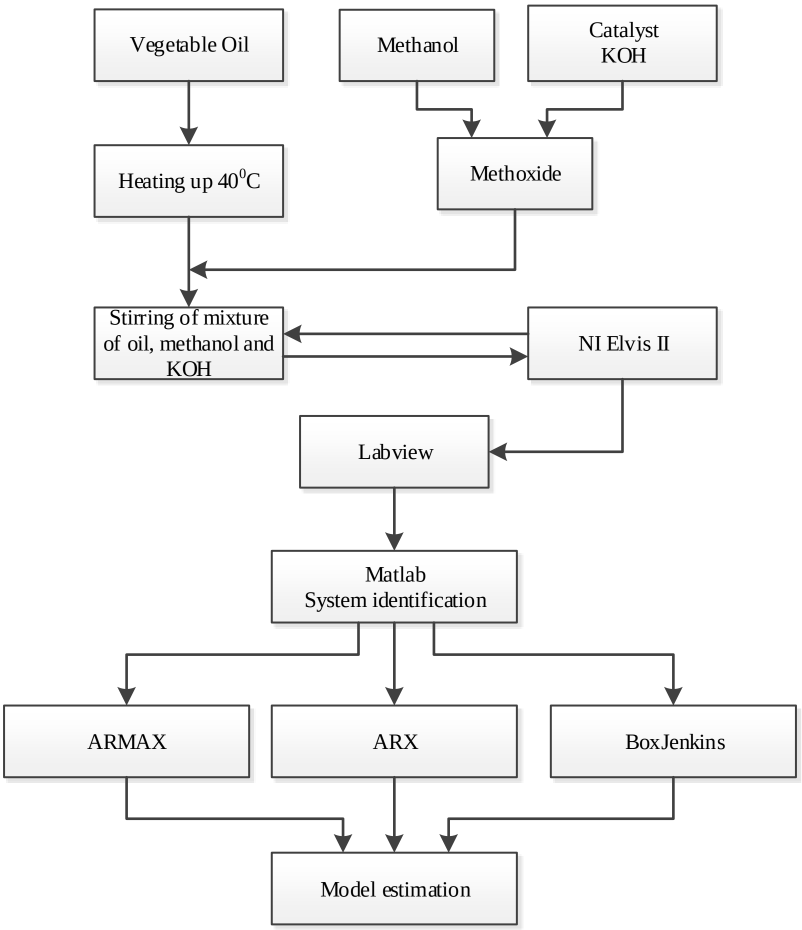


Figure 1.5 Research flowchart

## 1.7 Aims

The goal of the research is to study and develop Inter digital sensor to be implemented on biodiesel transesterification process as feedback input. Using impedance measurement as method to measure capacitance and resistance simultaneously. The main purpose of the sensor and measurement technique to monitor the state of the reaction. This feedback sensor is very important to optimize the transesterification process. Based on signal information from the sensor, control strategies can be implemented.

- Develop an alternative inter digital sensor for biodiesel based capacitance and impedance measurement.
- Propose an alternative method to direct measurement by means of single frequency Impedance measurement to assess process reaction.
- Propose the monitoring of reaction on biodiesel process in the point of permittivity and conductance changing.
- Using National Instruments Hardware and software to implement impedance measurement to possibility using low cost digital signal measurement system.
- Evaluate the chemical biodiesel process reaction related with capacitance-resistant properties during the reaction in order to understand the concept of impedance measurement on biodiesel process.
- As the system is conducted in batch reactor, the system identification is tested using open loop system with the step test input. The output recorded to produce a process reaction curve. A process estimation of the system developed using Matlab System Identification toolbox from step response to develop a model for biodiesel transesterification process.

## 1.8 Objectives

The objective of this research was to find and alternative for monitoring biodiesel process lead to process optimization. With process monitoring state of the process can be predicted. The complete mixing from batch transesterification process can be determined by steady state curve on graphic measurement. The optimization of biodiesel process by stopping or reducing of process stirring can lead to increase process efficiency. As previous research state that it is possible to reduce energy process after the reaction reach equilibrium.

Impedance measurement is proposed in this thesis along with Interdigital capacitance based sensor. With benefit of digital signal processing it is bring impedance measurement is less sophisticated and simple to implement In particular the impedance measurements have provided an approach to understanding in intrinsic material properties and chemical reaction mechanism. To optimize transesterification of vegetable oil to safe energy during chemical reaction, it is important to employ a system monitoring.

## 1.9 Thesis structure

The thesis is consist with 8 chapter with first chapter is description of energy today, renewable energy, using of biofuel and discussion about the objectives.

Chapter 1 present the concern of biodiesel, aims, objective and methodology of the thesis.

Chapter 2 present the literature survey in biodiesel utilization, current technology for biodiesel process, catalyst for the biodiesel process, Feedstock for biodiesel, debate utilization of vegetable oil as food or fuel.

Chapter 3 describes the transeterification process and the condition which affect the reaction process such as temperature, catalyst, mechanical agitation. Transesterification or methanolysis is highly affect by mass transfer between fluid the discussion will be presented in this chapter. Process monitoring is discussed in this section.

Chapter 4 provide a brief discussion about the impedance measurement and its application, measurement method and equipment used. Basic electronic circuit is foundation of impedance measurement.

Chapter 5 present a design of inter digital planar sensor and its application, basic concept of operating sensor explained. Resistance and capacitance is main basic calculation. The chapter explain the design and material used to create the planar sensor.

Chapter 6 this chapter discusses the detailed of experiments, materials and equipment used. Acid transesterification has chosen as a method for experiment. Feedstock (vegetable oil) and methanol and catalyst used,

Chapter 7 this chapter discuses modelling using system identification, with system identification it is possible to create a mathematical equation for the process based on input output measurements.

Chapter 8 Conclusions are drawn and recommendations for further work made.

# *Chapter 2*

# *Biodiesel*

## 2.1 Introduction to Biodiesel

Diesel engine has been used for prime mover in many heavy duty applications in agriculture, construction, industrial, high way transport and electric generation. Diesel engine is popular because its ability to use petroleum crude oil as a fuel compare with its close competitor, the petrol engine, diesel engine has long durability, high torque capacity, and fuel efficiency ensures diesel engine its domination in the most demanding application. In United States the diesel engines for passenger car is less than 1% in contrast with European country is around 58% of new registration on 2011 (Cames and Helmers, 2013).

Going concerns about the future petroleum oil reserves, and increasing awareness of the effect of air pollution to the health and consciousness the important Of reducing the GHG (greenhouse gases) for long term application it is crucial to find alternative fuel which has less emission and pollutant and renewable for diesel engine.

ASTM international has defined biodiesel as a fuel composed of monoalkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats meeting the requirement of ASTM D6751 (ASTM 2008a). Biodiesel is remarkable compare with the other biofuels, it is nearly interchangeable with common diesel fuel. Compared with spark ignition engines, where the main alternate the alternate fuel is ethanol and has different performance characteristic compared to petrol. From engineering point of view the differences between biodiesel and fossil diesel fuel or petro diesel fuel are pretty small, and biodiesel offers it has better performance in some cases such as burning emissions.

Biodiesel is not a new development, the German engineer Rudolph Diesel (1858-1913) who invented diesel engine used biodiesel in the his earliest engine.

At the World's Fair in Paris a diesel engine can ran using peanut oil smoothly. During diesel engines development, petro diesel replaced the biodiesel because petro diesel was cheaper and more plentiful. After the oil crisis in 1973 the world interest on biodiesel has developed. Nowadays the biodiesel market is growing rapidly, often sold combined with petro diesel as blend, often identified as a blended percentage of biodiesel in petro diesel. Neat biodiesel is pure 100% biodiesel fuel, it is referred to as B100. A biodiesel blend is pure biodiesel blended with petro diesel. Biodiesel blend are referred to as Bxx, where xx indicates the amount of biodiesel in the blend in example, a B20 blend is 20% biodiesel and 80% petro diesel.

## 2.2 Biodiesel raw materials (biomass, waste and vegetable oil)

Vegetable oils mainly contain with triacylglycerol (TAG) often referred to as triglycerides. TAG are esters of fatty acids (FA) The TAG present in vegetable oils and animal fats typically contain several different fatty acids as different fatty acids can be attached to one glycerol backbone. The different fatty acids that are contained in the TAG comprise the fatty acids profile (or fatty acids composition) that differs for each vegetable oil or animal fat because different fatty acids have different physical and chemical properties. The fatty acid profile is probably the most important parameter influencing the corresponding properties of a vegetable oil or animal fat (Knothe *et al.*, 2005).

Vegetable oils can be derived from edible seeds like corn, canola, palm and rapeseed, or oil resource form non-edible oils like Catton seeds (Nabi *et al.*, 2009), jatropha curcas (Berchamans & Hirata, 2008), microalgae (Chisti, 2007), neem, karanja, rubber seed, mahua silk cotton tree (Ghadge & Raheman, 2005).

There are many advantages using vegetable oils over petroleum diesel fuel such as the availability, renewability, lower sulphur content, however vegetable oils have apparent problems as diesel fuel such as higher viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains (Dermibas, 2008). Vegetable oils have potential to substitute for a fraction of petroleum distillates and petroleum-based petrochemicals in the future. At the moment, vegetable oil fuels are more expensive compare with petroleum fuels. However, the world recently experiences high levels of uncertainty about the oil prices. Petroleum prices are influenced by a number of the factors, the political situation in producer countries, supply and demand, and uncertainties concerning petroleum availability these factors lead to renewed interest in using vegetable oils in diesels engines.

### 2.2.1 Biomass

Biomass is organic matter particularly cellulose or hemicellulosic matter, and its available on renewal basis. The variety of biomass are including trees, plants and associated residues, animal waste, paper components municipal solid waste, industrial waste and poultry litters The biomass is abundant and almost available in every part of the world more over it has zero emission of $CO_2$, since its growth absorb carbon dioxide from atmosphere. Biomass is converted in to biofuels using different processes mostly because biomass is a low energy density material with a low bulk density, it degrades in storage and also it is difficult and costly to transport store and use (Chartier *et al., 2013*).

Conversion of biomass basically can be done by three main process: physical, biological and thermo-chemical. Commonly physical process is used for oil rich seeds. Oils are extracted from oil seed and the extracted oil is refined by esterification with alcohol to reduce viscosity and improve the quality of biodiesel.

In biological process, there are two common method to be used, fermentation and anaerobic digestion. Biological process use wet biomass as raw materials, the wet biomass is treated with micro-organisms in the presence of absence of oxygen for a longer time. The main products obtained in this process are bio-ethanol and biogas. Common application for fermentation is bio-ethanol production, which using sugar as components of biomass. Sugar cane and sugar beets store the energy as simple sugar. Then simple sugars as converted to ethanol by fermentation process using yeast or bacteria as catalyst. In anaerobic digestion the biomass is treated with micro-organisms like yeast in absence of oxygen to produce biogases and the main product is methane. Depending upon the solid content in biomass, the anaerobic digestion process is classified as dry and wet digestion process.

In thermochemical processes the feed stock is heated in limited presence of oxygen or steam for a short time. Gaseous fuel then further processed by Fischer-Troopsch process to convert the gas into liquid.

### 2.2.2 Algae

In recent year's algae as source of biodiesel has more attention on academic and commercial biodiesel research. Algae is photosynthetic organism which capable of using sunlight and carbon dioxide to produce variety of organic molecules especially carbohydrates and lipids. Biomass can be generating from these kind of bio molecules or through extraction as source of fuel known as biodiesel. Algae species can grow in various water qualities, from fresh water through saline water. Algae use $CO_2$ efficiently and are responsible for more than 40% of the global carbon fixation. Also, algae can produce biomass very rapidly, with some species doubling in as few as six hours and many exhibiting two doublings per day. All algae have the capacity to produce oil – rich energy and some of them have been found to naturally accumulate high levels in total dry biomass (Hannon, *et al.*, 2010). Moreover, because of algae is an aquatic species, they do not require arable land for cultivation it means that algae cultivation does not need to compete with agricultural commodities for growing space (Campbell, 2008).

Some researcher believe that all superiority of algae, can be become perfect candidates and capable as replacement for liquid fuel, especially for transport fuels in the near future (Chisti, 2007). However, despite of all algae benefit, there are still barriers for algae development. Because the development of this technology is in its early stages and much remains to be done for the biology optimizing, engineering, business models and life cycle analysis (Larkum *et. al.*, 2012). The main challenges to making biodiesel capable to compete with petroleum Diesel is the cost of the process. Estimated cost of a barrel of algae-based fuel using current technology in 2009 is US$300 – 2600, compared with $40-80 for petroleum. In certain region some estimation for a barrel of algae oil can be reach as low as $84 (Hannon, *et al.*, 2010).

### 2.2.3 Waste

Compared to petroleum-based diesel fuels, the higher cost of biodiesel production is a major barrier to its commercialization, with 70%-85% (Knothe *&* Steidley, 2009) of the total biodiesel production cost arises from the price of raw materials estimated. Waste cooking oil (WCO) or waste cooking oil, which is less valuable than neat vegetable oil, is a promising alternative for biodiesel feedstock. The use of WCO in biodiesel production may also act to reduce the effects of fuel production on food availability in developing countries. The properties of WCO should be considered when using WCO to produce a diesel fuel. WCO have different fatty acid profiles from raw oils and the resulting diesel fuel may affect engine operation like cloud point. When used for cooking the properties of vegetable oil change throughout frying process at temperatures of 160-200$^{o}$C. The changes by the oil are both physically and chemically. Some common thermally induced physical changes observed in vegetable oil are (i) oil viscosity increase, (ii) an increase in the specific heat capacity, (iii) a change in colour, (iv) a change in the surface tension and (v) an increase tendency of fat to form. Thermolytic, oxidative and hydrolytic chemical reaction occur during the process of frying oils at least three reaction (Mittelbach, *et. al.* 1995).

### 2.2.4 Biodiesel from vegetable oil

#### 2.2.4.1 Triglycerides of vegetable oils

Vegetable oils are vital bio-renewable resources extracted from various plants and commonly called by their originally biological sources like corn oil and rapeseed oil. Vegetable oils have been known as food since ancient times and become good source of biofuels in recent years. Triglycerides are the main constituents of vegetable oils and animal fats as shows in figure 2.1. Triglycerides also known as triacylglycerol (TAG), and they have lower densities compare with water (they float on water) also at normal temperature may be solid or liquid form. TAG is chemical compound formed from one molecule of glycerol and three fatty acids. Glycerol possesses three carbon atoms and fatty acids have long chains of carbon atoms. The fatty acids vary in their carbon chain length and in the number of unsaturated bonds they contain (Sonntag, 1979).

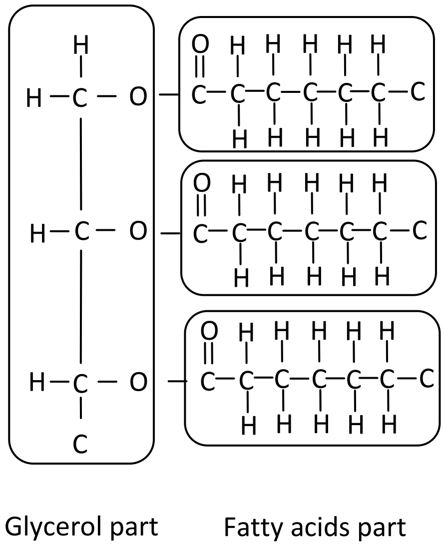
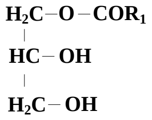
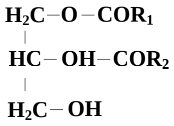
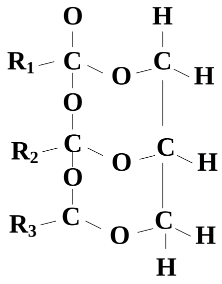
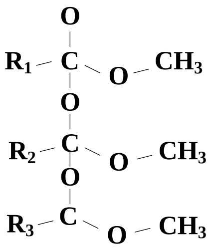


**Figure 2.1** Triglycerides structure contains glycerol and three fatty acid.

Glycerol is a trihydric alcohol which is containing three of –OH hydroxyl groups, it can combine with up to three fatty acids to form monoglycerides, diglycerides and triglycerides. Monoglycerides, diglycerides and triglycerides can be classified as esters which are compounds created by the reaction between acids and alcohols that release water ($H_2O$) as by product. Chemically the oil/fats consist of 90-98% triglycerides and small amount of mono and diglycerides. Triglycerides are esters of three fatty acids and one glycerol. These contain substantial amount of oxygen in their structures. When three fatty acids are identical, the product is simple triglycerides, when they are dissimilar the compounds is mixed triglycerides fatty acids which are fully saturated with hydrogen have one double bond and are called polyunsaturated. The use of fully saturated triglyceride can lead to excessive carbon deposit in diesel engines. The fatty acids are different in relation to the chain length, degree of unsaturation or presence of other chemical functions (Singh & Singh, 2010).

**Table 2.1** Chemical structure of common fatty acids (Singh & Singh, 2010)

| Structure of Monoglyceride | Structure of Diglyceride | Structure of fat and oil | Structure of ester |
|---|---|---|---|
|  |  |  |  |

Petroleum diesel, vegetable oil and ester have different number of carbon and hydrogen atom. Petroleum diesel does not contain oxygen in their carbon chain and it is a good quality fuel. Conversely, vegetable oils oxidation resistance is affected by fatty acid composition. The large size of vegetable oils molecules (typically three of more times larger than hydrocarbon fuel molecules) and the presence of oxygen in the molecules suggest that some fuel properties of vegetable oil would differ noticeably from those of hydrocarbon fuels (Goering *et al.*, 1982).

**Table 2.2** Chemical name of common fatty acids (Singh & Singh, 2010)

| Name of fatty acid | Chemical name of fatty acids | Structure |
|---|---|---|
| Lauric | Dodecanoic | 12 : 0 |
| Myristic | Tetradecanoic | 14 : 0 |
| Palmitic | Hexadecanoic | 16 : 0 |
| Stearic | Octadecanoic | 18 : 0 |
| Oleic cis-9- | Octadecanoic | 18 : 1 |
| Linoleic cis-9, cis-12- | Octadecadienoic | 18 : 2 |
| Linolenic | Cis-9, cis12, cis-15-octadecatrienoic | 18 : 3 |
| Arachidic | Eicosanoic | 20 : 0 |
| Behenic | Docosanoic | 22 : 0 |
| Erucle | ci-13-Docosenoic | 22 : 1 |
| Lignoceric | Tetracosanoic | 24 : 0 |

Composition of fatty acids in different vegetable oils is varied depending on the plant and the growing conditions. Table 2.1 and 2.2 summarized fatty acids compositions of the most common vegetable oils. Triglycerides vegetable oils and fats include not only edible vegetable oils but also inedible vegetable oils and fats such as jatropha curcas and castor oil.

More than 350 oil-bearing plants have been identified as resource for biodiesel production, but only few of them are considered as potential alternative fuel for diesel engines (Atabani, *et al*., 2012).. Availability of vegetable oils is varied from continents to continents, most used vegetable oil in European country is rapeseed, palm oil in Asian countries and soybean in USA.

**Table 2.3** Source of Biodiesel from vegetable oils

| Group | Source of oil |
|---|---|
| Primary Oils | Coconut, Corn, Canola from rapeseed, olive, peanut (groundnut), safflower, sesame, soybean, and sunflower. |
| Nut oils | Almond, Cashew, hazelnut, macadamia, pecan, pistachio, and walnut |
| Other edible oils | Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beechnut, ben, borneo tallow nut, carob pod (algarroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit, meadofoam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi (Caryocar brasiliensis seed), pine nut, poppyseed, prune kernel, quinoa, ramtil (Guizotia abyssinica seed or Niger pea), rice bran, tallow, tea (camellia), thistle (Silybum marianum seed) and wheat germ |
| Inedible oils | Algae, babassu tree, copaiba, honge, Jatropha curcas, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall. |
| Other oils | Castor, radish and tung |

During biodiesel production glycerol is a by-product, formed after the process of transesterification. The glycerol still contain catalyst which remain dangerous for environment and it need proper handling before further process. Glycerol is a valuable by product which has many applications including manufacture of drugs, cosmetics, toothpastes, urethane foam, synthetic resins and ester gums. Tobacco processing and foods also consume large amounts of glycerol.

Glycerol or glycerine a trihydric alcohol is a clear, water white, viscous, sweet-tasting hygroscopic liquid at ordinary room temperature above its melting point. Glycerol occurs naturally in combined form as glycerids in all animal and vegetable fats and oils, it is rarely found in free state in these fats. It is commonly present as a triglyceride combined with fatty acids. Coconut and palm kernel oils containing a high percentage of $C_6$-$C_{14}$ fatty acids, yield larger amounts of glycerol than fats and oils (Knothe *et al.*, 2005).

### 2.2.4.2 Biodiesel from edible vegetable oils

Although biodiesel can be processed from various sources including animal fats, vegetable oils and algae, most of biodiesel research concentration using vegetable oils (Hoekman *et al.*, 2012). Raw materials for biodiesel can be from various vegetable oils, animal fats and short chain alcohols. Generally, edible oil has been used as main materials in biodiesel production, however, it is growing concern about the debate about food or fuels has led to use of non-edible vegetable oils. Widely used edible vegetable oils as biodiesel raw materials are rapeseed oil, sunflower oil, soybean oil and other crops such as palm oil, sun flower, corn oil, palm oil. The other good resource for biodiesel are waste vegetable oils, animal fats like tallow, lard and non-edible oils such as jatropha oil, neem oil, castor oil, etc.

Current situation for biodiesel production raw materials more than 95% is come from edible vegetable oils, such as rapeseed oil 84%, sunflower oil 13%, palm oil 1 %, soybean and others around 2% (Atabani *et al.*, 2012). Those edible oil consider as first generation of biodiesel source, because they some kind of first corps used as biodiesel. Those main vegetable oil have been cultivate all around the world. Each continent has their major crops differ with other continents. In Asia especially Indonesia and Malaysia has become a largest producer of palm oil, while in Europe rapeseed is most popular and in USA soybeans and peanut become main resource as vegetable oils.

Using edible vegetable oils as biodiesel raw materials bringing many advantages, however it has negatives impact on food supply security. There has been long debate on using biofuels as replacement for petro fuel, these debates commonly in topics of liquid biofuels, solid biomass and adverse climate driven impacts. The debate on biodiesel and biofuel in particular, become controversy because it has largely been triggered by politics, ethical/moral consideration and vested interested rather than by science (Calle, 2012).

Biofuels demand has increased recently, due to some benefits of the fuels. Some agriculture product like vegetable oil, sugar cane or maize from corn can be utilized for both food and fuels. Majority biofuels supporters believed there is a weak link between biofuel productions with the increasing price for agricultural prices so higher agricultural prices have a small impact on food prices. On the contrary, biofuel opponent state that biofuels only exist because of subsidies, their existence and production increases agricultural prices for raw ingredients. For developed countries increasing agricultural prices may not impact on food prices, however for developing countries which are many people eat relatively unprocessed food, the food prices are most likely more responsive to dynamically commodity prices (Babcock, 2011).

Using edible oils as feedstock for biofuel competes directly with their use for food, it will risk the price of food as supplies tighten. In some agriculture countries with robust farming system, it will not disturb countries stability in the event of food price fluctuation. Such case can become disastrous in developing countries with weak food supply chain. In example, South Africa parliament has issued regulation that maize is restricted as feedstock for biofuels because the maize is considered as primary food for the nation (Diaz-Chavez *et al.*, 2010).

#### 2.2.4.3 Biodiesel from Non-edible vegetable oils

One of the main barriers for biodiesel commercialization from vegetable oil is the expensive of the biodiesel raw materials. In Biodiesel production cost, the price of raw material is around 70-95% of total production cost (Zhang, *et al.* 2003).

In order to make the price of biodiesel attractive, non-edible vegetable oil is preferred. Compare with edible vegetable oils, animal fats and non-edible vegetable oils are cheaper. Therefore they are found to be attractive as feedstock replacement to lower the cost of biodiesel production which dominated by the cost of raw materials. Sources of non-edible vegetable oil can be found easily in some Asian countries. The examples of non-edible vegetable oil in biodiesel production are Jathropa Curcas, Mahua indica, Karanja oil (Pongamia piñata), tobacco seed (Nicona tabacum) and polanga (Calophyllum inophyllum).

### 2.2.5 Direct use of vegetable oil on diesel engine

Application of vegetable oil as direct fuel replacement for diesel engine has been proposed in the early 1980s. The advantages of vegetable oil as diesel fuel over petro diesel as follows; ready availability, portability, renewability, lower sulphur content, lower aromatic content and biodegradability. Complete combustion of petro diesel requires the presence a stoichiometric amount of oxygen. In general, fully complete combustion is difficult to achieve even in the condition existence of stochiometric oxygen exist due to the petro diesel is not oxygenated (Dermibas, 2008). Whereas, vegetable oils have oxygen in their structural molecule, increasing mixing intensity with oxygen during combustion ans as a result increasing overall combustion efficiency. The structural oxygen content in vegetable oil caused the combustion efficiency and cetane number is higher compare with petro diesel.

**Table 2.4** Some fuel properties of vegetable oil with Diesel fuel (Dermibas, 2008)

| Fuel | Heating value MJ/kg | Density Kg/m$^2$ | Viscosity at 300 K mm$^2$/s | Cetane number |
|---|---|---|---|---|
| D2 fuel | 43.4 | 815 | 4.3 | 47.0 |
| Sunflower oil | 39.5 | 918 | 58.5 | 37.1 |
| Cottonseed | 39.6 | 912 | 50.1 | 48.1 |
| Soybean oil | 39.6 | 914 | 65.4 | 38.0 |
| Corn oil | 37.8 | 915 | 46.3 | 37.6 |
| Opium poppy oil | 38.9 | 921 | 56.1 | - |
| Rapeseed oil | 37.6 | 914 | 39.2 | 37.6 |

Direct use of vegetable oil has some advantages and disadvantages over petrol diesel, summaries as follows:

**Table 2.5** Benefits of straight vegetable oil on diesel engine (Misra & Murthy, 2010)

| Advantages | Disadvantage |
|---|---|
| It is renewable energy. | Straight vegetable oils have higher viscosity compare with petro diesel. |
| It balances carbon dioxide in environment ($CO_2$ neutral) | Varying in seed crops source has varied in oil yield, varied in oil content and long crops growth. |
| oil seeds borne trees also remove carbon from atmosphere, stores it in the woody tissue and assists in the build-up of soil carbon | The distribution of the crops availability is widespread and scattered. |
| The fuel production technology is simple and proven | Most of the production scale is small. |
| Non edible oil crops are common and are not affected by climatic changes | Heating value of vegetable oil is smaller because the existing of chemically oxygen bonding. |
| Cetane number is similar or even higher to that petro diesel. | Poor fuel atomizations caused by higher viscosity interfere with the injection process. |
| Heating values of various vegetable oils are nearly 90% to petro diesel. | Using straight vegetable oil in the diesel engine can caused some problems such as lubricant oil dilution, high carbon deposits, ring sticking, scuffing of the engine liner, and injection nozzle failure. |
| Reducing high risk of fire hazard for fuel storing because higher flash point. | Cloud and pour points are higher than petro diesel, this values may lead some problems during winter. |
| The engine performance and exhaust emission shows better results using small percentage of vegetable oil blends with petro diesel. | Longer storage for vegetable oil, oil viscosity gets further high. |
| Contains with oxygen contents in vegetable oils molecules increasing combustion performance. | Commercial production is feasible if the open land is used. |
| Less sulphur contaminants | |

Even though, the biodiesel has attracted more attention as alternative diesel fuel for diesel engine, the obstacle using the fuel for diesel engine must be addressed. Because of the higher viscosity of vegetable oil compare with common diesel fuel, it is required diesel engine modifications (Kerschbaum & Rinke, 2004). There was a carbon deposit around diesel injector even when blended 50:50 with petro diesel, carbon deposit is higher compare with biodiesel derived from trasesterification process. Vegetable and animal oils need modification before they can be used as fuel in diesel engine. Basically, some methods are available to convert vegetable and animal oil has purpose to reduce the viscosity to a value similar to petro diesel viscosity. Four major methods to reduce vegetable and animal oils have been developed and studied are:

a. Blend with petro diesel

Biodiesel can be used as diesel fuel without further process blended with petro diesel. In 1980 Caterpillar Brazil had showed the successful application using blend biodiesel from sunflower oil with petro diesel during the oil embargo in South Africa. A pre-combustion diesel engine had use a mixture of 10% sunflower oil to maintain total power without any alterations or adjustments to the engine. At that time, it was not possible to substitute 100% vegetable oil to replace petro diesel, but a mixture of 20% sunflower oil and 80% diesel fuel operated successfully. A short investigation using coconut oil blended with petro diesel in 412 cc diesel engine shows that coconut engine operation resulted in better emission, lower NOx and lower smoke emission compared with standard diesel fuel (Machacon *et al.*, 2001). Vegetable oils are not suitable for long term application in direct injection diesel engines, most previous research concluded that vegetable oils dilution in some degree may result in engine problems. Proper fuel atomization can be achieved with a composition of maximum 34% of vegetable oil with diesel fuel. In Asia some countries are producing both edible and non-edible oils vegetable oils. Blending vegetable oils with petrol diesel is interesting option in rural areas where diesel engine operation which is very frequently used for agricultural, irrigation and electricity generation purposes. Linseed oils, mahua oil and rice bran oil have been tested, the engine performance and emission is closed to petro diesel (Agarwal *et al.*, 2008). Another researcher reported using coconut oil blended with ordinary diesel fuel has an optimum coco blend of 30 per cent, lower exhaust emission and can be able to prolong lubrication oil lifespan. Testing on jatropha curcas, a non-edible oil shows blends 30:70 or 20:80 with petrol diesel have slightly higher viscosity than petrol diesel alone but these blends are within ASTM limits viscosity of diesel fuel (Agarwal, 2007).

b. Micro emulsion

   The formation of micro emulsion is one of the four solutions for solving high vegetable viscosity and gumming problems. It is quite a simple method of blending various vegetable oils with conventional fuel to decrease the viscosity of biodiesel.

c. Transesterification or alcoholises; is the reaction of vegetable oils or animal fats with short chain alcohol in order to derivate the triglycerides and fatty acid into esters. These contribute to the low viscosity property of derivative biodiesel. Alcoholises can be carried out without a catalyst. In catalytic transesterification acid base or enzyme catalysis is used to promote the alcoholises derivative reaction. Catalysts include sulphuric acid, hydrochloric acid, sodium hydroxide, sodium methoxide, potassium hydroxide and Candida Antarctica enzyme etc.

## 2.3 Biodiesel production Consideration

The opponents of biofuel argue that a main problem to direct application for large-scale adoption of biodiesel from vegetable oils is the adequate production of the oilseed without any substantial disturbance in food supply and cost. A lot of effort has been proposing and developing sources to produce biofuels by researcher and industries. A large portion of these efforts are focused on conversion of lignocellulosic feedstock to ethanol, some strategies to design new crops to produce biodiesel are highlighted (Durret *et al.,* 2008). In developed countries, the link between agricultural products with biodiesel production is weak mainly confined with diesel production cost, fertilizer and other agro chemicals which all energy intensive. However the link is clearly establish through a demand from the energy sector in developing countries. Moreover, some governments give the subsidies to biodiesel or biofuels, this create new demand on renewable energy led to increase in commodity agricultural prices. In the United States traded food commodities prices increased 130% from January 2002 to June 2008 and 56% from January 2007 to June 2008 according to IMF's index of internationally traded food.

Estimates of the contribution of biofuels production to food price increases are difficult. The estimates can differ widely due to different time periods considered, different prices (export, import, wholesale and retail) considered and different coverage of food products. Furthermore, the analyses depend on the currency in which prices are expressed and whether the price increases are inflation adjusted (real) or not (nominal). Different methodologies will have different results and the other markets have influence to short and long term dynamic price. Despite of discrepancy in methodology and approach, many scholars recognise biofuel production as a major caused of food prices. Increasing demand of biofuels rendered for 70 % of the increase in maize prices and 40% of the increase in soybean prices. A mathematical simulation has been used to estimate increasing maize price from 2006 to 2008 may have been due to the increase in maize used as ethanol feedstock. (Lipsky, 2008; Collins, 2008; Mitchell 2008).

Since the demand on biofuel increase and the concern of food supply security, agriculture land should be expanding to fulfil biofuel demand. Since 2003 The European Union (EU) has to promote the use of biofuels on its members as described in the EU Directive 2003/30/EC. The targets for their country members to achieve 5.75% blending biofuels in their fuels in 2010. Furthermore, in march 2007 EU leaders committed to mandatory 10% biofuels target in each country to be achieved by 2020 (Lucia *et al.,* 2012). According to FAO bioenergy production tripled in the last decade and until 2020, 15% of global cereal and plant oil production as well as 30% of sugarcane production is expected. The increasing bioenergy production followed by increases land grabs and increases food prices. Many publications believe that, biofuels are responsible to the global food spike in 2008. Furthermore, land expanding for biofuel may lead to destruction of the rain forest for oil palm and sugarcane (mainly in Indonesia, Malaysia and Brazil). A direct land use change converts their purpose like forest and grasslands or other natural ecosystem to biofuel production. The expansion of biofuel production into forests and grassland releases carbon stored releases carbon stored in the plants and soil into the atmosphere through decomposition or burning, which will result in a net increase in greenhouse gas emissions, the following effect rendering another problem for the environment with the destruction of major global carbon and biodiversity reservoirs (Tscharntke, 2012).

Inspite of all opposed biofuel application, the use of bioethanol or biodiesel has some advantages over fossil fuel (Calle, 2012; Brown & Brown, 2012):

- There is plenty of land available to produce both food and a reasonable portion of biofuels it is around 5-20% of transport fuels demand, without affecting food supply. The focus of biofuel production depend on the geographical area.

- For countries with volatile and sensitive food security and the do not own their fossil fuel reserves, can allocate a sensible amount of biofuel production without harm their food reserved. That is a good alternative to fossil fuels import exchange by other investment.
- Millions of people living without access to modern energy system. Agriculture in developing countries needs more energy investment and bio energy availability can actually enhance food production.
- Multifunctional agricultural production systems already exist in most countries, are mutually beneficial and can produce both food and non-food products in a sustainable and socially balance manner.
- Marginal or degraded land can utilise or reclaim by certain biofuels crops.
- Good management practices should be applied to achieved harmony in the social, economic and environmental benefits also to avoid potential negative impact of biofuels.
- Bioenergy can boost of new investment in agriculture, increasing modernization, diversification and consequently productivity.
- In general crop yields is low, it can be enhanced by biofuel.
- The case example from Brazil that Biofuels can play a significant role in modernising and diversifying agriculture.

The use of perennial energy corps for the production of lignocellulosic biofuels (lignocellulosic or plant dry matter), such as Miscanthus has been proposed as energy resource. This type of grass crops which is not compete directly for use for food also does not require large amounts of inputs in terms of annual cultivation and fertilizer application or not involve the destruction of native forests with severe negative effects on carbon sequestration and biodiversity (Valentine *et al.*, 2012).

## 2.4 Summary

In this chapter a review of biodiesel utilization has been presented the following summaries highlight the review:

- There are many sources of biodiesel; it is mainly derived from vegetable oil triglycerides.
- Triglycerides of vegetable oils contain long chain of carbon atoms; these make vegetable oils unsuitable use directly in internal combustion engines due to higher viscosity compared with that of common diesel fuels. Therefore further processing of triglyceride rich vegetable oils is required before it can be used as diesel fuel.
- Edible vegetable oils should be utilised with consideration to avoid competition between food and fuel.

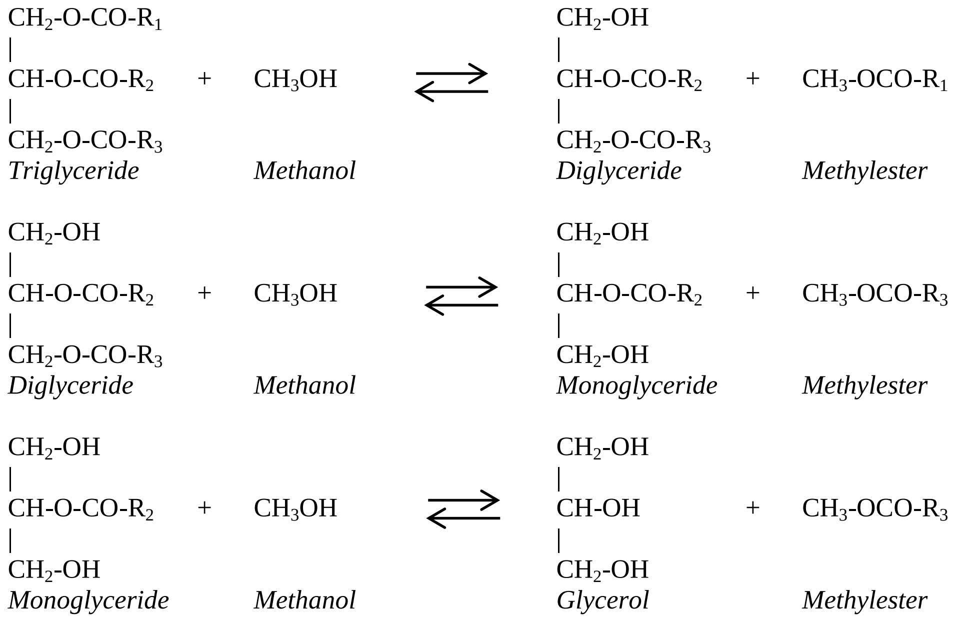
# *Chapter 3*

# *Transesterification, mass transfer and process monitoring*

The feasibility using vegetable oil as diesel fuel has been known in the early times of diesel engine development. Straight vegetable oils have high viscosity which is become problems for diesel engine. In order to make vegetable oil usable as fuel in diesel engine the viscosity must be lowered. The are some methods to reduce vegetable oil viscosity such as transesterification, micro emulsification, pyrolysis and dilution. Transesterification is chemical conversion of the vegetable oil into fatty ester, this conversion has been widely adopted and implemented. Alcoholises is the other name of the transesterification process as in this process vegetable oil is mixed with alcohol (methanol or ethanol) to form methyl ester and glycerol. To achieve higher conversion and shorter reaction time a catalyst is needed in this reaction.

## 3.1 Transesterification reaction

The reaction mechanism for the alkali catalyzed transesterification is formulated in three steps as illustrated in figure 3.1. The first step involves the triglyceride molecule being attacked by an anion from methanol to form a fatty acid methyl ester (FAME) and diglyceride (reaction 1). This is followed by the diglyceride undergoing the same mechanism to form the second FAME and monoglyceride (reaction 2). Finally, the monoglyceride is converted to a third FAME and glycerol in a same manner (reaction 3) (Ellis *et al.*, 2008).



$$\begin{array}{llcll}
CH_2\text{-}O\text{-}CO\text{-}R_1 & & & CH_2\text{-}OH & \\
| & & & | & \\
CH\text{-}O\text{-}CO\text{-}R_2 \quad + & CH_3OH & \rightleftarrows & CH\text{-}O\text{-}CO\text{-}R_2 \quad + & CH_3\text{-}OCO\text{-}R_1 \\
| & & & | & \\
CH_2\text{-}O\text{-}CO\text{-}R_3 & & & CH_2\text{-}O\text{-}CO\text{-}R_3 & \\
\textit{Triglyceride} & \textit{Methanol} & & \textit{Diglyceride} & \textit{Methylester} \\
 & & & & \\
CH_2\text{-}OH & & & CH_2\text{-}OH & \\
| & & & | & \\
CH\text{-}O\text{-}CO\text{-}R_2 \quad + & CH_3OH & \rightleftarrows & CH\text{-}O\text{-}CO\text{-}R_2 \quad + & CH_3\text{-}OCO\text{-}R_3 \\
| & & & | & \\
CH_2\text{-}O\text{-}CO\text{-}R_3 & & & CH_2\text{-}OH & \\
\textit{Diglyceride} & \textit{Methanol} & & \textit{Monoglyceride} & \textit{Methylester} \\
 & & & & \\
CH_2\text{-}OH & & & CH_2\text{-}OH & \\
| & & & | & \\
CH\text{-}O\text{-}CO\text{-}R_2 \quad + & CH_3OH & \rightleftarrows & CH\text{-}OH \quad + & CH_3\text{-}OCO\text{-}R_3 \\
| & & & | & \\
CH_2\text{-}OH & & & CH_2\text{-}OH & \\
\textit{Monoglyceride} & \textit{Methanol} & & \textit{Glycerol} & \textit{Methylester}
\end{array}$$

**Figure 3.1** Chemical reaction of biodiesel transesterification process

The main components of biodiesel are free fatty acid methyl esters which are derivative from free fatty acids. The most common free fatty acids in soybean oil and animal fats are palmitic (16:0), stearic (18:0), linoleic (18:2) and linolenic (18:3). Fatty acids can be recognised by two numbers, the first one is the total number of carbon atoms in the fatty acid chain and the second is the number of double bond in the chain. There is a much lower free fatty acid content in virgin vegetable oils and some rapeseed oil contains less than 0.5%. The highest percentage of oil content in vegetable oil is triglyceride; also termed as triolein. Free fatty acids and water content are two major negative factors in producing good quality biodiesel as they promote formation of soaps and gels when employing a basic catalyst. Manufacturers therefore prefer to use virgin oil such as rapeseed to make biodiesel due to its consistent quality and because only single basic transesterification process is needed and it becomes easier to control the biodiesel quality (Van Gerpen *et al.*, 2004).

Transesterification (also called alcoholises) is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. Figure 3.1 shows trasesterification reaction of triglycerides. A catalyst is usually used to improve the reaction rate and yield, because the reaction is reversible excess alcohol used to shift the equilibrium to the product side. The biodiesel reaction requires a catalyst such as sodium hydroxide to split the oil molecules and an alcohol (methanol or ethanol) to combine with the separated esters. The main by product is glycerine. The process reduces the viscosity of the end product (Demirbas, 2007).

One popular process for producing biodiesel from fats/oils is transesterification of triglyceride by methanol (methanolises) to make methyl esters of straight-chain fatty acids. The transesterification reaction proceeds well in the presence of some homogeneous catalyst such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) and sulphuric acid or a heterogeneous catalyst such as metal oxides or carbonates. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield (Demirbas, 2003).

Transesterification is the general term used to describe the important class of organic reactions where one ester is transformed into another through interchange of the alkoxy moiety (functional group of alkoxy). When the original ester is reacted with an alcohol, the transesterification will be used as a synonym of alcoholises. There is an agreement in most publication in this field, the term of transesterification can be used as synonym of alcoholysis. Transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. To achieve a high yield of the ester, the alcohol has to be used in excess and presence of a catalyst accelerates considerably the achievement of equilibrium. These reactions are often catalyzed by addition of a base or acid. Base can catalyse the reaction by removing proton from the alcohol, thus making it more reactive, while acid can catalyse the reaction by donating a proton to the carbonyl group, thus making it more reactive (Schuchardt *et al.,* 1998).

In alkali catalytic methanol transesterification method, the catalyst (KOH or NaOH) is dissolved into the methanol by vigorous stirring in a small reactor. The oil is transferred into biodiesel reactor and then methanol is pumped into the oil. A product of successful trasesterification reaction is two liquid phases, ester and crude glycerine. Crude glycerine, the heavier liquid, will collect at the bottom after several hours of settling. Phase separation can be observed within 10 minutes and can be complete within 2 hours of settling, however complete settling can take as long as 20 hours. After settling is complete, water is added at the rate of 5.5% by volume of the methyl ester of oil and the stirred for 5 minute, and the glycerin is allowed to settle again. After settling is complete, water is added at the rate of 5.5% by volume of the methyl ester of oil and then stirred for 5 min, and the glycerin is allowed to settle again (Acaroglu *et al.,* 1999).

Several factors, including the type of catalyst (alkaline, acid or enzyme), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of transesterification. In the conventional transesterification of fats and vegetable oil for production, free fatty acids and water always produce negative effects.

The reaction rate of each step of transesterification has examined by Komers (Ellis, *et al.*, 2008) and is described by the following equations (3.1-3.3) and table 3.1 details the equilibrium constant for the 3 equations.

Equations :

$$\mathrm{TG + M} \underset{k4}{\overset{k1}{\rightleftarrows}} \mathrm{DG + FAME} \tag{3.1}$$

$$\mathrm{DG + M} \underset{k5}{\overset{k2}{\rightleftarrows}} \mathrm{MG + FAME} \tag{3.2}$$

$$\mathrm{MG + M} \underset{k6}{\overset{k3}{\rightleftarrows}} \mathrm{G + FAME} \tag{3.3}$$

**Table 3.1** Rate constants for each transesterification step (Ellis, *et al.*, 2008)

| | |
|---|---|
| Forward | |
| $k_1$ (dm$^3$mol$^{-1}$min$^{-1}$) | 5.005 |
| $k_2$ (dm$^3$mol$^{-1}$min$^{-1}$) | 4.929 |
| $k_3$ (dm$^3$mol$^{-1}$min$^{-1}$) | 29.67 |
| Reverse | |
| $k_4$ (dm$^3$mol$^{-1}$min$^{-1}$) | 3.545 |
| $k_5$ (dm$^3$mol$^{-1}$min$^{-1}$) | 2.987 |
| $k_6$ (dm$^3$mol$^{-1}$min$^{-1}$) | 0.7932 |

The kinetic of transesterification, rate constants for each transesterification step can be used to simulate the reaction. Using a spreadsheet, the result are shown in figure 3.2. The concentration profile of all components reaches a plateau at equilibrium in certain times, the curves indicate the time series of the composistion in the reaction mixture,

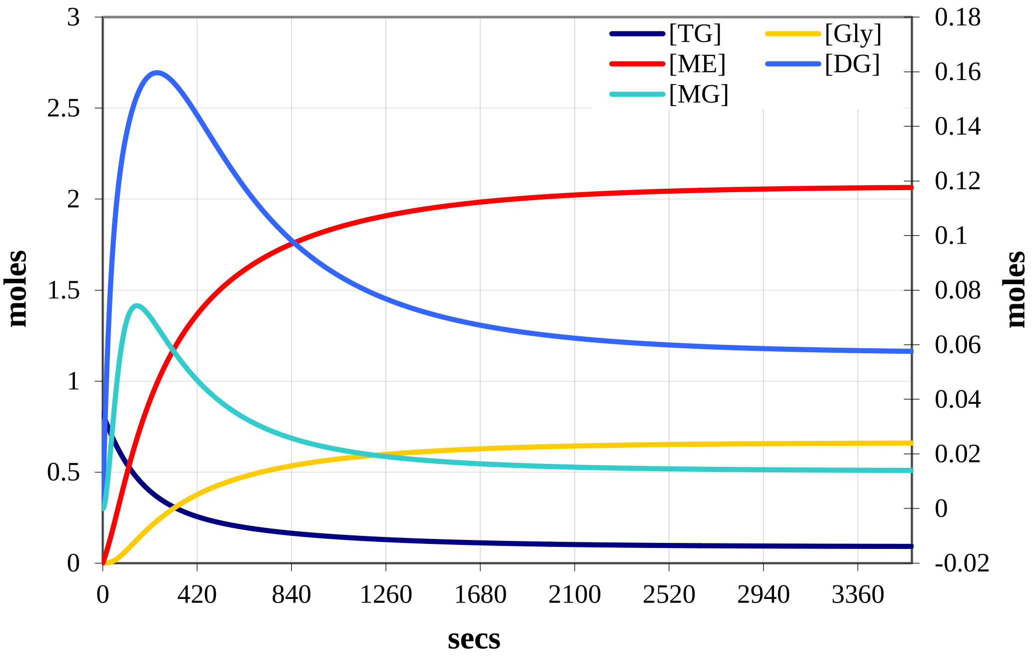


**Figure 3.2** Simulated concentration profile of glycerol (G), tri-glyceride (TG), di-glyceride (DG), mono-glyceride (MG) and fatty acid methyl ester (FAME) during transesterification (MG and DG using right scale).

The figure 3.2 shows individual reactants during transesterification, it can be seen triglycerides decreased during the reaction, the branch of triglycerides break up into smaller diglycerides and monoglycerides while Glycerol build up until all reactants reaches a plateau steady state. During the reaction Methyl ester raise up until it reach stability.

## 3.2 Catalytic transesterification process

A catalyst is commonly used on a chemical reaction to increase the rate of the process, and it is not consumed by the reaction. A catalytic chemical reaction has a lower activation energy compared to a reaction without catalyst, generating a faster reaction rate at the same operating temperature. The transesterification reaction can be enhance by acids (Furuta *et al.*, 2004), alkali (Zhang, *et al.*, 2003) and enzymes (Noureddini *et al.*, 2005).

Catalysed trasesterification biodiesel reaction may be employ to gain highest methyl ester conversion by acids catalyst (Furuta *et al*., 2004), alkali (Zhang *et al*., 2003) or enzymes (Du *et al.*,2004; Noureddini *et al.*, 2005). Many researches has been done using different oils as raw materials, different alcohols (methanol, ethanol, butanol). Different catalyst including homogenous catalyst such as sodium hydroxide, potassium hydroxide, sulphuric acid and supercritical fluids and heterogeneous ones such as lipases (Marchetti *et al*, 2007). On transesterification process homogenous and heterogeneous catalysts are often used (heterogeneous catalyst differs from homogeneous catalyst has different phase with reactants). Homogeneous catalysts offer simplicity and are capable of generating a high yield of biodiesel in short reaction and moderate reaction conditions (temperature and pressure) but they have some drawbacks. Homogenous catalyst has shortfalls including high cost for corrosion resistant equipment, unwanted side reactions, a significant amount of waste water (leading to waste water treatment), separate additional equipment for separation and purification process and difficulties and catalyst recovery (Yan *et al.*,2010).

Homogeneous catalyst may also restricted percentage number of free fatty acid and water in the vegetable oils. When the raw materials contain high percentage of free fatty acid or water, alkali catalyst will reacts with free fatty acid to form soaps and the water can hydrolyse the triglycerides into diglycerids and form more free fatty acids (Leung *et al*., 2010).

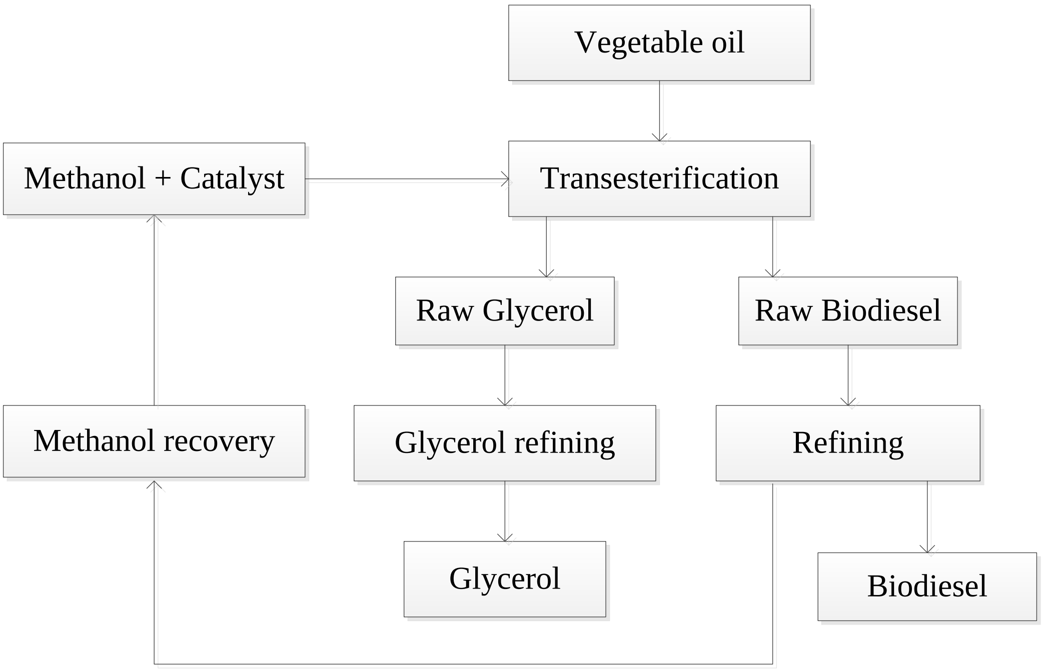


**Figure 3.3** Large scale biodiesel productions via transesterification

As heterogeneous catalysts are solid, the process for biodiesel separation is made relatively easy by filtration, and this reduces the washing requirement. Moreover this solid heterogenous catalyst is particularly useful for those feedstock with high free fatty acid content (Kulkarni *et. Al.*, 2006).

Figure 3.3 shows general process for large scale biodiesel production, it can be seen that the product transesterification is raw biodiesel. Raw biodiesel need to refine before it can use as engine fuel due to it contains some catalyst, unreacted methanol and some water. Raw biodiesel can be refining by washing with water. This thesis will focus only on monitoring of transesterification process in a batch reaction process.

Commonly catalyst on chemical reaction may be divided in to three categories, alkalis, acids and enzymes. Alkali and acid catalyst is widely used commercially in biodiesel production, this kind of catalyst includes homogeneous and heterogeneous catalyst. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) as alkali homogeneous catalyst and alkali catalysed transesterification are the most preferred in biodiesel production due to homogeneous catalyst cheaper than heterogeneous catalyst.

For acid catalysed trasesterification method sulphuric acid, hydrochloric acid and sulfonic acid are usually preferred as acid catalysts. Both Methanol and catalyst is dissolved in small reactor by vigorous stirring in a small reactor. When the oil is ready in biodiesel reactor the catalyst-methanol mixture is transferred into the oil.

### 3.1.1 Base catalytic biodiesel transesterfication

In the biodiesel transesterification process base catalysts are popular and widely used in early development of biodiesel transesterification process due to low cost and simple operation. The use of base catalyst is generally divided into two types heterogeneous base catalyst and homogenous base catalyst. Figure 3.4 shows the homogenous base catalytic transesterfication.

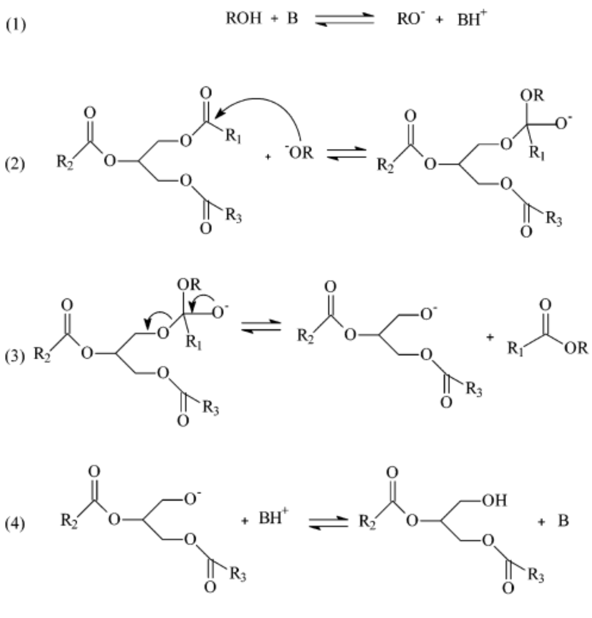


**Figure 3.4** Homogenous base catalysts (Lotero, *et al.*, 2005)

#### 3.1.1.1 Homogenous base catalyst

A reaction of biodiesel transesterification process that using a base catalyst in the same phase or form with vegetable oils. There are many types of homogenous base catalyst are used for vegetable oils transesterification. Most popular for this type of catalyst are potassium methoxide, potassium hydroxide, sodium methoxide and sodium hydroxide.

Potassium hydroxide *(KOH)* is base catalyst which is commonly used in transesterification process. A comparison of performance catalyst using waste frying oil as biodiesel as feedstock from waste oil between KOH and NaOH has been reported that performance KOH was better than that of NaOH (Encinar *et al.*, 2005). Furthermore Encinar *et al.*, mention that separation of biodiesel and glycerol was easier when KOH was used as catalyst. Transesterification of neat sunflower oil and waste frying oil can be optimized by use 1% KOH and methanol to oil ratio of 6 and 65$^{o}$ C reaction temperature, it gained 96% biodiesel (Refaat *et al.,* 2008).

Sodium hydroxide (NaOH) is a low cost catalyst for transesterifiation process and causes less emulsification compare with potassium hydroxide. The use of different vegetable oil have been investigated. High conversion rate of cottonseed oil to fatty acid methyl ester (90%) can be achieved by 3:1 methanol oil ratio but for economically conversion 6:1 ratio is most favourable. The optimal conversion temperature according to Hoda is 50-60$^{o}$C for favourable conversion. At higher temperatures (more than 60$^{o}$ C) some difficulties is observed in separation and washing step as at a higher temperature a small amount of formed gelation is occurs (Hoda, 2010). Other researcher reported that the optimal concentration of NaOH catalyst with Canola oil is 1% wt. Excess catalyst will not enhance the conversion but can significantly decrease the yield of biodiesel product. Another study on karanja oil transesterfication shows decreasing yield when sodium hydroxide was replaced with potassium hydroxide as catalyst, the biodiesel conversion was reduced from 85% to 82.5%. The separation of potassium hydroxide from the karanja methyl ester is easier than sodium hydroxide. During the washing of methyl ester with water, $Na^+$ and $K^+$ ions form sodium and potassium soap. Sodium soap sinks at the bottom of separating funnel and the product had to be decanted from the top, whereas potassium soaps are lighter and do not sink to the bottom but remain suspended (Sharma, 2008).

#### 3.1.1.2 Heterogenous base catalyst

Heterogeneous catalysts has some advantage over homogenous catalysts such as the catalyst can be recovered and reused and are potentially cheaper in continuous fix bed operation (Helwani, 2009). Homogenous catalyst like sodium hydroxide and potassium hydroxide is widely used because they are very effective catalyst. However the use of these catalysts have some drawbacks in methyl ester purification due to thorough cleaning is required therefore excessive water should be needed.

There are some common heterogeneous base catalyst such as alkaline earth metal oxides, zeolite, $KNO_3$, loaded on $Al_2O_3$, $KNO_3$/ $Al_2O_3$, BaO, SrO, CaO, MgO etc (Shadid & Jamal, 2011). The experimental result reported by Liu shows that using SrO as transesterification catalyst to convert soybean oil into biodiesel yield methyl ester more than 95% within 30 min. furthermore for best economically operation process 12:1 molar ratio of methanol to oil, 3% SrO catalyst by weight and 65°C. Liu has showed that SrO demonstrated good activity catalytic activities and stability due to strong basicity, insoluble in methanol and can reusable until 10 times without significant degradation in catalytic activity (Liu *et al.,* 2007). However the price of the SrO catalyst is more expensive than homogenous base catalyst.

### 3.1.2 Acid catalytic biodiesel transesterfication

The base catalyst have some benefit as catalyst in biodiesel transesterification process such as very efficient and lower costs which lead to efficient biodiesel process operation. However, when the raw materials contains a small quantity of water, high free fatty acid and high value in acid number the base catalyst do not exhibit a good results (a measure for the content of free fatty acids in the vegetable oil, commonly exist in waste vegetable oil). Base catalyst can be very sensitive to water contents which cause soap formation and the separation of methyl ester and glycerol becomes difficult.

Vegetable oil from non-edible seeds commonly have higher acid number compare with edible oils, in this case the use of acid catalyst is favourable. However, the use of acid catalyst has some disadvantage such as higher amount of alcohol, higher reaction temperature, pressure and slower reaction rate.

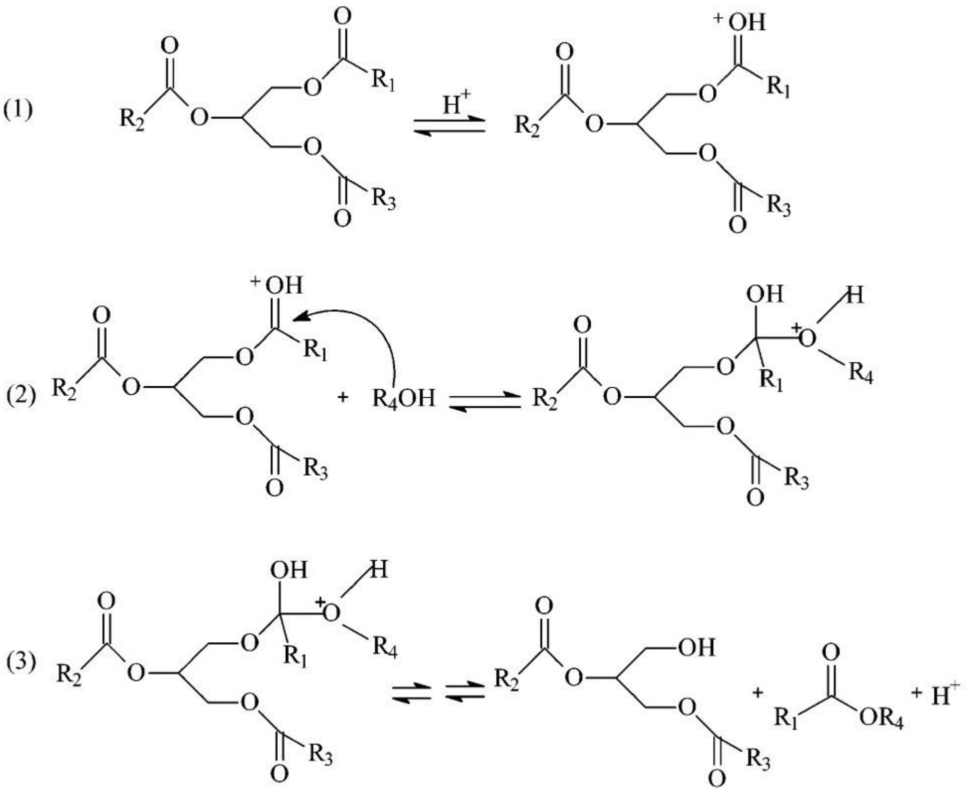


**Figure 3.5** Homogenous acid catalyst (Lotero, *et al.*, 2005).

Furthermore, acid catalyst required reactor corrosion protection or good material reactor, also it is environment hazard become an issue (Shahid & Jamal, 2011).

Figure 3.5 shows the sequence reaction mechanism for homogenous acid catalyst in triglyceride transesterification. The first reaction is protonation (addition of a proton to an atom, molecule, or ion) to the carbonyl group by acid catalyst. Second stage is nucleophilic ( a molecule or group, having a tendency to donate electrons or react at electron-poor sites such as protons) of the alcohol forming tetrahedral intermediate (a reaction intermediate in which the bond arrangement around an initially double-bonded carbon atom has been transformed from trigonal to tetrahedral). The final stage is proton migration and breakdown of the intermediate (Lotero, *et al.*, 2005).

### 3.1.2.1 Homogenous acid catalyst

Miao studied the use of homogenous acid catalyst trifluoroacetic acid with vegetable oil from soybean, the result showed that the soybean oil can be converted directly in one step process without extreme temperature and pressure conditions. Suggested process parameters were 2 M catalyst concentration with 20:1 M ratio of methanol to oil at temperature of 120°C. the reaction took over 5 hours and methyl ester and the yield was 98.4% (Miao, *et al.*, 2009).

An investigation the use of Linseed oil with acid catalyst and subsequent engine tests shows good results. Linseed crude oil is low cost inedible vegetable oil, making it a suitable candidate for biodiesel material. Under certain conditions like acid number and moisture content the base catalyst is not suitable for converting this vegetable oil into biodiesel, for those reasons the acid catalyst sulphuric acid ($H_2SO_4$) is used with a methanol to oil ratio 20:1 and 5% of sulphuric acid by weight, the reaction temperature was 62-65°C and reaction time 5 hours. The experiment results showed that Linseed methyl ester properties is closer to petro diesel fuel, also the emissions of diesel engines using Linseed methyl ester as fuel were lower in HC, CO and $CO_2$ contents except NOx which is slightly higher (Puhan, *et al.,* 2009).

### 3.1.2.2 Heterogeneous acid catalyst

Similar to heterogeneous base catalyst, heterogeneous acid catalyst offer some advantages such as it is not dissolve in the alcohol and raw materials, they are favourable to separate by filtration and can be reused for another process. Research conducted by Mittelbach involved a rapeseed oil transesterification using solid acid catalyst. They used a series of layered aluminosilicates with sulphuric acid with an alcohol to oil molar ratio 30:1 and 5% wt catalyst. The catalyst showed high activity depend on reaction condition (Mittelbach, *et al.*, 1995).

### 3.1.3 Enzyme Catalyst

The other route to manufacture biodiesel from vegetable oils and animal fats transesterification is using enzyme catalyst. The use of an enzyme catalyst is an attractive choice because the enzyme has advantages over base and acid catalyst, soap formation will not occur, giving fewer problems with purification, washing and neutralization. Enzyme catalysts also have less energy requirements since enzymatic catalyst can be operated at lower temperature conditions (35 – 45$^{o}$C) and the enzyme catalyst is recyclable. More than 90% triglyceride conversion can be achieved with high free fatty acid contents which is a serious problem in common transesterification process. Despite of superiority of enzyme catalyst over conventional transesterification processes the main barrier to commercial application are higher costs and longer reaction times (Shahid & Jamal, 2011).

## 3.2 Non Catalytic Transesterification

The conversion of vegetable oil into methylester in catalytic transesterification is slow due to methanol and triglycerides is immiscible and mass transfer resistance exists between the two fluids. The non-catalytic method is designed to overcome the problem of low solubility. One promising method is to use a solvent which is soluble between methanol and oil. The experimental results indicate a complete reaction can be achieved from 5 to 10 minutes without traces of catalyst residue. Tetrahydrofuran is one co-solvent which has low boiling point (near methanol boiling point) and need only low temperature reaction ($30^{o}C$). The BIOX is a patented production process, convert up triglycerids and free fatty acid into biodiesel in less 90 minutes at atmospheric pressure and ambient temperature. The BIOX can convert vegetable oil into biodiesel methylester with more than 99% conversion rate, even the feedstock contains up to 10% water. 99.9 % of cosolvent can be recovered from the process and the excess methanol can be recycled and reused (Mandolesi, *et al.*, 2013).

Another method for non-catalytic transesterification is supercritical methanol, the process takes place in extreme condition with a high pressure and high temperature operation. Supercritical methanol has some benefits (Balat & Balat, 2008; Vera *et al.*, 2005);

- Tolerates a higher percentages of water.
- With high ratio methanol to oil, the conversion can be done in few minutes.
- Catalyst removal is not necessary.
- The single phase can eliminate mass transfer resistant.
- Glycerides and free fatty acids react with equivalent rate.

Supercritical methanol has some drawbacks such as:

- The process take place in high pressure (25-40 MPa).
- The high temperatures operation 350 – $400^{o}C$
- High methanol oil ratios about 42:1 is potential losses because of ureacted methanol evaporation.
- High pressure and high temperature operation lead to inefficient operation process caused economically not feasible.

## 3.3 Parameters that effect biodiesel transesterification

The main operational parameters of biodiesel trasesterification that influence yield of methyl ester. Feedstock, process temperature, reaction time, alcohol quantity and catalyst are the factors of biodiesel process that should be considered for optimum process.

### 3.3.1 Biodiesel feedstock treatment

Feedstock for biodiesel can come from various materials of vegetable oils waste frying oils (WFO) and animal fats. Vegetable oil can come from different crops with different properties. Waste frying oils often have a higher level contaminants which can affect the transesterification process. Common contaminants in biodiesel feedstock are free fatty acid (FFA) and water content. Both fatty acid and water content will significantly reduce the conversion of vegetable oil into biodiesel. The content of FFA in vegetable oil or WFO can determine the feasibility of economic biodiesel transesterification process. The presence of FFA can detect by the number of acid value, there is direct correlation between acid number and FFA percentage. Higher acid value indicate that biodiesel raw materials contains a higher proportion of FFA. Insufficient catalyst quantity and excess contaminants (water and FFA) lead to soap formation (Dorado *et al., 2002*).

To gain higher conversion of vegetable oil with high FFA and water content pre-step transesterification process may be required to reduce water and FFA content to the desired percentage. Suggested FFA contaminants in vegetable oils is less than 2% (Naik *et al.*, 2008), furthermore, small amount of water about

0.1% content on vegetable oil could reduce triglycerides conversion of biodiesel (Canakci & Van Gerpen, 2001).

In order to reduce FFA contaminants, biodiesel feedstock should pre-treatment by neutralizing the acid value. The experiments undertaken by Naik successfully reduced the acid number of Karanja oil containing 20% of FFA with acid value 41.9 to 3.9 KOH/g in in one hour using $H_2SO_4$ acid. And the water as simply removed the water content by heating the oil into 65$^o$C (Naik *et al*, 2008).

### 3.3.2 Process temperature

Temperature is one key factor in successful biodiesel transesterification reaction. At higher temperature vegetable oils are less viscous than in lower temperature. Higher temperature reactions have higher activation energy which speed up the transesterification reactions giving increased reaction rate and shorter reaction time. However the operational temperature for catalytic transesterification is below the boiling point of the solvent. If the reaction temperature is higher than the alcohol boiling point, the alcohols will evaporate and the rate of oil conversion of methyl ester will be low. Higher reaction temperature accelerates the saponification (process that produces soap) (Eevera *et al.*, 2009).

### 3.3.3 Reaction time

The conversion rate of fatty acid esters increases with reaction time. Slow reaction detected at the beginning of the conversion process due to methanol and vegetable is immiscible. In the next few minutes the reaction proceeds faster, after around 60 minutes the reaction reaches steady state (Alamu *et al.*, 2007). An experiment was conducted by Freedman using four types of vegetable oils, peanut, cotton seed, sunflower and soybean with molar ratio oil methanol to oil 6:1, catalyst 0.5% sodium methoxide and 60°C reaction temperature. Most of the triglyceride conversion observed to have occurred in the first one minute of transesterification reaction about (80% for soybean and sunflower oil). When the process extended until one hour the methyl ester yield reached 93-98%, the other oils have similar results (Eevara *et al.,* 2008). It is clear that most of the conversion processes take place in the earlier stages of the process, after successful mixing of the reactance and that extending time will provides process completeness.

### 3.3.4 Alcohol quantity and variety for biodiesel conversion

Theoretical calculations stated that complete reaction of biodiesel transesterification requires 3 mole of alcohol for 1 mole of triglyceride and generates 1 mole of glycerol and 3 mole of fatty acid ester. Molar ratio of alcohol to triglyceride have been well known as one of main factors in achieving a good conversion yield. Methanolysis is a reversible reaction therefore excess methanol is required to shift the equilibrium towards the product side. Generally practical biodiesel conversion uses the optimal ratio of 6:1 alcohol to vegetable oil molar ratio (Leung *et al.,* 2010; Demirbas, 2008). Furthermore, excess alcohol beyond optimal ratio will not increase the yield but will increase the cost of alcohol recovery.

The solvent type for biodiesel conversion can be a variety of alcohols including methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are the most widely used alcohols for transesterification. Depending on geographic location, methanol is used frequently because of availability, good chemical reaction with vegetable oils, good physical properties and a lower cost compare with the other solvents (Ma & Hanna, 1999). The drawback of using methanol as solvent is the risk of unexpected combustion due to its relatively low boiling point. Moreover methanol vapours difficult to detect because they are colourless and odourless. In addition, adding catalyst into methanol to make methoxide makes an even more hazardous solution that should be handled with care.

### 3.3.5 Catalyst

Among all process operational conversion, catalyst amount and methanol/oil ratio exhibit higher influences on the result biodiesel conversion compare with temperature and reaction time in the reaction stage (Leung, 2006). The amount of catalyst use in transesterification is critical for good yield of product. Incomplete conversion of vegetable oil in to methyl ester may be caused by insufficient catalyst. As the catalyst amount increases the methyl ester yield increases. The optimal value for catalyst concentration for biodiesel conversion is 1.5% by weight, beyond the optimal value the biodiesel conversion is less effective and gives less yield in methylester conversion. The yield reduction due to excessive catalyst react with triglycerides to form soap formation (Eevera *et al.*, 2009).

### 3.3.6 Mixing intensity

Methoxide (methanol solution catalyst) is not miscible with both vegetable oils and animal fats, therefore a mixing speed is one of the key factors to optimise biodiesel conversion. Because of mass transfer resistant exists between two fluids and the reaction is not effective in initial stages of mixing. Once the vegetable oil and methoxide are totally mixed with each other an increase stirring speed is unnecessary. The effect of stirring speed has observed using 3 different speeds 180, 360 and 600 rpm. 180 rpm stirring speed has shown lower result in methylester yield compare 360 and 600 rpm. While 360 and 600 showed insignificant differences in conversion yield. It has been observed the reaction rate for three stirring speed have the  same profile (Meher *et al.*, 2006).

Rigorous mixing is clearly needed to achieve the completeness of the transesterification process, to minimalize the effect of mass transfer resistant. Wave propagation can be replaced a physical mechanical agitation, ultrasonic and microwaves has been research to use on transesterification.

Ultrasonic stirring is found more efficient than conventional mechanical agitation in biodiesel transesterification. The efficiency of ultrasonic agitation is better compare the mechanical agitation it accounted the reaction rate constants that are higher than mechanical agitation.

The use of microwaves on biodiesel process is more beneficial because the method provide instantaneous heating and is possible for continuous operation. An experiment using microwave heating for a continuous flows biodiesel plant have been successful to convert 98% triglyceride in to methyl ester (Azcan & Danisman, 2008).

Microwave propagation method is more efficient than common heating in transesterification process. However, the largest drawbacks to use microwave heating for promoted reaction is the efficiency of magnetron which has efficiency 60% - 67 % (Barnard *et al.,* 2007).

## 3.4 Mass Transfer resistant

Mass transfer can be described as a components (compound, fraction) movement from one phase to another phase due to concentration differences between phases such as concentration gradient. The term mass transfer encompasses diffusion and convection currents set up due to flows, laminar or turbulent, temperature differences and concentration differences, which are complementary to one another, across phase boundaries. Mass transfer commonly occurred in the most chemical engineering problems and become very important factors for following reasons (Cussler, 2009):

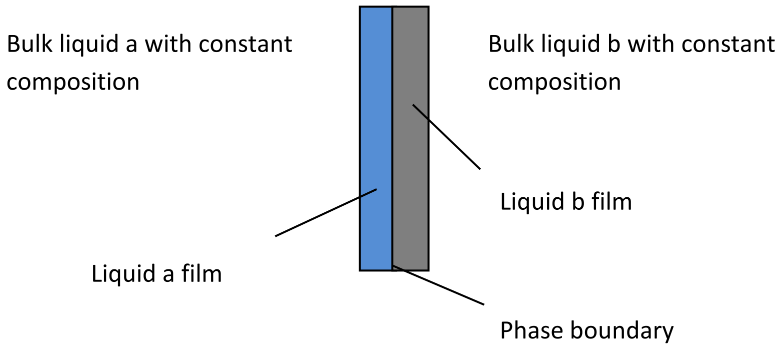
- Design and operation of chemical process equipment involves preparation of reactants, carrying out chemical reactions and separation of the resultant products.
- Mass transfer has a mixture of components tendency to travel high concentration region to lower concentration region.

Mass transfer phenomena may explain by film theory with following assumption and constraint (Cussler, 2009):

- The phase in bulk, all composition variations under turbulence condition is negligible, and the compositions considered uniform.
- The phase boundaries are conceived of as a sharp transition between the two phases.
- The phase boundaries are considered rigid that causes damping of the turbulent eddies in the bulk near the interface.
- Film theory assumes presence of an imaginary stagnant laminar fluid film for each phase next to the phase boundary and the resistances for mass

transfer are within the imaginary films and concentrations remain constants within the bulk phases.

Figure 3.6 illustrate the two film theory on liquid to liquid transfer. In the biodiesel process two immiscible layers occur with a distinct interface forming between oil and methoxide. The chemical reaction is initially very slow due to a small contact area at the fluid interface. In order to increase the area of contact the two immiscible fluids can be mixed by mechanical agitation and the supply of energy via heat transfer and/or microwave excitation.



(simplified)

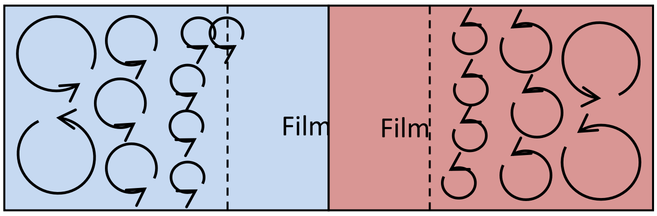


**Figure 3.6** Illustration of two film theory on liquid to liquid mass transfer

Transesterification reaction is categorized as a liquid-liquid systems mass transfer with chemical reaction. In modelling of the process it is advantage to incorporate in equation for mass transfer with the equation describing the chemical reaction. The coupling of both two factors describe overall mass transfer rates. Once the chemical reactions start it will further enhance the mass transfer rate because diffusing solute is consumed in the region of the interface producing a steeper concentration gradient (Raju, 2011).

The general equation for mass transfer plus chemical reaction is an unsteady state mass transport equation that incorporates not only diffusion but also convective mass transport and chemical reaction contributions.

### 3.4.1 Mass transfer control region and chemical control region

Some factors have influence on the biodiesel conversion rate and directly affected the yield of methyl ester. In order to improve and enhance the biodiesel conversion the dynamics of the transesterification process should be understood. Biodiesel conversion of vegetable oil via transesterification consists of three consecutive and reversible chemical reactions. Vegetable oils contains a large branch of triglycerides which are to be converted into smaller straight chains of methyl ester in the presence of a catalyst. Within the process diglycerides and monoglycerides are formed before the formation of the final products methylesters and glycerol.

Vegetable oil and alcohols are immiscible inconsequence the process need agitation to promote chemical reaction otherwise the reaction will take place for long time. The biodiesel conversion in a batch reaction may be considered as homogenous reaction with no mass transfer indication (Encinar, *et al.,* 2002; Marjanovic *et al.,* 2010). However, mass transfer maybe not visible in the process with high energy intensity.

Well known proposed theory on the transesterification process has been introduced with the reaction mechanism consisting of an initial mass transfer-controlled region followed by kinetically controlled region. The initial mass transfer region is containing two immiscible fluids, non-polar vegetable oil and a polar fluid alcohol with catalyst. Figure 3.7 shows general reaction rate of transesterifiation process with $40^oC$, 6:1 alcohol to triglycerides with 200 rpm stirring conducted by several researchers in this field such as Darnoko, Noureddini, Freedman, Boocock, Olivera and Marjanovic. Stoichiometry reaction of biodiesel transesterification required three moles of methanol for each mole of oil. Because of transesterification is reversible reaction excess methanol is needed to shift the equilibrium condition towards the direction ester formation.

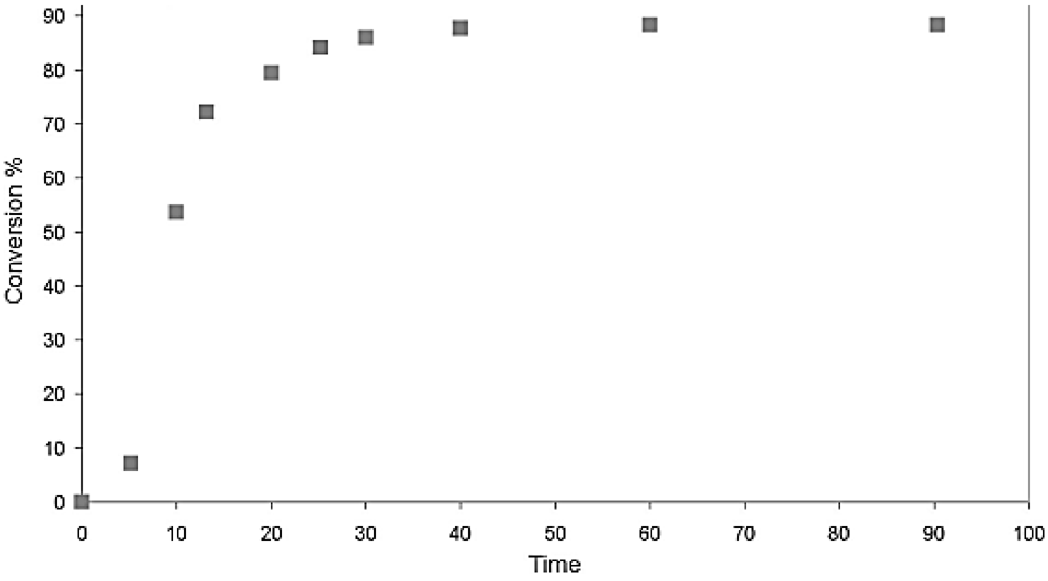


**Figure 3.7** The typical conversion from triglycerides into methylester at $40^oC$, 6:1 Ratio methanol to vegetable oils in batch reactor using mechanical stirrer.

Since mass transfer reduction of resistance is one of the important keys to enhance the transesterification process there is an increased interest in new technologies such as the use of heterogeneous catalyst to shorten mass transfer controlled region (Leung *et al.*, 2010). Influence of mass transfer clearly visible in transesterification employing Lewis catalyst (a metal-based Lewis acid acts as an electron pair acceptor to increase the reactivity of a substrate), although Lewis acid catalyst are active in the both esterification and transesterification but the reaction is very slow (Hou *et al*, 2007). Transesterification of vegetable oils with methanol is a two phase reaction system and the reaction occurs in the methanol phase. The immiscibility of methanol and vegetable oil leads to mass transfer resistance (Guan, *et al.*, 2009). The common and conventional base catalyst transesterification owned the characteristic of slow reaction rates at the beginning of the reaction and final reaction stages limited by mass transfer between polar methanol phase/glycerol phase and non-polar oil phase (Zhang, *et al*, 2009). Mixing was identified as a crucial factor in transesterfication process to reduce the mass transfer resistant with mixing leading to a large increase in the area of the interface between vegetable oil and methoxide. Without mixing the reaction occurred only at the limited interface of the two layers and was considered too slow to be feasible (Ma, *et al*, 1999). The process model developed by Liu indicates that the trasesterification reaction is controlled by both mass transfer period and reaction period, the mass transfer period having a greater effect than the reaction resistance. Therefore the reaction rate could be increased by increasing the external surface area of the catalyst, when the surface area is big enough the reactions dominate further process (Liu, *et al.*, 2010).

Experiments to study the mass transfer resistance can be conducted at ambient temperature, indicated by the presence of a triglyceride induction period during acid catalysed transesterification reaction (Ataya *et al.*, 2008). Stamenkovic conducted biodiesel conversion experiments at temperature 30$^{o}$C to confirm the existence of mass transfer. The sigmoidal kinetics as illustrated in figure 3.7 of the process is explained by the mass transfer controlled region in the initial heterogeneous regime, followed by the chemical reaction controlled region in the pseudo homogenous regime. The mass transfer rate is related to the drop size of the dispersed methanol phase, which is reduces rapidly with the progress of the methanolysis reaction. It is observed that the droplet size has main influence in reaction result and the reaction is mass transfer limited (Stamenković, *et al.,* 2008).

Variation in different mixing methods has influence the mass transfer on the biodiesel conversion. Lifka & Ondrusschka conducted a series of experiment with different mixing methods using magnetic stirrer, ultrasound and ultra turrax, their result have different varied conversion for the transesterification of rape oil with methanol in both acidic and basic systems (Lifka & Ondruschka, 2004). Bambase state that the mixing it the most critical requirement that must initially be met in order to achieve any practical conversion of the oil into methyl ester. When the mass transfer resistance can be minimised, temperature becomes the most influential factor affecting the rate of methanolysis reaction. Lower temperatures slow done the rate of conversion and extending the reaction time required to achieve maximum methyl ester yield (Bambase, *et al.,* 2007).

Optimization of the mixing method and the evaluation of mass transfer resistance are very important to gain maximum conversion in biodiesel production and high efficiency transesterification process. The significant contribution in mass transfer research by some researcher leading to idea to save more agitation energy. Most of biodiesel process is prolonged over an hour with intensive agitation speed. By agitation optimization it is possible to save mixing energy by reducing the rotational speed or stopping the agitation after a short mixing time (Frascari, *et al*, 2009).

The sigmoid shape of the biodiesel conversion curves has been observed during the process. This is shows a slow reaction rate or delay at the beginning of the process followed by rapid increase and then a smaller rate of the reaction as the reaction reach completion and reaches equilibrium at last. This behaviour exhibited by the chemical reaction is typical for auto catalytic reactions or reactions with changing mechanisms. However transesterification reaction for triglycerids is not identified as an autocatalytic reaction. The second hypotheses suggested by the sigmoid graph is that of a mass transfer controlled region with slow progress then a kinetically controlled region with fast conversion rate and finally equilibrium region marked by a slow reaction (Noureddini & Zhou, 1997). In transesterification the reactants is a biphasic liquid, where poor miscibility and limitations results in a slow rate reaction. During the reaction methylester are formed and they act as a mutual solvent for the reactants and the phase changing from biphasic to single phase, this promotes a rapid chemical reaction. However, Stamenković argued that methyl ester (after it is formed) is still not immiscible with methanol or glycerol. He has observed in his research the methanol-glycerol-methyl ester system is heterogeneous and separates into the two conjugated three component solutions, one is rich in methyl ester containing glycerol and less than 2% methanol and the other is rich glycerol and methanol containing less than 3 % methyl ester whereas non reacted methanol will be distributed predominantly in the methanol/glycerol phase therefore methyl ester as mutual solvent is questioned (Stamenković*, et al.*, 2007).

Stamenković *et al.*, conducted an experiment during which they measured drop size distribution during the transesterification. They had a hypothesis that in the kinetically controlled region other products such as monoglycerides, diglycerides and soaps act as emulsifying agents inhibiting the droplet coalescence and favouring formation of a stable emulsion of small drops. Furthermore the process of drop breakup will be favoured by reduction of viscosity of the reaction mixture. The experiments confirm variations of drop size distributions which become narrower and shift to smaller sizes with the progress of the methanolysis reaction. The volume of methanol would decrease with time due to methanol consumed by the reaction except glycerol. This is create the specific interfacial (called self enhancement) area that promotes the rate of mass transfer and total mass interface, causing an increase of the mass transfer rate in the fast region (Stamenković, *et al.,* 2007). This also explained why the agitation was no longer needed once the two immiscible phases were mixed and the reaction was started (Ma, *et al.*,1999; Stamenković *et al.,* 2008). Frascari *et al.*, conducted an experiment validation to verify the possibilities of saving mixing energy and to fasten the decantation process by reducing the rotational speed of stopping the agitation after a short mixing time. They used sun flower oil with Rushton turbine (a flat disk with vertical flat blades vertically mounted), 60$^{o}$C reaction temperature, methanol to oil ratio is 6:1 and KOH catalyst. They achieved 99% oil conversion with 1-2 minute mixing period followed by a complete halt and this led to reduced energy mixing. The energy consumption was 3.6 J/kg biodiesel, and it is 200 times lower than the typical common un-optimized liquid to liquid biodiesel transesterifacation process (Frascari *et al, 2009*).

The last control region is that of approaching equilibrium. According to Tsuji, the slow conversion rate in the final stage of transesterification is not caused by equilibrium limitation but it is most likely due to catalyst depletion by the side reactions contributing to the low conversion of triglycerides. As long as the catalyst remained in the system excess methanol may not be necessary to drive the process toward complete conversion. For homogenous alkali catalysts the process is not only transesterification of the triglyceride with methanol but also the saponification of the triglycerides with catalyst (Tsuji, *et al*, 2009).

### 3.5 Methods for Biodiesel monitoring process

#### 3.5.1 Offline Biodiesel Determination Chromatographic Methods

To meet the requirements of biodiesel standards, the quantization of individual compounds in biodiesel is not necessary but the quantization of classes of compounds is important. For example, for the determination of mono-, di- or triacylglycerol (in European standards), it does not matter which fatty acid(s) is attached to glycerol backbone. Virtually all methods used in the analysis of biodiesel are suitable (if necessary, with appropriate modifications) for all biodiesel feedstock even if the authors report their method on one specific feed stock. Also, the ideal analytical method would reliably and inexpensively quantify all contaminants even at trace levels with experimental ease in a matter of seconds at the most, or even faster for on-line reaction monitoring. No current analytical method meets these extreme demands. Therefore, compromises are necessary selecting a method for analyzing biodiesel or monitoring the transesterification reaction (Knothe, 2005).

Gas Chromatography Methods (GC), high performance liquid chromatography (HPLC), Gel permeation chromatography analyses were reported for biodiesel content determination. GC has been the most widely used for the analysis of biodiesel due to its generally higher accuracy in quantifying minor components. However, the accuracy of GC analyses can be influenced by factors such as baseline drift and overlapping signals. It is not always clear that factors are compensated for in related reports on biodiesel analysis. Most reports on the use of GC for biodiesel analysis employ with flame-ionization detection (FID). A general advantage of HPLC compared with GC is reducing in processing time and consuming reagent, which reduces the time for analyses. The report on the use of HPLC described the use of chloroform with an ethanol content of 0.6%. The system was useful for quantifying various degree or conversion of the trasesterification reaction (Trathnigg & Mittelbach, 1990). Gel permeation chromatography (GPC) which is similar to HPLC in instrumentation except for the nature of the column and the underlying separation principle, namely, molecular weight of the analytic for GPC for the analysis of trasesterification products. The method was tailored for palm oil and standards selected accordingly (Darnoko, 2000).

A Various analytical methods have been studied in biodiesel research such as: gas chromatography (GC) (Freedman, 1986). Liquid chromatography with gas chromatography (LC-GC)( Plank & Lorbeer,1995), thin layer chromatography (TLC), high performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR) spectroscopy, near infrared (NIR) spectroscopy and gel permeation chromatography (GPC). GC has a wide application in the analysis of triglyceride (TG) or petroleum diesel mixtures containing acylglycerols.

Freedman et. al first applied GC in their study of soybean oil transesterificaiton. GC is also generally regarded as the most precise and the reproducible method (Plank & Lorbeer, 1995). However, the reproducibility of GC analysis can be influenced by factors such as baseline drift, overlapping signals, etc. GC also requires derivation of samples which is laborious and time consuming.

LC-GC was also applied to the analysis of sterols in biodiesel from derived different vegetable oils. Kusdiana et.al developed a reliable online LC-GC quantification of monoglyceride (MG), diglyceride (DG) and triglyceride (TG). However, they also mentioned the methods did not work well on the analysis of fuel derived from waste frying oil, LC is a simple method using sample preparation. LC is basically a qualitative method, quantification being difficult. LC has therefore not been used extensively for quantitative analyses of oils.

HPLC is less time and reagent-consuming compare than GC, Mittelbach first developed an isocratic solvent system on a cyno-modified silica column two GPC columns. The systems was utilised for quantitation of various degrees of transesterification conversion. Holcapek et.al carried out an extensive study on transesterification using different detection methods they found that the sensitivity and linearity of each detection method varied with the individual TG.

NIR spectroscopy has attracted a lot attention because it provides a possible method of rapid, easy to handle and cost effective monitoring of the transesterification reaction and of biodiesel fuel quality. At 6005 cm$^{-1}$ and 4425-4430 cm$^{-1}$, the absorbance of methyl esters was stronger than that of TG, which were used in the conversion monitoring of the transesterification, the monitoring results from NIR spectroscopy were all compared with $^1$H NMR, the results of the two methods showed good agreement(Knothe, 2001). NIR spectroscopy and $^1$H

NMR were also used to determining the blend level of mixtures of biodiesel with conventional petro diesel fuel (Knothe, 2001). However, there are no further reports about whether the NIR spectroscopy can identify other components in the transesterification such as diglyceride or monoglyceride or whether on-line monitoring of the transesterification reaction can be carried out by NIR spectroscopy.

Among these analytical methods GPC appears to be the most promising. Darnoko et.al. reported excellent linearity of calibration curves for the mass calculation of MG, DG, TG and methyl esters components moreover the method showed good reproducibility. Their analysis of a mixture of these standards with different compositions showed a relative standard deviation of 0.27% - 3.87%. In the kinetic study of alkali catalysed palm oil transesterification in a batch reactor, Darnoko et.al. used GPC for their analysis.

### 3.5.2 Real time Biodiesel Determination

Although chromatographic methods are accurate in analysis of biodiesel and they provide very detail contents of the compounds, even the minor one. However the process it is time consuming of extremely expensive, more over the samples need to be extensive preparation. e

For some practical purposes quantity measurement is important as in process control and monitoring activities. Process monitoring and control activities have to deliver a highly efficient conversion process that uses less energy and less reactants. The purpose of process monitoring and control is to identify undergoes process which reaches a certain stage of process and executes another control sequence.

Some methods such as long-period grating or near-infrared spectroscopy can shorten the test and lead to considerably less expensive. Online monitoring commonly used affected physical parameters under chemical process such as viscosity, colour changing, pH value and dispersed bubble. Each online monitoring technique has unique characteristics reading.

### 3.5.2.1 Spectroscopic Method

Spectroscopic method such as nuclear magnetic resonance (NMR), near infrared (NIR), Fourier transform infrared spectroscopy (FTIR) and FT-Raman spectroscopy have gained more attention because they are non-destructive, need minimal sample preparation and much faster than chromatographic (Cabeça *et al.*, 2011).

Spectroscopic methods are being increasingly utilized for quality qontrol purposed. Near-infrared (NIR) spectroscopy is one of the methods which increasingly used for reasons of operational ease and rapid measurement. The sensor uses a fiber-optic probe, which makes the acquisition especially easy and provides the possibility of developing on-line reaction monitoring. Felizardo, et.al.2007, used this technique to determine the content of water and methanol in biodiesel, the results show that NIR spectroscopy may be used in combination with multivariable calibration to asses biodiesel quality and to identify the type of oil used for biodiesel production. After the NIR calibrations have been established, it will only take less than two minutes to obtain an almost complete analysis. Knothe used the fibre optic NIR spectroscopy to quantitatively monitor the transesterification reaction of a vegetable oil also showed that NIR can be used for biodiesel fuel quality assessment. NIR is attractive method because it ease, rapidity and cost analysis (Knothe, 2000).

Siatis *et al.,* used FTIR to determine the percentage of fatty acid methyl ester in the n hexane layer of the reaction and to monitor the reaction process. They used the FTIR to measure the biodiesel conversion from seed cakes processed by ultrasonic agitation (Siatis *et al., 2006*).

Ghesti *et al.,* conducting some experiments using Raman spectroscopy to assessing biodiesel yield and quality. In their experiment Raman spectroscopy was used to measure biodiesel transesterification of soybean oil with ethanol to produce fatty acid ethyl ester. The Raman spectroscopy measurement result compared with $^1$H NMR spectroscopy. Their correlation coefficients obtained from the linear fit between FT Raman measurement and the $^1$H NMR methods were 0.9974; 0.9847 and 0.9972 (Ghesti, *et al.,* 2006; Ghesti, *et al.,* 2007).

### 3.5.2.2 Viscometry method

The viscosity differences between triacylglycerol of vegetable oils and their corresponding methyl esters resulting from transesterification is approximately one order of magnitude. The viscosity difference from the basis of an analytical method, viscometry, applied to determining the conversion of a vegetable oil to methyl ester. Viscosities determined at 20 and 37.8$^o$C were in good agreement with GC analyses conducted for verification purposes. The viscometric method (especially when employed at 20$^o$C), is reported to be suitable for process control purposes due to its rapidity of measurement. Similar results were obtained from density measurements (De Filipis et.al.1995).

Ellis, et.al. 2008, using a commercial viscometer sensor (Vismart) measured the acoustic viscosity without any moving parts. The sensor is a semiconductor built to continuously measure viscosity and temperature and can determine the viscosity of a liquid rapidly. A quartz oscillator in the device generates resonance waves which travel through the liquid film to an acoustic sensor that detects the amount of waves that absorbed by the media. Data is output through extension wires to a handheld device with LCD monitor.

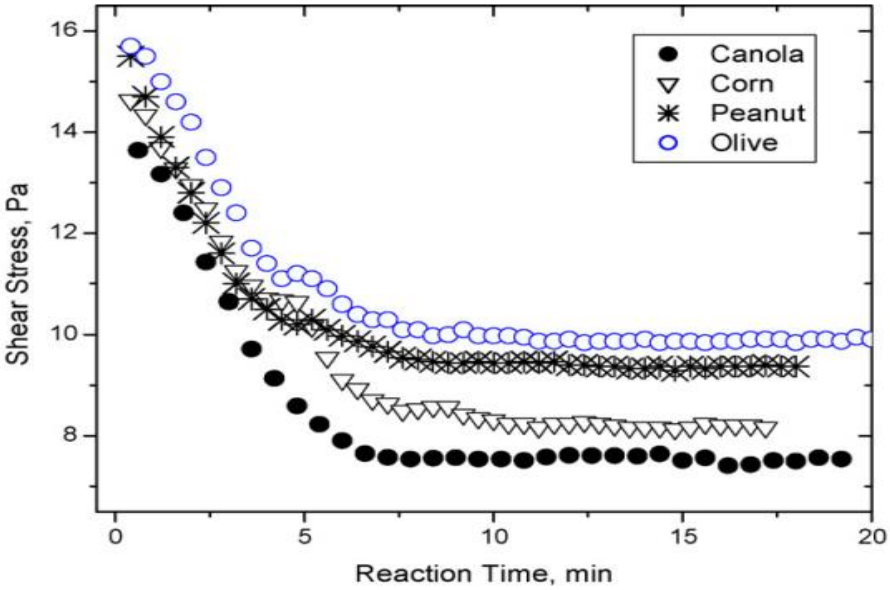


**Figure 3.8** Comparison of change in shear stress of reaction mixture with time for different feedstock oil (Ellis, *et al.*, 2008*).*

Data can also be logged to a controlling device. Acoustic viscosity is a function of the absolute (dynamic) viscosity, the density of fluid and the frequency of vibration. Through the means of acoustic viscosity, process engineers can monitor the process more effectively without considering the inter dependence of density and viscosity of the mixture. Figure 3.8 presents the results from the most recent work undertaken by Ellis, et al, using in process viscosity measurement for a range of oil feedstock. The results presented each oil clearly show shear stress differences at the beginning of the process due to differing triglyceride content and different terminal shear stress values following transesterification.

### 3.5.2.3 Optical Fibre Long Period Grating Sensor

A particular type of optical fibre device namely, the long-period grating (LPG) is sensitive to changes in the surrounding mediums refractive index this allows its uses as a chemical sensor. This makes possible the application of the LPG sensor in petroleum and natural fields and for environment control. The LPG in an axially periodic modulation in the optical fibre refractive index with periods of 100-700 µm, which couples light from the fundamental core propagation mode to co-propagating cladding modes. The LPG is an in-fibre compact and cheap device that presents real time response and can be easily integrated in an optical link, it is high sensitivity to refractive index changes. The LPG response to the sample refractive index and consequently, to the oil mass proportion in the biodiesel results in error in the determination of this parameter of about 0.4% for pure biodiesel (Falate,2007), however there is not further report in application of LPG for on line biodiesel measurement.

### 3.5.2.4 Laser

Laser spectroscopy may also use to monitor biodiesel process. De Boni & Lima conducted a research on transesterification monitoring process on soybean oil with a 60$^{o}$C reaction temperature, 3:1 alcohol to molar ratio and 1% KOH catalyst. A laser source of 650 nm wave length and a LDR have been used.

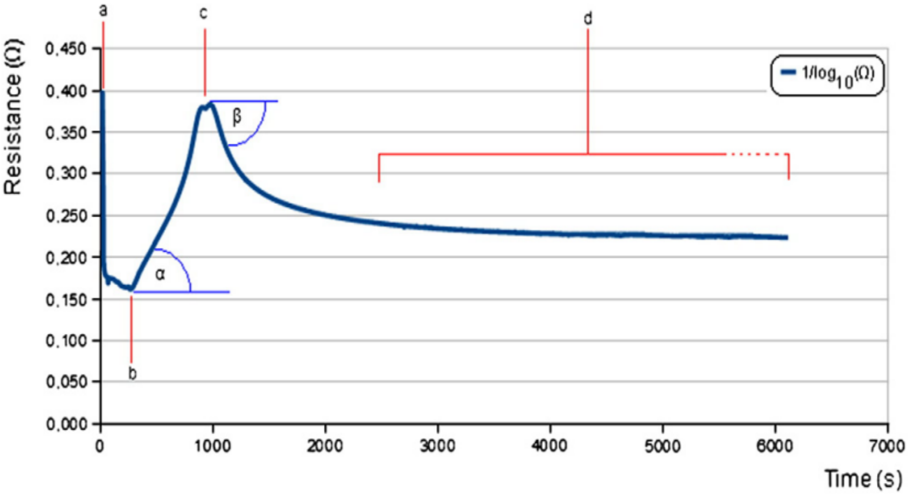


**Figure 3.9** The variation of LDR resistance (Ω) as function of time (De Boni & Lima, 2011)

Figure 3.8 represent the resistance value received by a LDR during biodiesel transesterification process. Point a is denote the addition of the methoxide solution and the refraction index from this point is triglycerides. Between point a and b exhibit the mixing between vegetable oils and methoxide, high degree of optical activity show the medium reaction. From point b and c multiple reaction has occurred simultaneously it is denote by reduction of the refraction index. At point c the reaction begin to reach a state of chemical equilibrium.

They used to monitor the reaction by pointed continuous laser beam in reaction environment, measuring the refractive index of the reaction medium during the reaction time. The light intensity will cross through the liquid and the intensity measured by LDR (De Boni & Lima, 2011).

### 3.5.2.5 PH monitoring

In literature most pH measurement technique are used to monitor aqueous reactions which one of the reactants or products is an acid or base. In non-aqueous situations pH measurement is rarely used. However, according to Komers one indication of completion of the biodiesel reaction is indicated by the exhaustion of the strong basicity ($OH^- = CH_3O^- = 0$) because of the consumption of $OH^-$ via saponification. Clark (Clark, *et al.*, 2013) described a reaction conducted with a methanol to oil ratio of 6:1, 0.49 % KOH catalyst by weight. They demonstrated that the reading of the pH can be continuously recorded after methanol and KOH are dispersed in oil.

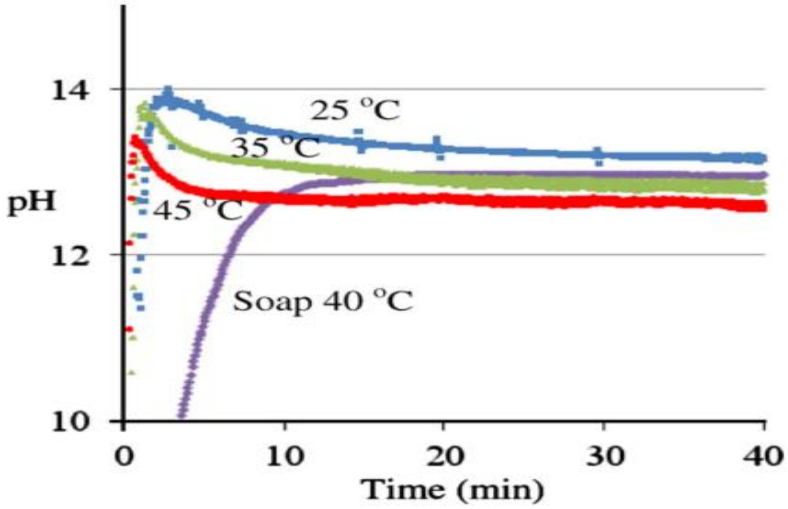


**Figure 3.10** pH as a function of reaction time for biodiesel and soap (Clark *et al.*, 2013).

Figure 3.10 illustrate the pH measurements resulting from Clark *et al.*, for experiments for a range of reaction temperatures. The result also show the pH of the result of soap formation. It can be seen that the transesterification process the pH process the pH gradually increased until it became constant value. Slightly different is exhibited for the different reaction temperature. It can be seen that there is a rapid increase in pH before the pH decreases and the process reaches equilibrium. It can also be seen that the final pH is a function of reaction temperature, with higher temperature giving rise to a lower terminal pH.

### 3.5.2.6 Microwave

Recently new methods have been developed by BEST research institute to determine vegetable oil type using microwave technologies. The technique developed employs microwave cavity resonators that operate based on the principal of interaction between electromagnetic waves and the material being tested and how the electromagnetic wave is transmitted and polarised. The sensor is excited by sweeping the microwave frequency from 6.62 to 6.92 GHz. The measurement result shows clearly differentiated resonant peak frequency amongst tested oil (Korostynska *et.al.,* 2013).

### 3.5.3 Biodiesel measurement purpose

Measurement of the biodiesel production process can be divided in to two functions, the monitoring of quality and real time process monitoring as shows in the aim of monitoring of the quality of the biodiesel process is to characterise all ingredients in the transesterification process. Monitoring for quality assurance purposes requires that all ingredients and the resulting products (methylester, diglyceride, monoglyceride and glycerol) are identified accurately. The state of the reactants having an influence on reaction setup. The injection of methoxide will reduce process temperature however the hot plate is controlled and the temperature shortly back to process temperature. To minimize the temperature variation methoxide may be pre-heating. To monitor the changing of the process, the sensor is immerse in the oil from the beginning of the process conversion.

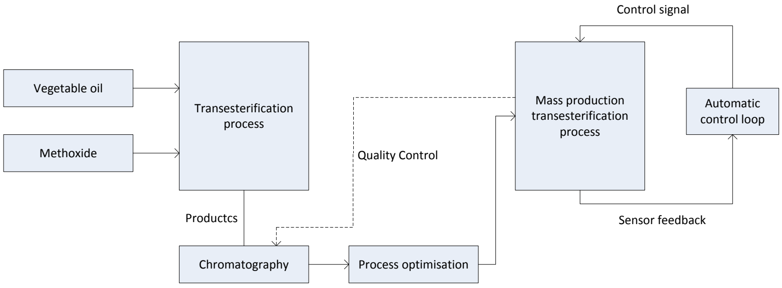


**Figure 3.11** Biodiesel conversion monitoring flow

Process monitoring on the other hand aims to control the actual conversion process in real time so as to ensure successful implementation of the previously identified optimal conversion process as seen in figure 3.11

During the biodiesel conversion process the need for in process measurement to control particular pre-determined requirement the conversion process or particular requirements is clear with employing process monitoring the state of the conversion progress can be determine in real time. On batch reaction processes monitoring can be applied to achieve a faster process with lower energy and more economically viable operation. Application of chromatography process monitoring for a batch reactor biodiesel conversion process is difficult and often prohibited expensive. As an alternative real-time measurements can be used to identify each stage of reaction. Physical quantities can be used (as already discussed) such as viscosity change and light transmission. Each measurement method has its own advantages and disadvantages when compare each others.

Viscosity method has shown a good result as on line indicator of biodiesel conversion by observing viscosity changing as a result of chemical reaction, however the digital version of viscometer sensor unfortunately is expensive, it caused overall cost for batch reaction plant increase significantly. The other method is using laser measurement as monitoring tools. It is interesting method uses laser through the reactants, reducing intensity of the light caused by chemical reaction will received by the light receiver in the function of resistance. However light measurement is excellent in small particles free environments, therefore light method is prone to interference by tiny contaminants, which is possible its existence in methoxide and triglycerids mixture.

Batch reactor transesterification process is widely used as low cost biodiesel conversion process which needs to be enhancing by a monitoring method to increase its efficiency. Base on this idea simple interdigital sensor and impedance measurement has proposed as a solution for inexpensive monitoring tools for online biodiesel conversion process.

### 3.6 Summary

The subject of transesterification process has been reviewed and the main points as follows:

- Catalyst summary

| | Homogeneous | Heterogeneous |
|---|---|---|
| Base | Widely used as cheaper compare to the others catalyst<br>Required excessive water for cleaning. | can be recovered and reused<br>more expensive than homogenous |
| Acid | Suitable for high acid number oil.<br>Need higher amount of alcohol, higher reaction temperature, pressure and slower reaction. | Not dissolved with alcohol<br>Can be reused<br>more expensive than homogenous |
| Enzyme catalyst | Reduce soap formation, simple purification, washing and neutralization.<br>More expensive and longer reaction time. | |
| Non Catalytic | Supercritical methanol with high pressure and high temperature, the process can tolerates water presents<br>Inefficient process conversion<br>Potential losses of methanol due to high molar ratio operation | |

- Transesterification is one widely used method to convert vegetable into biodiesel. The optimum conversion is 6:1 methoxide to triglyceride molar ratio due to it is reversible reaction to shift reaction towards equilibrium.
- Some types of catalyst can be used to enhance transesterification process. Homogeneous alkali catalyst like KOH is commonly used due to its price

is cheaper compare to other catalyst like heterogeneous and enzyme catalyst.

- Transesterification process is determined by some process condition such as raw material, temperature reaction time, molar ratio, catalyst and mixing intensity.
- Transesterification process consists of two mechanism, mass transfer and kinetically control region. Monitoring the mechanism of the process can lead to process optimization by saving mixing energy.
- There are two methods for biodiesel determinations, offline and real time method. Real time biodiesel determination can be used for process monitoring deliver efficient conversion process that uses less energy and less reactant.

# *Chapter 4*

# *Electrical Impedance*

When a closed circuit (conjunction path) contains a source of electro motion force (emf), electrical charge will flow around the circuit under the influence of the applied electric field. Movement of charge can be expressed as an electric current, the current have the rate of how of charge per unit time. For simple resistive devices the current and applied voltage are proportional and can be modelled using Ohms law. Figure 4.1 shows simple electric circuit contains with emf and resistance.

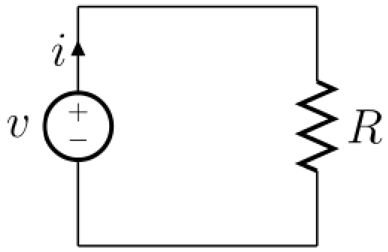


**Figure 4.1** closed loop circuit with emf

The relationship between the voltage (V) and resistance (R) and current (I) is Ohm laws

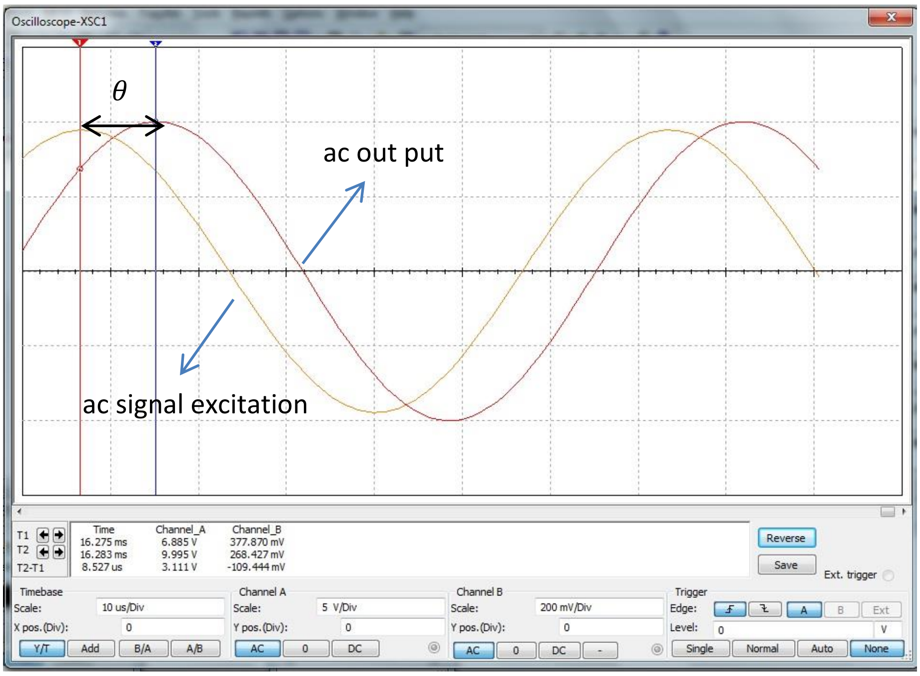
$$V = I.R \tag{4.1}$$

## 4.1 Impedance of resistance

Differs with dc (the flow of electric charge is only one direction), the flow of an ac electric charge is constantly being reversed back and forth. All materials to varying degrees have the ability to pass current. Ohm’s law provides the relationship between the applied voltage V, and measurement current, I, where R is the ratio of these two parameters, defined as the resistance of the material. This equation holds for application of the fields. When an ac (alternating current) is applied, however, this relationship becomes

$$V(t) = I(t).Z(\omega) \qquad 4.2$$

Where V(t) is the time varying voltage, I(t) is the time varying current, and $Z(\omega)$ is the constant of proportionality defined as the frequency dependent impedance. The impedance is a complex function having both in-phase and out-phase components as the ratio of the voltage and current (time-varying functions) has both magnitude and phase angle components. The in-phase of the impedance, Zr, provides information on the resistance of the material just as in the dc case. The out-phase on the contrary comes about because of the system's ability to not only dissipate but also to store energy. The information is not available from steady state measurements and relates to the capacitance or less often the inductance of the material. Because of this dual nature concerning a material's ability to dissipate and store energy, the impedance response of phenomena in materials systems is often modelled as a resistor in parallel with a capacitor. The impedance response of these circuit elements will now be discussed as a primer for understanding the response of real materials systems.



```
      Time        Channel_A   Channel_B
T1    16.275 ms   6.885 V     377.870 mV
T2    16.283 ms   9.995 V     268.427 mV
T2-T1 8.527 us    3.111 V     -109.444 mV
```

Timebase
Scale: 10 us/Div
X pos.(Div): 0

Channel A
Scale: 5 V/Div
Y pos.(Div): 0

Channel B
Scale: 200 mV/Div
Y pos.(Div): 0

Trigger
Edge: A
Level: 0 V

**Figure 4.2** The relationship between the applied voltage and the induced current in an impedance measurement.

Figure 4.2 represent the relationship between a sinusoidal ac voltage and the sinusoidal output current. The output signal is changed in magnitude as well as in phase. The angle θ is phase difference of ac signal excitation and signal response, if the voltage is given by:

$$V(t) = V_\theta \sin(\omega t) \qquad 4.3$$

The current is given by ;

$$I(t) = I_0 \sin(\omega t + \theta) \qquad 4.4$$

And the frequency-dependent impedance is calculated as

$$Z(\omega) = \frac{V(t)}{I(t)} = |Z|(\cos\theta + j\mathrm{Sin}\,\theta) \qquad 4.5$$

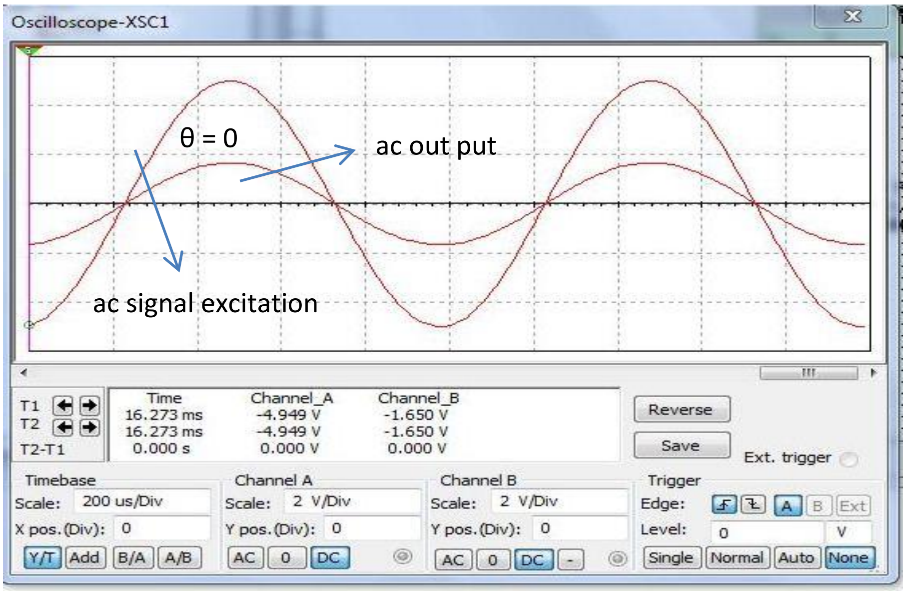
Where |Z| is the total impedance and j is defined as $\sqrt{-1}$ . To simplify this relation further the impedance is commonly depicted as the sum of its imaginary and real components:

$$Z = Z_r + jZ_i \qquad 4.6$$

Where $Z_r = |Z| \cos\theta$ and $Z_i = |Z| \mathrm{Sin}\,\theta$, Plotting the impedance in the complex plane as $Z_r$ versus $Z_i$ then provides a concise and convenient tool for determining various electrical response behaviours as will discussed below.

The following figure 4.3 shows the complex plane plot for a single resistor. This corresponds to a system in which no charge storage (capacitance or inductance) occurs. As shown a pure resistance is depicted as a single point on the complex plane. This is because the impedance of a resistor is given by :

$$Z(r) = R \qquad 4.7$$



| | Time | Channel_A | Channel_B |
|---|---|---|---|
| T1 | 16.273 ms | -4.949 V | -1.650 V |
| T2 | 16.273 ms | -4.949 V | -1.650 V |
| T2-T1 | 0.000 s | 0.000 V | 0.000 V |

Timebase
Scale: 200 us/Div
X pos.(Div): 0

Channel A
Scale: 2 V/Div
Y pos.(Div): 0

Channel B
Scale: 2 V/Div
Y pos.(Div): 0

Trigger
Level: 0 V

**Figure 4.3** A Schematic showing the relationship between the applied ac voltage and the pure resistant where phase shift θ is zero.

Where R is the same resistance defined in equation 4.1. As can be seen in equation 4.7 the impedance of a resistor contains no imaginary component as would be expected from its lack of a charge storage mechanism. The phase difference between the applied and measured signal in this case is zero. It is important to note that the impedance is frequency independent. The impedance of a pure resistor will be constant at any frequency.

## 4.2 Impedance of capacitance

Capacitance represents the energy capability of a capacitor. The most common form of charge storage device is a two-plate capacitor as figure 4.4. A parallel plate capacitor is a circuit element with two conducting plates at the terminals and a nonconductive material, known as the dielectric material, to separate them. When a charge source such as a battery, transfer charges to a capacitor, the voltage builds up across the two conductive terminals.

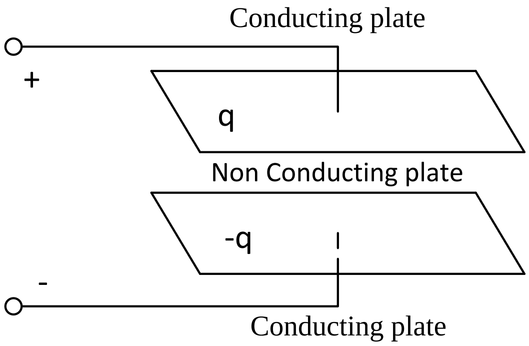


**Figure 4.4** Parallel plat capacitor

The charges accumulate at the two plates of the capacitor and can be expressed as:

$$q = CV \qquad 4.8$$

C is the capacitance in farads (F), q is the accumulated charge in coulombs (C) and V is the voltage measured between the two conducting plates in volts (V). The capacitance value (C) of a parallel-plate capacitor is related to the geometry of the capacitor and the dielectric constant of the nonconductive material in the capacitor by the following equation :

$$C = \frac{\varepsilon A(8.854x10^{-12})}{d} \qquad 4.9$$

Where C is the capacitance, ε is the dielectric constant of the insulating material, A is the surface area in square metres ($m^2$) and d is the thickness of the dielectric material in metres (m). Some representative dielectric constants are 1.0 for air, 5 for mica, 6 for glass and 7500 for ceramic.

The behaviour of capacitor in a DC circuit like an open circuit (Figure 4.5). In other words, when the circuit reaches its steady state the current through the circuit is zero. However, if a current or voltage is impressed on or switched out of the circuit with a capacitor. There will be a transition change in the current and voltage. Between the moment of switching and the steady state the current phasing through the capacitor is not zero. The time dependence of the voltage across the capacitor during the transient state in a DC circuit.

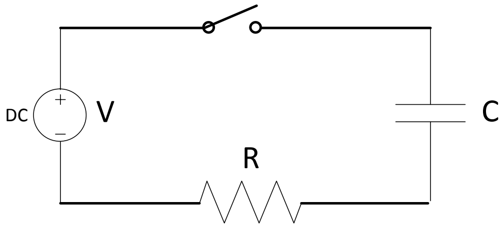


**Figure 4.5** A capacitor and resistor circuit

The current can be difined as the change rate of the charge, we can obtain the equation by differentiating:

$$I_{(t)} = C\,\frac{dV(t)}{dt} \qquad 4.10$$

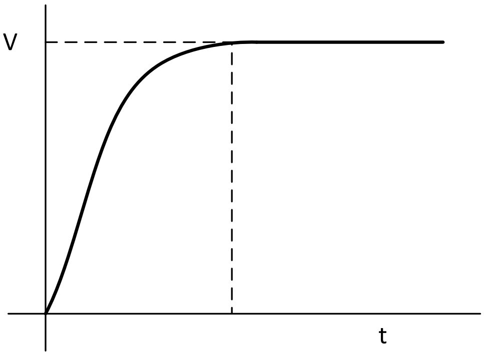
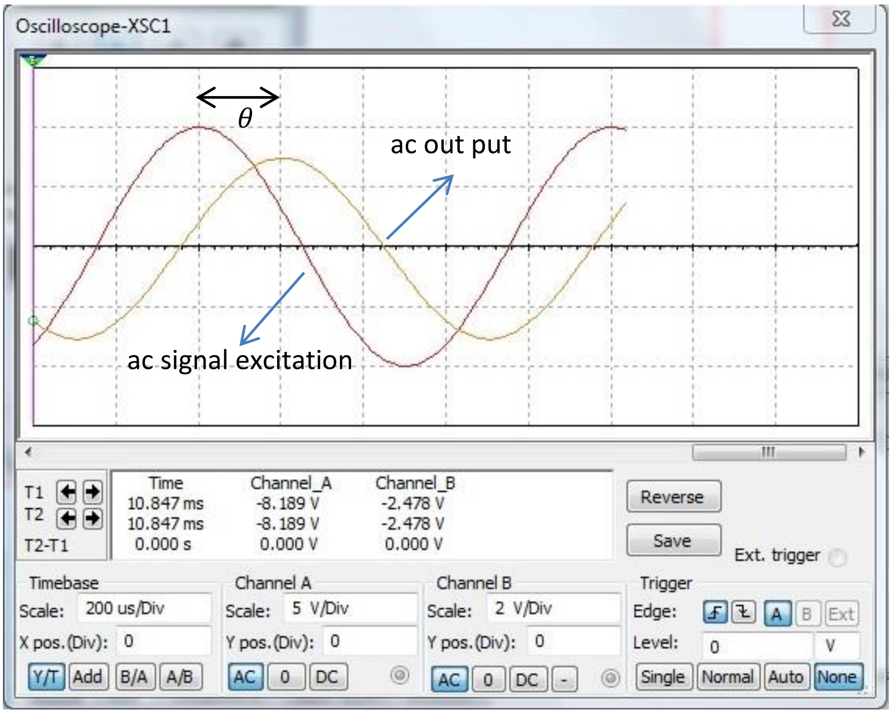


**Figure 4.6** Charging time and voltage rising in capacitor

When applying an ac voltage to the capacitance, the impedance of a capacitor is not quite as simple. Its impedance is given by the relationship:

$$Z(\text{capacitor}) = \frac{-j}{\omega C} \qquad 4.11$$

Where C is the capacitance and ω is the angular frequency, figure 4.6 shows a chaging time and voltage rising in capacitor. The figure 4.7 shows the complex plane plot for a capacitance. This corresponds to a system in which charge storage or capacitance occurs



```
      Time        Channel_A    Channel_B
T1    10.847 ms   -8.189 V     -2.478 V
T2    10.847 ms   -8.189 V     -2.478 V
T2-T1 0.000 s     0.000 V      0.000 V
```

Timebase
Scale: 200 us/Div
X pos.(Div): 0

Channel A
Scale: 5 V/Div
Y pos.(Div): 0

Channel B
Scale: 2 V/Div
Y pos.(Div): 0

Trigger
Edge:
Level: 0 V

**Figure 4.7** The relationship between the applied ac voltage on the capacitance circuit where phase shift θ.

As the frequency of the applied signal is increased the impedance of the capacitor decreases. Because the two quantities are inversely proportional. This can be understood if we consider how materials store charge in an ac field. Although there are several mechanisms that may lead to a capacitance the basic phenomena all involve the oscillation of charge carriers (i.e. electronic atomic orientation and space charge) creating a polarization (Van Roggen, 1990).

At very low frequencies approaching dc, the polarization is stagnant flow and no current is passed through the capacitor. Thus the impedance approaches infinity. At very high frequencies, however, the phenomena involved in polarization cannot keep up with the applied field, and the capacitor is effectively a short circuit. Thus the impedances approaches zero.

## 4.3 Impedance of Inductance

An inductors is a coil of wire or solenoid which can be used to store energy in the magnetic field that it generates. The inductors is similar to capacitor mathematically but has opposite behaviour, at low frequency it behaves as short circuit and as an open circuit for high frequencies. The impedance of an inductor is given as follows:

$$Z(\text{inductor}) = j\omega L \qquad 4.12$$

Where L is the inductance of the material. Inductance is rarely a dominant electrical response in material systems, but as can be shown the impedance response is analogous to that of a capacitor with no real component present. For this reason, the influence of inductance impedance is simply neglected (Cho, 2009; Romano & Sorichetti, 2011).

## 4.4 Impedance complex

An impedance can be used to evaluate the electrochemical behaviour of electrode or electrolyte materials using two identical electrodes immerse in the liquid sample the sensor may take in the form of circular cylinder or planar electrodes. Electrical excitation is applied to the electrodes, usually in the form of a voltage or current with particular pattern such as step excitation or random excitation. The response of measured system as results in the detection of current or voltage difference across the sensor electrodes.

The measured response will depend on the properties of the material between and surrounding the electrode. The range of impedance measurement application includes (Macdonald, 2006):

- the transport of electrons through the electronics conductors.
- the transfer of electrons at the electrode-electrolyte interfaces.
- Investigation of electrochemical reactions and their underlying mechanisms.
- Measurement of the dielectric and transport properties of materials.
- Exploring the properties of porous electrodes
- Investigating the properties of passive surfaces

In impedance measurement applications three different types of electrical stimulus are usually used depending on the purpose of the measurement (Barsoukov & Macdonald, 2005). In transient measurements usually a step voltage excitation with $V_{(t)} = V_0$ for $t > 0$, $V_{(t)} = 0$ for $t<0$, it can be applied to the system at t=0, and the response of the system is a time-varying current i(t). The ratio of $\frac{V_0}{i_{(t)}}$ can be called the time varying resistance. That results from impedance at the electrode and liquid interface. Further analysis from time varying results can be extended in to frequency dependent impedance using Fourier or Laplace transform.

The second technique is to apply an excitation signal containing random white noise to the interface and then measures the resulting current. Fourier transformation can be used to convert the time domain data into frequency domain data.

The third technique is the most common and standard impedance measurement. To measure impedance by applying a single frequency of voltage or current to the material under test and then measuring the phase shift and amplitude or real and imaginary parts. This approach offers a lower cost and more readily available solution.

The application of impedance spectroscopy using high frequency sweeps was conducted by Cho, 2009. Cho studied the characteristic of biodiesel in the range frequency of biodiesel. The measurement dielectric properties were shown to provide a critical approach to understanding the structure of material as well as the chemical reaction mechanism. The changes in dielectric properties can be used in a simple method for monitoring biodiesel operations (Cho, 2009; Inoue *et al.*, 2002). It has been reported that permittivity values obtained by impedance measurement may be used to determine the quality of biodiesel product (Corach *et al.*, 2012).

Other experiments have been undertaken using a similar method by Romano and Sorichetti, to determine electric characteristic of biodiesel before and after the conversion process. Transesterification of waste frying oils which required treatment water contents and filtration was investigated. The conductivity was measured using portable measurements, and dielectric properties of the reactants measured in the range frequency 100 Hz to 15.7 kHz. They summarized that the method of monitoring the physico-chemical and electrical properties is an efficient technique for controlling different stages of the process raw material from preparation to the quality control of the finished product (Sorichetti & Romano, 2005; Romano & Sorichetti, 2011).

Figure 4.8 shows the complex plane plot for the impedance of a parallel RC circuit. The semi-circle centred on the $Zr_{\text{-axis}}$ is a common feature of impedance spectra for materials systems. Knowing that the reciprocal of the total impedance of parallel components is equal to the sum of the reciprocals of the individual component impedances, the impedance of a parallel RC circuit, $Z_{RC}$ can be calculated to be :

$$Z_{RC} = \frac{R}{1+(\omega RC)^2} - \frac{\omega R^2 C}{1+(\omega RC)^2} \qquad 4.13$$

Thus it can be seen that at frequencies approaching zero (dc) $Z_{RC}$ is equal to the resistance of the circuit. Because the capacitor is basically an open circuit at zero frequency, all of the current must pass through the resistor. The diameter of the semicircle is the resistance of the circuit. At frequencies approaching infinity, $Z_{RC}$ approaches zero. This is as expected, because at high frequencies the capacitor is short circuited and current flows unimpeded. This is the characteristic or relaxation frequency for the parallel RC circuit. At this point real part of the impedance is exactly equal to the imaginary component can be written:

$$\omega = \omega_{max} = \frac{1}{RC} \qquad 4.14$$

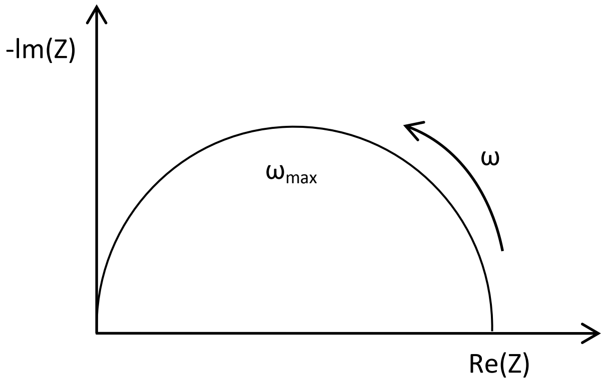


**Figure 4.8** Nyquist plot for the Parallel RC circuit with the parameters of interest labelled. Frequency increases right to left.

Thus knowing the diameter of the arc, R, and the frequency at the top of the arc, $\omega_{max}$ the capacitance of the circuit can be calculated. Therefore, from the Nyquist plot, all of the pertinent electrical information for a system can be obtained. An important feature of equation 4.13 is found when the equations for resistance and capacitance are expanded as follows:

$$R = \frac{\rho l}{A} \qquad 4.15$$

and

$$C = \frac{\varepsilon_r \varepsilon_{oA}}{l} \qquad 4.16$$

Where ρ is the resistivity and $\varepsilon_r$ is the dielectric constant of the material/process in question, A and l are the area and length of electrode, respectively and $\varepsilon_0$ is the permittivity of free space (8.85 – 12 $C^2/Nm^2$). It can be seen from equation 4.17 then that the characteristic frequency of a parallel RC circuit is completely geometry independent and is a function only of material parameters and a constant.

$$\omega_{max} = (RC)^{-1} = (\rho.\varepsilon_r.\varepsilon_0)^{-1} \qquad 4.17$$

This is an important concept in analysis of the impedance response of real material systems. Because the impedance of series components is additive, the impedance of multiple phenomena is series is a simple extension, and several consecutive semi-circles would be evident in the complex plane assuming, that the characteristic frequencies of the phenomena are far enough removed from one another (approximately two decades of frequency). Thus, in given materials system the impedance characteristic of several processes occurring within the system can be deconvoluted/separated if a broad enough range of frequency is swept in measuring the impedance spectrum.

## 4.5 Material permittivity

Every substance has particular responds to applied magnetic field, their electrical properties merely depend on its dielectric and permittivity properties. The permittivity commonly described as resistant deal with the electric field excitation in a substance. The dielectric properties of most materials depend on the frequency of the applied alternating electric field, the temperature, mixture, density, material structure and pressure (Lizhi *et al.*, 2008). A dielectric material can transmit the electric field force without conduction effect in other words perfect dielectric materials is insulator. If a dc current is places across a parallel plate capacitor, more charge is stored when a dielectric material fill in between the plates than is a vacuum. In capacitor, dielectric materials increases the storage capacity of the capacitor by neutralizing charges at the electrodes. The relationship between dielectric constant $\varepsilon_r$ (relative permittivity) of materials with capacitance:

$$\varepsilon_r = \frac{C}{C_0} = \frac{\varepsilon}{\varepsilon_0} \qquad 4.18$$

Where C is the capacitance with a dielectric substance and $C_0$ is the capacitance without the material, ε material permittivity and $\varepsilon_0$ is vacuum permittivity. If the same parallel plate excited by sinusoidal alternating current, the resulting current will be made up charging current and a loss current. Permittivity has two parameters have direct relationship:

$$\varepsilon = \varepsilon' - i.\varepsilon'' \qquad 4.19$$

Figure 4.9 shows the simple diagram of complex permittivity where the real and imaginary parts are $90^o$ out of phase. The angle δ is sum of the vector with real axis. The permittivity ε be composed of real part ε' and imaginary part ε'', the real part of permittivity represent the ability the media to store the electromagnetic and imaginary part indicate the loss.

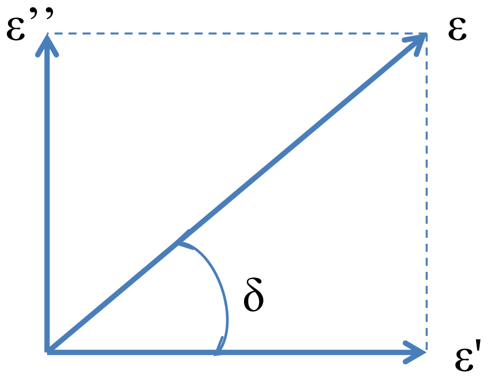


**Figure 4.9** Diagram complex permittivity

For most solid and liquids ε'>1, the loss factor from imaginary parts indicate how dissipative of lossy a material to the external electric field. ε'' commonly smaller than ε' and the value is ε''>0. The factor influence the loss in imaginary part is both dielectric loss and conductivity.

If material under test there are presents charge transport effects or ionic solution, there will be dielectric polarization and the imaginary part will be included in complex relative permittivity.

$$\varepsilon \quad = \quad \varepsilon' - i\varepsilon'' - i\frac{\sigma}{\omega\varepsilon_0} \qquad 4.20$$

$\varepsilon''(\omega)$ is describes the dissipation of energy associated to the relaxation of dielectric polarization.

$$\varepsilon_r = \varepsilon' - i\frac{\sigma}{\omega\varepsilon_0} \qquad 4.21$$

However because the dielectric relaxation only happen in the frequency more than 4 Ghz, and this dissipation no longer applicable in biodiesel process (Sorichetti & Romano, 2005) Thus the equation become equation 4.21

## 4.6 Summary

Impedance has been reviewed in this chapter, some notes from impedance as follows:

- Impedance is consist two components real parts and imaginary parts. Real parts is represent pure resistant and reactance. The reactance consists with capacitance which the value depend on material permittivity. Permittivity is consist real parts and imaginary parts. The real part is indicate the ability the media to store electromagnetic and imaginary part indicate the loss due to polarization.
- Impedance can be used to evaluate a material properties with examine material permittivity.

# *Chapter 5*

# *Interdigital Planar Sensor*

Resistive and capacitive sensors may be becoming the most commonly used sensor. The applications of this sensor have been used widely for, home automation, space, aviation and medical industries. Resistive and capacitive sensors apply a broad are applicable to range of phenomena from the fields of physics, material science biology, electrochemistry and electronics (Du & Yelich, 2008; Korostynska *et al.*, 2013). Application of resistive sensor can be found on automobile applications such as coolant and air temperatures, air flow rates and throttle position. Impedance measurement and analysis also have been used to characterize the human body, enabling the doctors to evaluate and diagnose certain diseases and facilitate the related monitoring of health conditions.

## 5.1 Interdigital capacitance sensor

The application of planar inter digital sensor in this report can be classified as an electrochemical sensor. An electrochemical sensor maybe defined as a small device that as the result of chemical interaction or process between the tested materials and sensor device, transforms chemical or biochemical information of quantitative or qualitative type into an analytically useful signal (Stetter, *et al.*, 2003). This chapter will discuss the operating principle of inter digital (ID) sensor and the development of sensors for the monitoring of the transesterification process. Common ID sensor are used to measure capacitance or conductivity however in this thesis, both measurement of resistance and capacitance can be obtained in one measurement. The ID sensor uses periodic electrode structures and often given names like periodic sensor, grating sensor, comb sensor or micro strip sensor. The term inter digital sensor is used in this thesis. This sensor has been used in many applications including chemical sensing, biotechnology, micro electro-mechanical system and non-destructive testing. Inter digital sensors can be defined as a digit-like or periodic comb pattern of the parallel in plane electrodes used to build up capacitance associated with the electric fields that penetrate into material sample (Mamishev, 2004). Depend on the excitation signal applied to the electrode, the application of inter digital sensor can be measure capacitance and conductance detection or both of them. Applications of the ID sensor started from 1960s and continues for various scientific and industrial applications.

The configuration of the ID sensor can be described in to direct contact between metal electrode and liquid in case of invasive sensor and non-invasive which is no contact between metal electrode and liquid. Depend on the purpose of measurement, direct contact sensor is highly influence by liquid conductivity and the effect of conductivity is presented by a resistive element in parallel. For non-invasive electrodes, more complex equivalent circuit models should be represented (Golnabi, et al, 2007). Moreover, direct contact electrodes have measured capacitance to be a linear function of liquid permittivity (Heidari et al, 2010).

### 5.1.1 Capacitive ID sensor

The ID sensor also has been the subject of extensive research in areas such as, bio impedance measurement, quality monitoring of dairy products, biological contaminants on fish meat, moisture content, detection of nitrate levels in natural water and leather quality. The application of the ID sensor is limited not only to biological contaminants but also it can be extended to the evaluation of near surface material. In this application the ID electromagnetic sensors is not only to inspecting conducting materials in which eddy currents are generated but can be used to evaluate non-conducting materials which no eddy current is generated. Applications of the ID sensors have been successful in determining the conductivities of near surface materials, electroplated materials and detection of cavities (Mukhopadhyay, 2005).

ID sensors have been used to estimate the moisture content in paper pulp which contains calcium carbonate. This method provides non-intrusive method evaluation material. The sensor design applied to this partially application have 40 mm spatial periodicity, finger length of 160 mm and an effective penetration depth of 7 mm width. The sensor electrodes not direct contact with paper pulp. Measurement equipment using LCR meter with one volt sinusoidal ac voltage. The experiments clearly demonstrate that the ID sensor can measure the capacitance value of the content in pulp in the presence of calcium carbonate (Sundara-Rajan, *et al.,* 2004, 2005). Tsamis & Avaritsiotis designed a planar capacitive sensor with nine electrodes with 1 cm width and the gap 1 cm to monitor water content on standard sheets of A4. He concluded that ID sensor has an optimum distance range for the proposed application (Tsamis & Avaritsiotis, 2005).

Mohd Syaifudin designed a dielectric inter digital planar sensor to discriminate different chemical contaminants on seafood products. Mussels from the sea are prone contaminating with some bio toxins like domoic acid and proline. Using 10 volt excitation and 10 kHz frequency applied to the sensor then comparing voltage output to the excitation voltage. This sensor was able to detect the presence of bio toxins (Mohd. Sayifudin *et al.,* 2009).

An inter digital capacitance design also has been used to predict the fat content of pork meat. The meat is cut with a thickness 20-30 mm, to have adequate electric field penetration into the meat sample, electrodes gaps should be more than double of meat thickness. The measurement was using fixed excitation frequency of 5 kHz. The sensor performance shows meat measurement using ID sensor can responds very well to fat content on pork meat (Mukhopadhyay & Gootneratne, 2007).

Recent research BEST research institute was using a co planar sensor for biomedical applications. The sensor has designed to sense glucose dilutions. Sensor construction is based upon a coplanar waveguide with sweep frequency between 3610 and 3630 MHz, the sensor has a good respond for 0-10% concentration of glucose (Mason *et.al.* 2012). An inter digital electrode has been used at BEST to verify some types of oil, the frequency excitation for the sensor from 5-8 GHz, with good repeatability. The result shows different frequency shift occurred with different type of oils (Blakey, *et.al.* 2012). Another flexible inter digital microwave sensor has been used to analyse water contaminants in real time. Microwave excitation in the range of 1-15 GHz used to sweep the test material. Water quality indicator can from the microwave measurement using the changes in microwave part of the electromagnetic spectrum. The experiment result shows the sensor has instant respond to water contaminants (Korostynska *et. al.,* 2013)

### 5.1.2 Conductometric ID sensor

The ID sensor is used not only for capacitance measurement but also for conductivity measurement. Conductivity has been widely used in electrolytic conductivity to monitor a progress of chemical reaction (often called conductometric). Application of an ID micro biosensor for environmental monitoring has been reported by Renault & Dzyadevych. Early application of conductometric sensors for monitoring bio catalytic reactions has been investigated, further application is widely used for pollutant detection for environmental monitoring. Compared with other types of sensor conductometric ID sensors have advantages over other types of transducer. The cost of production of the conductometric sensor is low based on standard photolithography method and no reference electrode needed (Renault & Dzyadevych, 2008).

An ID planar sensor based on a biosensor has been used to detect toxic compounds in water samples. The ID biosensor is based on the principle of change of conductivity of the enzyme membrane when tyrosine (a binuclear copper containing metalloprotein) interacts inhibited by pollutants. The sensors was possible to detect and determine the present of some toxic compounds such diuron, copper ions or atrazine (Anh *et al.*, 2006).

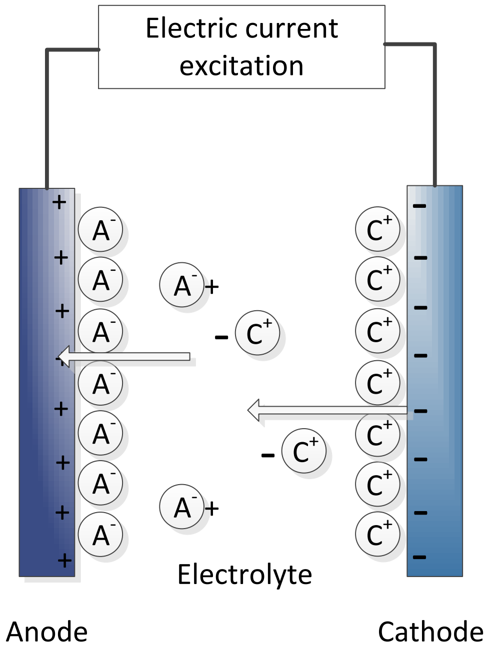


**Figure 5.1** Ion migration in the solution volume and electrolyte conductivity

The conductivity of the fluid is defined as the ability of materials to transmit heat or electricity. Electrical conductivity occurs in a liquid where the substance contains mobile charge carries like electrons or ions. When electrical potential is placed on two conductors, separated such a fluid then depending on the number of ions per unit volume, the movement of charge carriers under the influence of an applied electric field result in the flow of an electric current.

## 5.2 Advantages of Inter digital sensors

The Inter digital (ID) sensor displays some advantages that attract sensor researchers. ID sensors are categorized as non-destructive testing sensors, in that they have a most important feature that the sensor surface only requires single-side access to the test material. The electromagnetic field created by sensor excitation can penetrate the sample under test and the properties of the tested materials will response to the excitation in a readily understood way. Some sensitive chemical or biological layer deposited over the electrodes, can further sensitively interact with a gas or liquid. Monitoring and measuring of chemical concentration can be undertaken using single surface. In some difficult situation where parallel plat is unable to the placed due to design limitations for the electrode, then one sided access is very important.

Signal strength of the ID sensor can be controlled by changing the design of the sensor. By varying the number of comb fingers and the spacing between them and also changing the area of the sensor, the output signal can be controlled.

The other capability of the ID sensor in the research field of inter digital frequency wave length dielectrometry, a close relative to impedance tomography. This technology application applies inter digital electrode pairs of variable spatial periodicity. The operational principal is the depth of penetration of electric field lines into the material is frequency independent and proportional to the spatial wavelength, defined as the distance between centrelines to the neighbouring electrodes in the same polarity. Movement of the sensor along the material surface with subsequent signal process can generate three dimensional imaging of dielectric properties of insulating materials. The dielectric properties can be related to many other physical properties such as porosity, density and chemical content of material (Mamishev, *et al*, 2004).

## 5.3 Planar inter digital sensor structure

The operating principle of planar inter digital sensor is similar with operation to the conventional parallel plate or coaxial cylinder capacitor. Voltage excitation is applied to the electrodes and the impedance across the electrode is measured. Compared with a parallel plate cell or coaxial cylinder, the ID sensor is not required two side access to the material sample. The basic operation relays on the capacitance and conductance between two electrodes depending on the properties of dielectric material, electrode and material geometry.

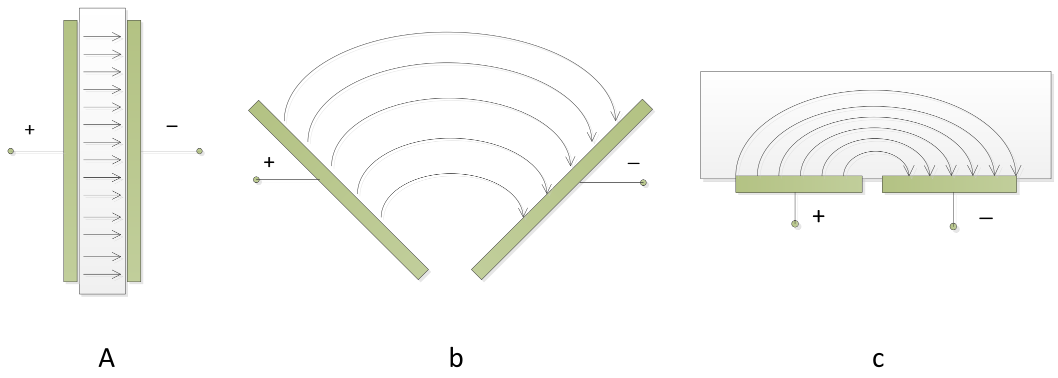


**Figure 5.2** a. parallel plate b. open up electrode c. one sided access electrode

The Inter digital sensor contains of one set of electrode and directly measures the dielectric properties of material sample. when a periodic stimulus signal is applied on the surface of the sensor. The electromagnetic field formed between sensor fingers and the variation of the permittivity and charge carrier potentially provides extensive information about the conductivity and dielectric (impedance) properties of the surrounding material. Changes of the dielectric properties of the surrounding materials are usually induced by changes in various physical, chemical or structural properties of materials. Therefore by measuring the capacitive reactance of the sensor, the system properties can be evaluated. The sensor excitation takes the form of an alternating current (AC) type excitation applied between the positive terminal and negative terminal. An electric field is formed positive terminal the negative terminal.

The output of ID sensor has low signal to noise ratio because the design of the sensor is coplanar. The comb pattern of ID sensor has been adopted in order to gain a strong output signal has purpose to get strong signal.

Capacitance sensors may vary in design and structure, most of them are based on a parallel plate structure. Standard capacitors often contains two parallel plates arranged at a distance apart from one another with a dielectric medium of some sort in between the two. The capacitance of this geometric arrangement is proportional to the area of the plate (A) and proportional to the distance separating the paltes (d) as described by equation (5.1).

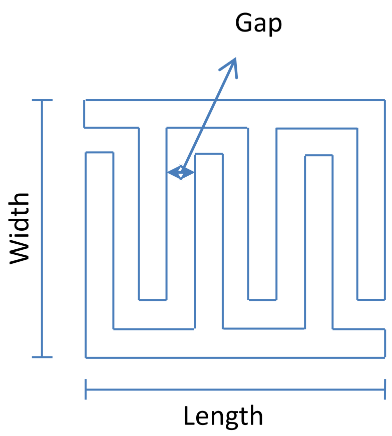


**Figure 5.3** Interdigital sensor

In general ID sensor has equation as follows:

$$C = \varepsilon_r \cdot \varepsilon_0 \frac{A}{d} \qquad 5.1$$

Where $\varepsilon_0$ is the permittivity of free space and $\varepsilon_r$ is the relative permittivity of the material. From the equation 5.1 is possible to determine the capacitance measurement by changing the related variables. Tuning of the sensor maybe achieved by tailoring the sensor geometry to a particular application. The thickness and spacing of the sensor fingers maybe easily changed. Figure 5.4 illustrates the plot between capacitance value and finger gaps with constant area A. It can be seen that decreasing the gaps between the sensor fingers reduces the capacitance of the sensor.

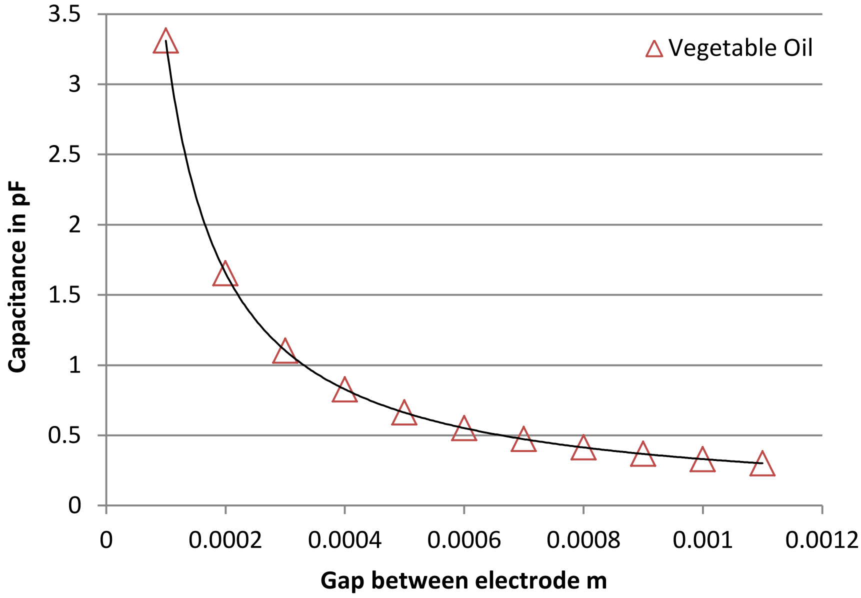


**Figure 5.4** Calculated ID sensor capacitance values with electrode gap variation using equation 5.1

The control variables can be the area A and the sensor gap d by varying both parameters the measured capacitance will change accordingly. The sensing area is determined by the thickness of the fingers, width of the fingers and number of the fingers, increasing those parameters can increase the capacitance value.

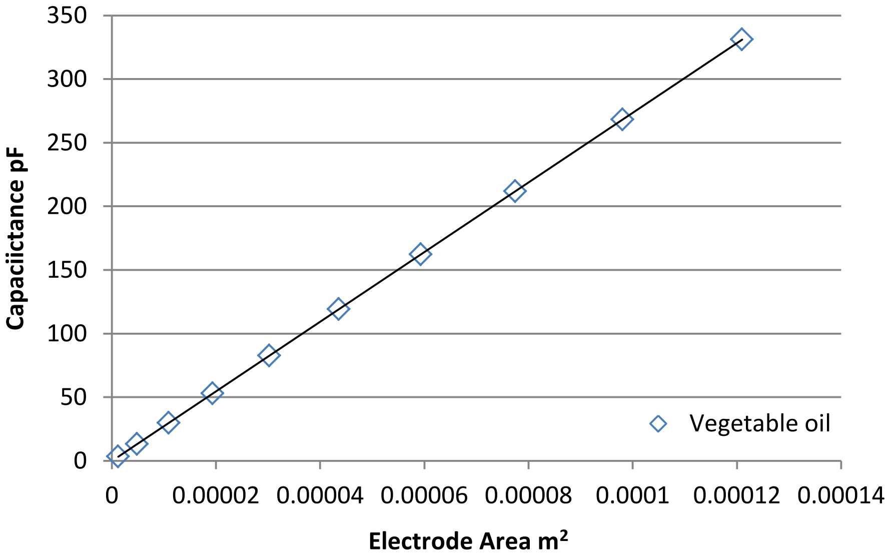


**Figure 5.5** Calculated capacitance values with electrode area variation using equation 5.1

The design of the ID sensor can be varied to achieve the desired sensor sensitivity, for example double the area of electrodes will double the capacitance and increase signal output and hence the sensitivity (figure 5.5).

## 5.4 Interdigital Sensor Analysis

### 5.4.1 Impedance and Resistance

When ac excitation is applied to the sensor with the voltage of v and the current i, electromagnetic fields will be build up in the fringing area and penetrate into the materials. The impedance of the ID sensor will depend on the material being tested. The complex impedance of the system is defined as:

$$|Z| = \sqrt{R^2 + X^2} \qquad 5.2$$

The real part of the complex impedance is the resistance R (the inverse of G the real conductive) and corresponds with to the energy dissipation process occurring in the sample. The imaginary component of impedance is the reactance X, the value is influenced by the capacitance and inductance.

$$X = X_L - X_C \qquad 5.3$$

Where :

$X_L$ is inductive reactance

$X_C$ is capacitive reactance

In inter digital measurement systems sensors measurement only read to Capacitance reactance, the inductance reactance element having negligible. Ignoring the effect of inductance the impedance on ID sensor can be calculated become:

$$|Z| = \sqrt{R^2 + (-\frac{1}{2\pi fC})^2} \quad 5.4$$

Where :

f is frequency

C is capacitance

R is resistance

It can be seen the capacitance reactance is dependent on the value of frequency and capacitance, when the single frequency applied the value is dependent on the capacitance value. Measurement of impedance is common way of measuring the capacitance value and hence dielectric properties of materials. In this thesis the both real part and imaginary part of impedance measured. The value of imaginary part of impedance Xc (ohm) is influence by frequency the capacitance does not change the capacitance impedance changes by the frequency.

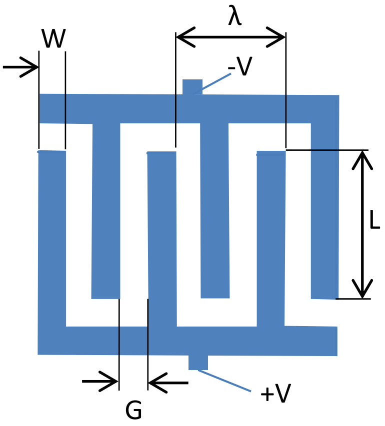
$$X_c = \frac{1}{2\pi fC} \quad 5.5$$

Increasing the frequency f will reduce reactance and vice versa.

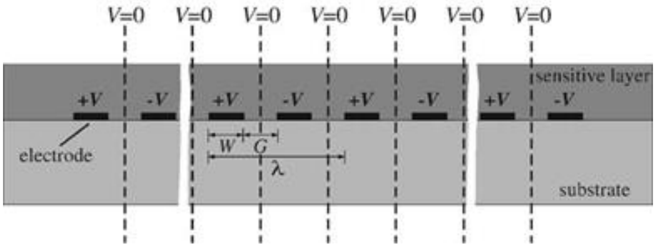
### 5.4.2 Equivalent Circuit

Analytical evaluation of ID sensor using conformal mapping (CM) technique firstly appear by the publication by Wei (Wei, 1977), he evaluated the capacitance of an ID sensor with infinite top air layer. This technique cannot be applied for calculate the capacitance for a sensor having a finite layer of a multi-layer structure over the electrode.

The technique was used in equivalent circuit calculations based on the work of Igreja and Dias defined as conformal mapping technique as shows in figure 5.6 a and b (Igreja & Dias, 2004).



a.



b.

**Figure 5.6** Configuration of electrode (a) and electrode cross section (b)

The design ID sensor proposed in this thesis for biodiesel measurement and process monitoring is based on single layer sensor design. The geometry of the ID sensor can be considered as a repeating set of parallel capacitors and resistive elements as illustrated in figure 5.6.

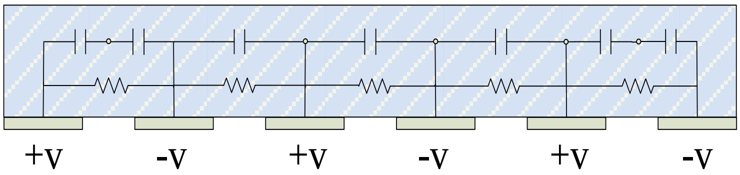


**Figure 5.7** The equivalent circuit for ID sensor

Figure 5.7 illustrate Igreja & Dias technique using conformal mapping, the technique assumes that we can consider the thickness of the substrate as infinite if the thickness is much greater than the spatial wavelength (λ=2(W+G)) The electrodes is separated by the gaps G and W is fingers width, and the fingers thickness can be ignored due to it is much less than the width. All of the fingers are connected in two opposite position with different potential +V and –V, the fingers length is defined by L. Because there is no sensitive layer above the conductor, the calculation will use a single or semi-infinite layer equivalent electric circuit. The capacitance of a single layer can be evaluated as a function of two capacitance, C1 being half the capacitance between exterior electrode and the ground. The total capacitance of one single layer sensor system can be written :

$$C_s = (N - 3)\frac{C_I}{2} + 2\,\frac{C_I.C_E}{C_I+C_E}\,,\ N > 3 \qquad 5.6$$

This equation in only applied to N >3, for sensor N<3 can be calculate by few modifications from equation 5.1. IDC value calculate is pair of inside electrodes :

$$C_I = C_{I,\,media} + C_{I,\,SiO2} + C_{I,\,Si} \qquad 5.7$$

$$= \varepsilon_0 L\ (\varepsilon_{media}\,\frac{K(k_I\infty)}{K(k'_I\infty)} + (\varepsilon_{SiO2} - \varepsilon_{media})\frac{K(K_I,SiO2)}{K(K'_I,SiO2)} + \varepsilon_{si}\frac{K(k_{I\infty})}{K(k'_{I\infty})}) \qquad 5.8$$

and $C_E$, is the capacitance of an outside electrode and given as :

$$C_E = C_{E,\,media} + C_{E,\,SiO2} + C_{E,\,Si} \qquad 5.9$$

$$= \varepsilon_0 L\,(\varepsilon_{media}\,\frac{K(k_E\infty)}{K(k'_E\infty)} + (\varepsilon_{SiO2} - \varepsilon_{media})\,\frac{K(K_I,SiO2)}{K(K'_I,SiO2)} + \varepsilon_{si}\,\frac{K(k_{I\infty})}{K(k'_{I\infty})}) \qquad 5.10$$

The parameters of $k_{I\infty\,;}$ and $k_{E\infty}$ can be written as :

$$k_{I\infty} = \sin\frac{\pi}{2}\,\eta \qquad 5.11$$

and

$$k_{I\infty} = \frac{2\sqrt{\eta}}{1+\eta} \qquad 5.12$$

The k' is the complex modulus of k and is equal to the square root of $(1-k^2)$. The parameters of η is non-dimensional value :

$$\eta = \frac{W}{W+G} = \frac{2W}{\lambda} \qquad 5.13$$

### 5.5. Sensor fabrication

The planar sensor has been widely used in many applications and many varied sensor fabrication techniques have been used for its design and development. Electrochemical planar sensor materials can be divided in some way such as insulators, metals, catalytic materials, semiconductor materials or commonly called solid state sensor develop using Si or Ge Materials. To produce chemical planar sensor some available technology has been used such as photolithography, silicon technology and thick and thin film technology (Laschi & Mascini, 2006).

A thick film technology has been developed to produce hybrid circuit involving semiconductors, integrated circuit etc (figure 5.9). A thick film sensor is developed by films of particular pastes or inks sequentially onto surface of substrate. The developed pattern the printed and transferred by the mask on substrate surface. The next step is dry process of the film using oven. To build complex arrangement, printing step can be repeated. Thick film for sensor application has been used for pH sensor, gas sensor and humidity. There are many variant of these sensors and most of them technically can be classified as Impedance based sensor. The material under test is measured and evaluate by parameters changing in capacitance and resistance.

Photolithography is one method of thin film technology, the method also sometimes called UV lithography or optical lithography.  Photolithography is a process using a thin film or parts of a substrate to selectively remove unwanted section. The geometric patterns are transfer from a photo mask to light sensitive chemical photo resist using ultra violet light.

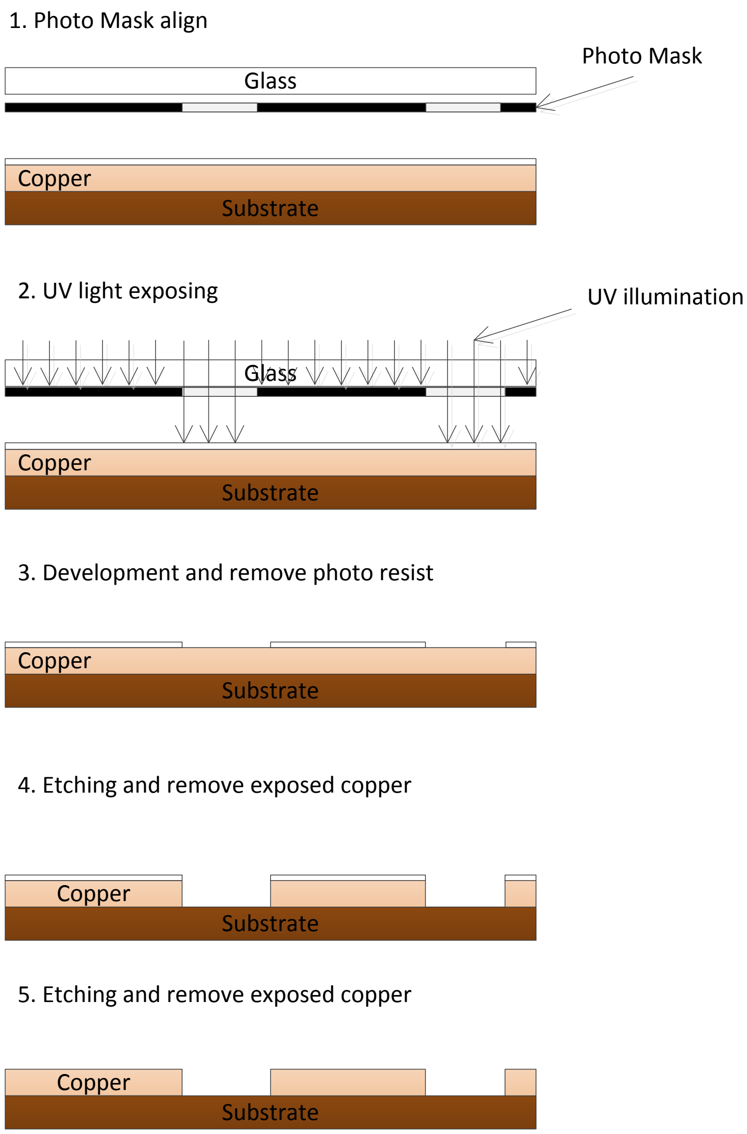


**Figure 5.8** Photolitography process

## 5.6 Summary

- Interdigital sensor has featured that the sensor surface requires single side access to the test material the operational of the sensor is similar with operation to the conventional parallel plate.
- The geometry of the ID sensor can be considered as a repeating set of parallel capacitors and resistive elements.
- Interdigital sensor can be develop using photolithography which is implemented in this thesis.

# *Chapter 6*

# *Experiments, Results and Discussion*

## 6.1 Inter digital (ID) sensor

In order to investigate the potential of using ID sensors to monitor transesterification reactions a simple sensor was fabricated, Figure 1. The resulting sensor had a 1.5 cm$^2$ effective area and 0.4 mm gap width between digits. A precision shunt resistor (40.2K 0.1% tolerance) was used to sense the circuit current. The method design and calculation was based on available publication (Mohd Syaifudin *et al.*, 2009*;* Mukhopadhyay *et al.*, 2005; Sundara-Rajan, *et al.*, 2005).

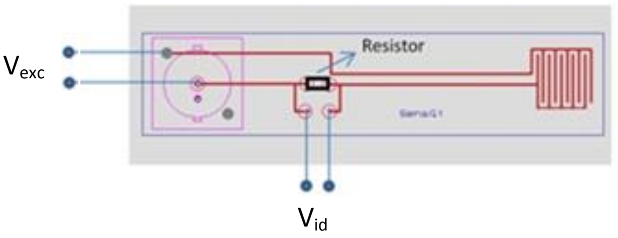


**Figure 6.1** Interdigital sensor layout

In order to determine the impedance of the sensor an alternative signal was applied across the electrodes. Generally when an electric current of a certain magnitude passes through a liquid solution, an effect known as polarization takes place due to electrochemical reaction.

The effects of polarization should be avoided and minimized so is not to cause inaccurate measurement. One of the detrimental polarization effects is electrolysis. Electrolysis will produce a gaseous layer on the electrode surface and this will lead to increased resistance between electrode and liquid solution. Therefore applied direct current voltage excitation is not recommended. Reversing the current will cause the layer to go back in to solution. Thus, if an alternating current is employed, the effect of polarization will be decreased as the gases and other polarization effects produced on one-half of the cycle are dissipated on the other half cycle. Figure 6.2 shows the circuit diagram of ID sensor, the equivalent diagram of current measurement technique. The excitation signal $v_{exc}$ is applied through the sensor.

When the ac excitation signal passes through the ID finger elements, an electrical field is build up and an electric current will flow across the other pair of ID fingers with different magnitude and phase to that of the input signal. The resulting sensing signal can be extracted by measuring the current flowing inside a precision shunt resistor. Since the ac current signal is in phase with the voltage across the shunt resistor, the measurement of current can be done by measuring the voltage in series with resistor. This impedance measurement is called I-V method, to calculate unknown impedance value Z.

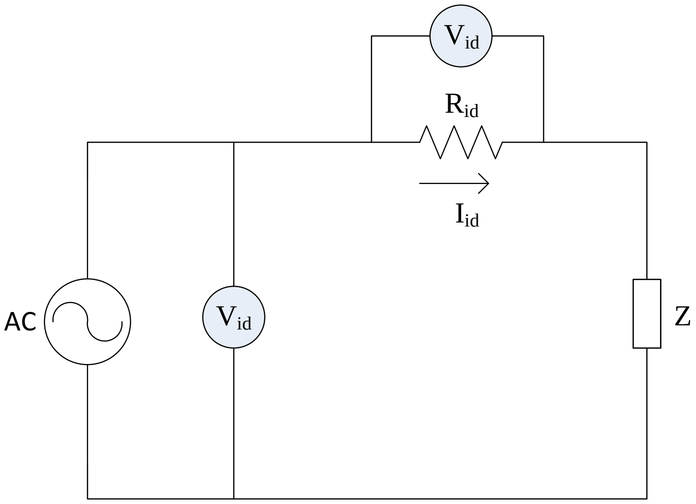


**Figure 6.2** Circuit diagram for ID sensor

This relationship can be expressed:

$$V_{exc} = I_{id} . Z \qquad 6.1$$

$$V_{id} = I_{id} . R_{id} \qquad 6.2$$

$V_{exc}$ is ac voltage excitation and $R_{id}$ is accurately known resistor, $V_{id}$ is voltage measurement from $R_{id}$, phase different between two signal $\theta$ is measured then impedance can be calculate :

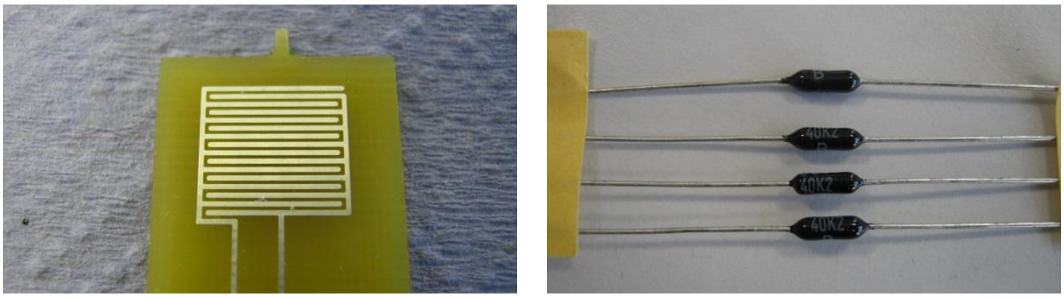
$$Z = V_{exc}/V_{id} . R_{id} \qquad 6.3$$

Real part of the impedance resistive component can be calculate by multiply the impedance with cosines $\theta$. The imaginary component of impedance or reactance can be found by multiply the impedance by sin $\theta$.

$$Z_r = Z . \text{Cos}\ \theta \qquad 6.4$$

$$Z_i = Z . \text{Sin}\ \theta \qquad 6.5$$

In this work the sensor was designed using Proteus 7 PCB design. The electrode pattern was created on a printed circuit board using a FR4 substrate. FR4 is commonly known as epoxy resin fiber glass substrate, this widely used as circuit board materials worldwide. A thin layer of copper foil can be laminated on to one or both sides of FR4 clad. In this research project the sensor design only used one sided copper foil and the fabrication process of the sensor was followed common electronic circuit board production technique. In this design sensor the copper plate thickness was 35µm; the width of the track forming the ID fingers was 1.6 mm and the surface finished by Ormecon (partial chemical tin for ultra-flat pads). The original layout was created by Proteus 7 PCB design software and a number of sensors were produced from a single PCB sheet. The fabrication process was done by professional printed circuit board supplier.



**a** **b**

**Figure 6.3** a. ID sensor and b. shunt resistor

The shunt resistor used in this experiment is manufactured by Welwyn with metal film materials and it has ± 0.1% tolerance.

## 6.2 Experiment Materials and procedure

### 6.2.1 Materials

Vegetable oil used for this experiment was sunflower which sold at a local general superstore, the composition was 100% of sunflower oil. The Methanol came from BDH laboratory supplies with minimum 99.5% with non-volatile matter around 0.005% maximum. Potassium hydroxide (KOH) standard Flake form has 90% purity non sediment.

Sodium hydroxide is highly caustic substances when mix with methanol it will be more dangerous. Methanol can be absorbed through the skin and is a serious contaminant to eyes therefore gloves and protective glasses must be worn when preparing these solutions as well as having a nearby running water supply.

### 6.2.2 Procedure

To make sure the transesterification process can reach maximum yield conversion, Materials composition refer to (Korus, *et al*, 1993; Ellis *et al*, 2008) using 80 grams, 1% catalyst and 28,8% methanol (by weight and 100% excess methanol by stochiometry)

1. Open the potassium Hydroxide (KOH) bottle and using a spatula or small spoon, add the KOH to measuring pan until the balance reads 5.0 grams, Protect balance with thin sheet of paper as any spills could be caught on the paper and disposed of more easily.
2. Add 5.0 grams of KOH to a bottle using a funnel. Place the bottle on the balance, open the methanol bottle carefully decants the liquid about 200.0 grams into the bottle using the funnel into the bottle. This acts to rinse the granules of KOH down into the bottle. Put the cap on the bottle and methanol bottle, this is to keep moisture in the air from being absorbed.
3. Close the lid, tip bottle back and forth until the KOH dissolves, this might take about five minutes, the bottle will get warms as the KOH dissolves, the KOH reacts with the methanol to form methoxide.
4. Safety goggles and rubber gloves must be wear to avoid contact with methoxide. Also dry ice (too cool down the reaction between methanol and KOH) and flow tap water should be available as well.

5. The injection of methoxide will reduce process temperature however the hot plate is automatically controlled and the temperature shortly back to targeted process temperature. To minimize the temperature variation methoxide may be pre-heating.
6. To monitor the changing of the process, the sensor immersed in the oil from the beginning of the process conversion. The changing of impedance can be monitored during the reaction.

Transesterification Process

1. Warm up oil, pour the oil into the flask and turn on the heater stirrer, the heating will make the oil less viscous so it will stir more easily and the heat helps the conversion to biodiesel go proceed at a fast rate. The temperature for the initial experiments was set to $50^{o}$C.
2. Fully immerse the sensor in the reactants in order to monitor the process.
3. Put flask on the magnetic stirrer, and put the magnetic bar (magnetic flea) in the flask.
4. Pour the methoxide in to the oil (open the bottle cap or lid and squirt it into the oil).
5. Turn on the magnetic stirrer to mix the methoxide and oil. Turn up the stirrer set to scale 1 on stirrer, slow enough to keep bar from jumping instead of spinning.

Cleaning procedure for ID sensor

1. Remove the sensor form flask
2. Carefully clean and rinse using alcohol to remove all visible oils

3. Immerse into alcohol
4. Keep the sensor in the air
5. Check the connector of the sensor

## 6.3 Data acquisition

### 6.3.1 Hardware

During the experiments a calibrated National Instruments ELVIS II in figure 6.4 (Educational Laboratory Virtual Instrumentation Suite) was used to generate the excitation signal and acquire the sampled output data. The ELVIS II main features used extensively for impedance measurement are the arbitrary waveform generator (ARB) or frequency generator (fgen) and the Oscilloscope (Scope) function. The ARB has function to generate a digital sinusoid signal with the magnitude of ± 5 volt peak to peak, using an analogue output with DAC resolution of 16 bits and update rate 2.8 MS/s. The measurement channel using 2 analogue input with 1.25 MS/s for single channel, because the ADC use multiplexing for multiple channel (8 differential) the speed for multichannel measurement is 1 MS/s (aggregate). As In impedance measurements two analogue input are needed, maximum measurement for each channel become 500 kS/s. The specification ELVIS II ARB and scope as follows:

Table 6.1 National Instrument Elvis II Specification

| | ARB | Scope |
|---|---|---|
| Number of channels | 8 Diff/16 SE | 2 |
| ADC/DAC resolution | 16 | 16 |
| Sample rate | 1.25 MS/S (single ch)<br>1 MS/s (multi ch aggregate) | 2.8 MS/s |

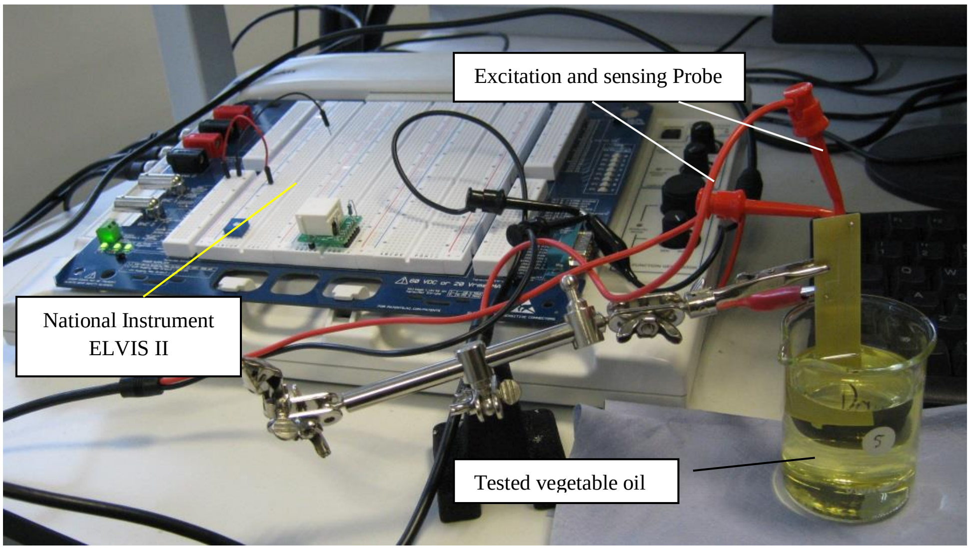


**Figure 6.4** National Instrument Elvis II

### 6.3.2 Sampling rate and aliasing

Sampling rate of a digital data acquisition system is how fast the digitizer converts the input signal, (in this case is analogue signal), to stream of digital values. The analogue input signal may be conditioned in several ways such as any attenuation, gain and filtering prior to the sampling. Nyquist theorem states that a signal must be sampled at a rate greater than twice the highest frequency component of interest in the signal to capture the highest frequency component of interest (NI, 2013).

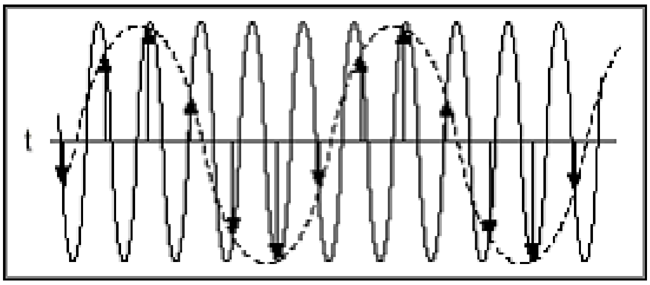


**Figure 6.5** Aliasing frequency

Failure to sample at the required rate will give rise to signal aliasing, where the under sampling of a higher frequency component will give rise to a low frequency oscillation in the digitised waveform. This Alias frequency can be predicted from known input signal and the sample rate. Equation 6.5 shows that alias frequency is a function of the difference between the input signal frequency and closest integer multiple of the sample rate.

$$f_a(N) = |f_{in} – Nf_s| \qquad 6.6$$

Where :

$f_a$ = alias frequency

$f_{in}$ = input signal frequency

$f_s$ = sample rate

$N$ = an integer greater than or equal to 0

Constant N is and integer that assumes the value necessary to bring the therm $Nf_s$ closest to the input signal frequency $f_{in}$. Example, if the input frequency is 150 Hz and the sample rate is 75 Hz it means N equals 2.

### 6.3.3 Labview software

NI Labview 2011 a program development environmental was used with the NI ELVIS II. Labview uses a graphical symbol programming language to create programs in block diagram form. The graphical language is named G, Labview is commonly used for instrument control, data acquisition and industrial automation on various system platforms including Windows, Unix, Linux and Mac OS X.

The programming language in Labview is a data flow programming language. Labview programs are named virtual instruments, vi, because their symbolic appearance and ability to emulate real instruments such as oscilloscopes and multimeters. The vi programs contains three main parts; the block diagram, the front panel and the symbol/connector.

The vi for impedance measurement consists of two main parts, generating waveform and the other undertaking the analogue input measurement.

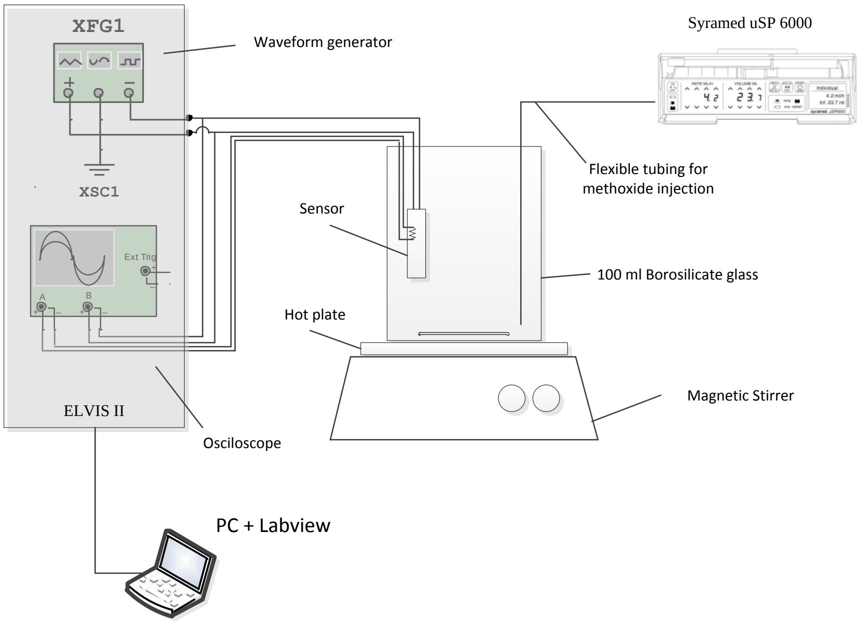


**Figure 6.6** The schematic diagram of impedance measurement

The voltage excitation is vpp ± 5 volt 15 khz generated by function generator (FGen), both sensor input is connected to function generator as well as one input analogue input scope0 (ai0). The sensor output which measures the voltage of the resistor is connected to analogue input scope1 (ai1). FGen of ELVIS II can be activated using fgen vi to generated sinusoidal waveform, maximum waveform can be generated is 2 MHz.

Figure 6.6 shows the layout of the conducted experiment, syramed dozing machine has been used to inject methoxide in to the bottom of the experiment flask. The flask with vegetable oil was put on magnetic stirrer with controller hot plate. ELVIS II unit connected with computer with NI LABVIEW, the output waveform was connected to sensor and the sensor output was link to Aio.

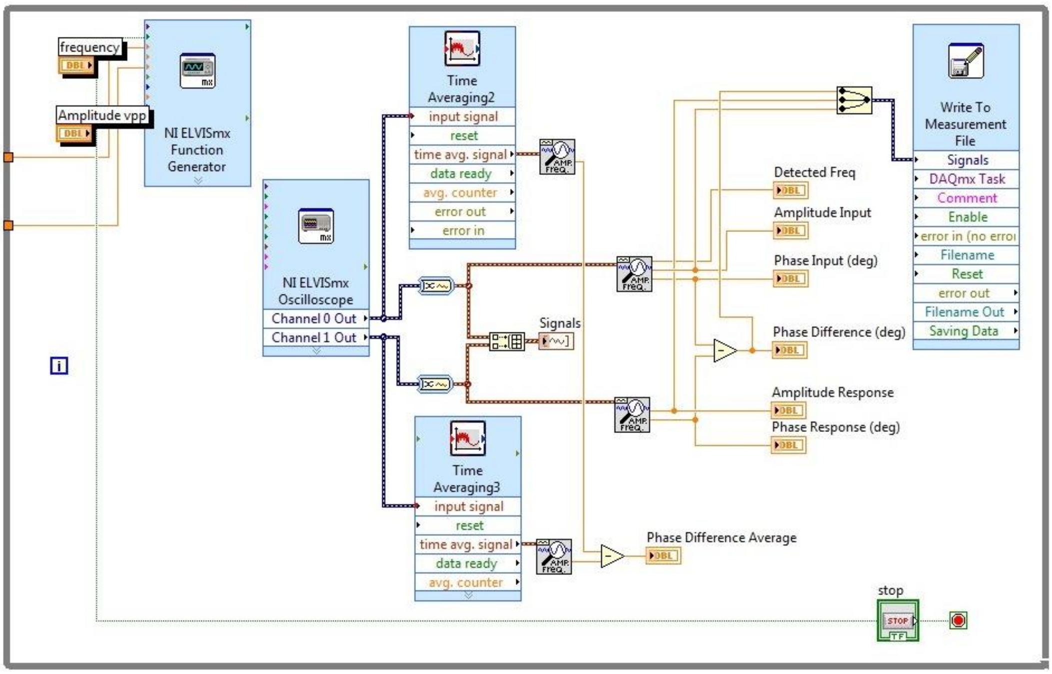
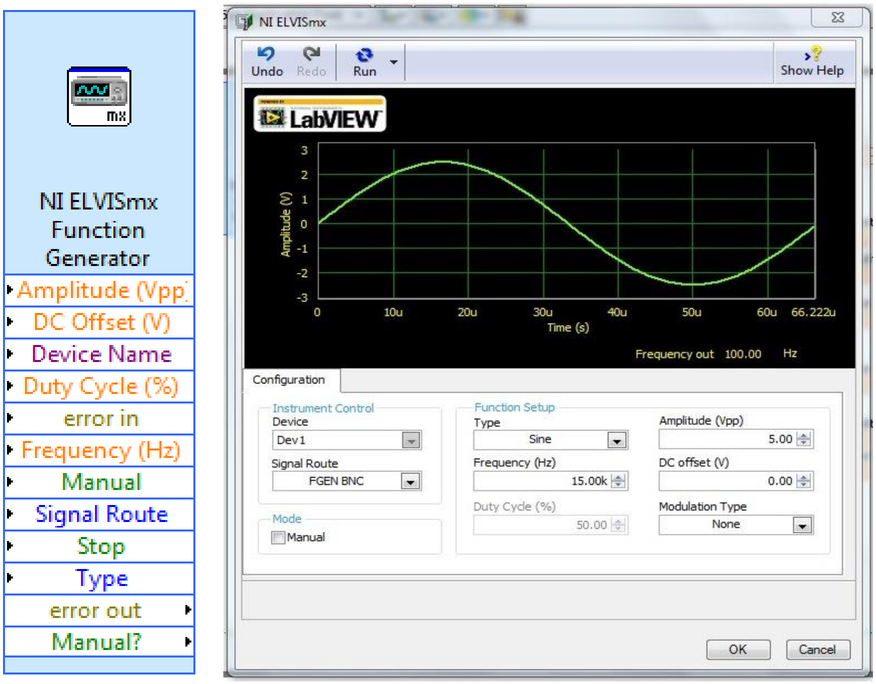


**Figure 6.7** Impedance measurement block diagram

Figure 6.7 shows the impedance measurement block diagram, the waveform which was generated by function generator was physically route to the sensor, and the output from sensor as an input for ai0 (analogue input 0) and ai1(analogue input 1) of the National Instrument hardware. The output signal from the sensor then converted from dynamic data into numeric data. extract single tone information vi is used to extract information from the data such as frequency, amplitude and phase input. By comparing two signal from original waveform with the sensor output, phase different can be known.

Figure 6.8 is function generator express vi, the variable can be adjusted is amplitude and frequency output. It can be seen from block diagram, the connection from function generator is physically connected to the sensors. The BNC connectors are connected to the input sensor and analog input scope0, this connection has the purpose of capturing the sinusoidal waveform source. The other pair connectors are connected to the shunt resistant. The data output from scope0 and scope1 cannot directly used as the output in the form of waveform dynamic data. It is necessary to convert dynamic data to numeric with the other express vi or function, the output dynamic data was processes by *convert form dynamic data* vi, the conversion can be in the form of numeric, Boolean or array in this case the data was converted into numeric. Figure 6.9 shows the express vi convert form dynamic data.



Frequency out 100.00 Hz

Device: Dev1

Signal Route: FGEN BNC

☐ Manual

Type: Sine

Frequency (Hz): 15.00k

Duty Cycle (%): 50.00

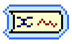
Amplitude (Vpp): 5.00

DC offset (V): 0.00

Modulation Type: None

**Figure 6.8** NI ELVISmx Function Generator

In Labview a vi which can be configured through a dialog box is called an express vi. The impedance measurement in this experiments involved using some built in express vi's. Express vi can be configured by setting options in the configuration dialog box and it is appear on the block diagram as expandable nodes.

|  | <br> |
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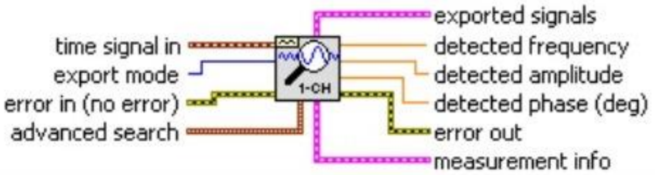
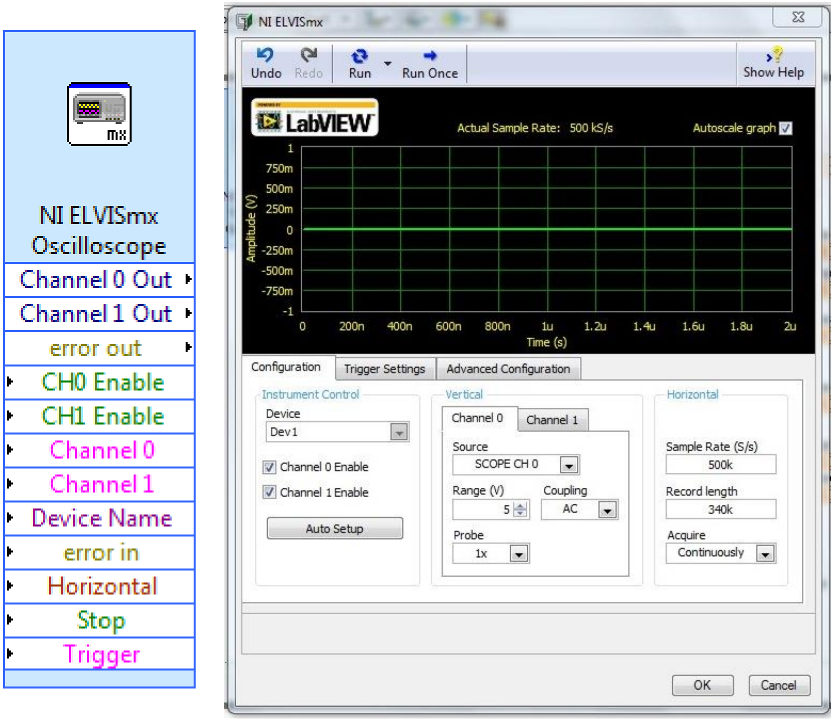
|  | <br> |
| a | B |

**Figure 6.9** Convert from Dynamic Data Express VI and extract single tone information vi



Actual Sample Rate: 500 kS/s

Autoscale graph ☑

Instrument Control

Device: Dev1

☑ Channel 0 Enable

☑ Channel 1 Enable

Vertical

Channel 0 | Channel 1

Source: SCOPE CH 0

Range (V): 5

Coupling: AC

Probe: 1x

Horizontal

Sample Rate (S/s): 500k

Record length: 340k

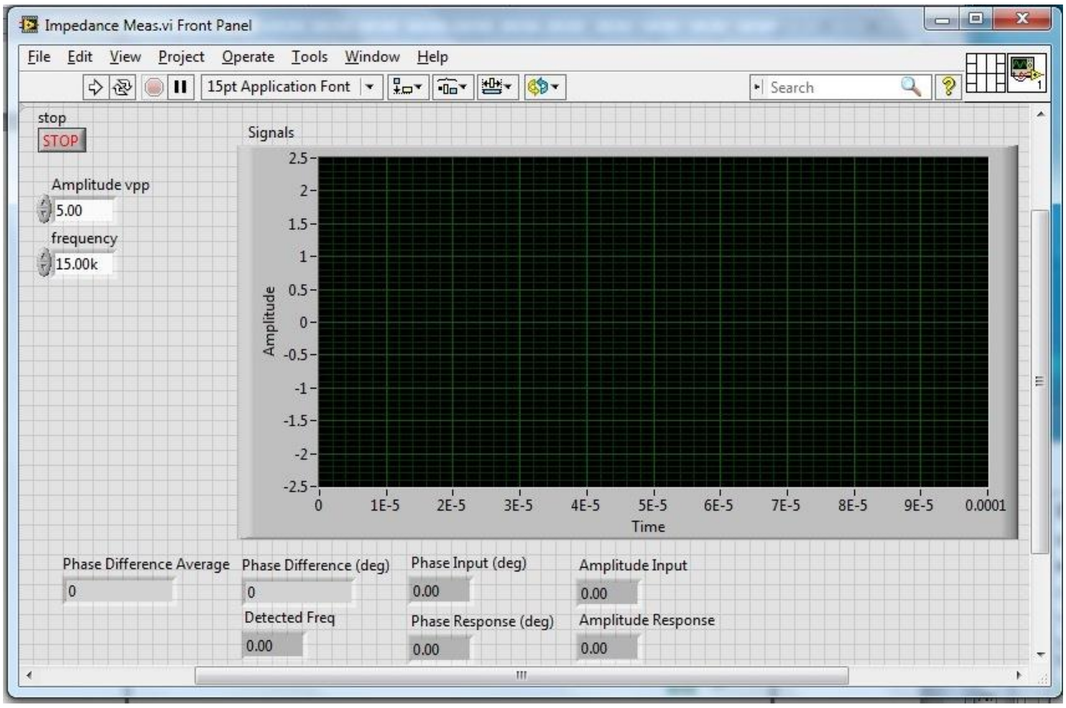
Acquire: Continuously

**Figure 6.10** NI ELVISmx Oscilloscope

Figure 6.10 shows the express VI for oscilloscope function, there are two channel input for ID sensor application. The scope has 1 MS/s multiplexing and single channel maximum. If two channel is used the analogue to digital converter is limited to 500 kS/s. However this speed is more than enough for the impedance experiment using 15 kHz excitation waveform.

The output from *convert form dynamic data* vi then split into two wired connections. One connection is joined with *build array* vi to create real time signal visualisation in the front panel software, it is appear as *signals* on front panel in the function of signal magnitude and time.

This graphical signal show in figure 6.11 is important as it enables the user to check whether the waveform is properly configured. The wired from sensor output has goes to e*xtract single tone information* vi to extract the signal waveform into frequency, amplitude and phase.



Amplitude vpp 5.00

frequency 15.00k

Phase Difference Average 0

Phase Difference (deg) 0

Detected Freq 0.00

Phase Input (deg) 0.00

Phase Response (deg) 0.00

Amplitude Input 0.00

Amplitude Response 0.00

**Figure 6.11** Impedance measurement front panel

The extracted frequency, amplitude and phase both input and output then fed into write to measurement file in numeric value. There are some choices to save the file in binary file using TDMS file and based text file LVM, in this experiment text based file have been used. Figure 6.11 is front panel of impedance measurement vi has some interface to check frequency and amplitude parameters have properly setting. Figure 6.12 shows the layout of the biodiesel impedance measurement layout inside fume cupboard.

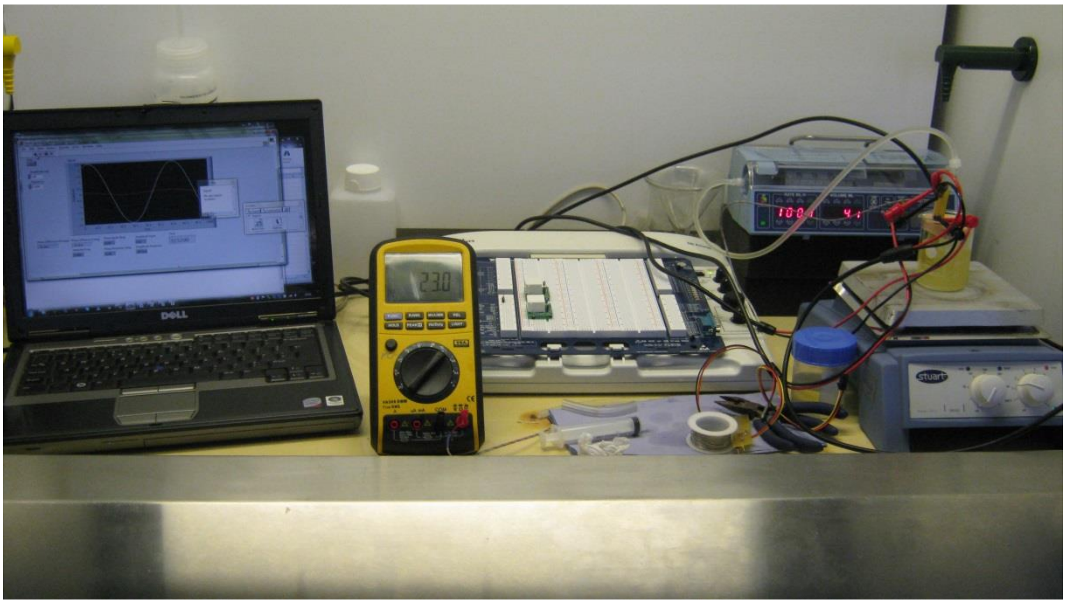


**Figure 6.12** Equipment for biodiesel single frequency impedance measurement

The experiment divided into two sections, initial experiment which was using digital multimeter with capacitance measurement and further experiment using waveform and impedance measurement. Early experiment conducted to evaluate the possibility using capacitance measurement using digital multimeter to measure chemical reaction in biodiesel transesterification process. Based on first investigation, the ideas is further expanded using impedance measurement which is capable to measure both conductance and permittivity.

## 6.4 Result

To explore the possibility of using capacitance measurement as a method of monitoring biodiesel process. Initial experiments were conducted using a digital multimeter with an auto range capacitance measurement capability.

### 6.4.1 Initial experiments capacitance measurement

The transesterification reaction was conducted at temperature of 50$^o$ C with methanol in stoichiometric molar ratio alcohol to oil 6 to 1, and 1 % of KOH catalyst. The transesterification process was monitored for 60 minutes and capacitance reading has taken every second.

The capacitance measurement system in general includes a sensing probe and a measuring module. The experimental setup was very simple one which used, interdigital capacitance (IDC) sensor probe and the measuring modules as shown in figure 6.13. In this setup includes the IDC and two digital multimeter modules (DMM) and a PC. As show in figure 6.14 on of the digital multimeter was used for the capacitance measurement and the other one used with a thermocouple temperature probe for temperature measurement. The DMMs used have features such as real time graphic display with scale grid, real time display of maximum and minimum values with time stamp and current measuring window.

The DMM provide advanced feature with optional accessories such as a temperature probe that is used in this experiment. Software (PC Link) allowed the DMM to send measured data to the PC via a usb connection. Capacitance measurements provided by DMM were based on the charge/discharge method and measured capacitance in the range of 0.01 nF to 9.99 mF can be measured with stated accuracy of ± (0.8% rdg +3) and a resolution of about 0.01 nF.

**Figure 6.13** Measurement and experiment lay out for capacitance measurement

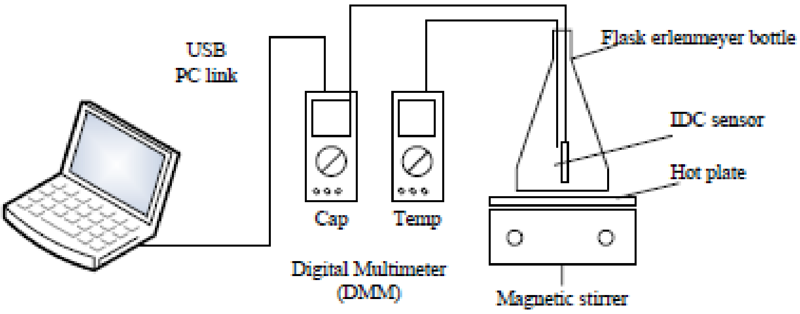


**Figure 6.14** Measurement and experiment lay out

The arrangement used for the initial experimental work is show in figure 6.14. The sensor was designed with Ares PCB design software, and the sensor was manufactured by engraving machine. The sensor as depicted in figure 6.15 was made from copper clad pcb board and the conducting layers of the board made of thin copper foil. A drawing of the sensor was transferred to a PC controlled engraving machine. The process then removed the undesired copper and left designed copper circuit on the surface. Following machining the sensor was cut to desired dimensions to make it suitable for testing.

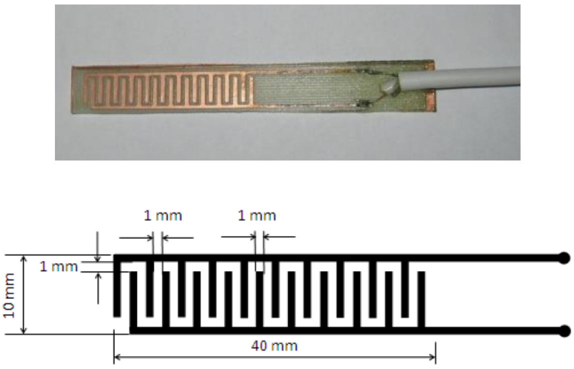


**Figure 6.15** Interdigital capacitance sensor

The technique used for the preliminary experiments was to continuously capture capacitance values every second throughout the entire reaction time. The capacitance values from IDC sensor were then converted from an analogue electrical signal, via an analogue to digital converter to give a digital output signal. The digital data was transferred to the computer by means of a software link and store in a spreadsheet file for further analysis. As dielectric value of the raw materials was different to dielectric value of final products a change in capacitance was expected.

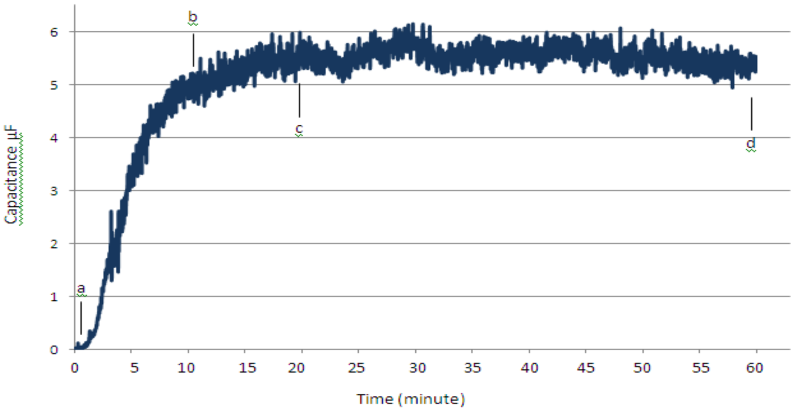


**Figure 6.16** Capacitance measurement during transesterification process using Interdigial Capacitance IDC sensor. Transesterification process using Alkali catalyst $KOCH_3$ mixed with rapeseed vegetable oil at $50^oC$, sample rate at 1 second

Figure 6.16 illustrates the results gained during the initial experiments. Different phases of the biodiesel transesterification reaction are indicated by a,b,c letters. Step a, indicates that the reaction begins with methoxide added into vegetable oil. Capacitance value of hot oil (50$^o$C) was approximately 86 pF only a 3pF increase from the value in air. Since the oil resistance is very high (the resistance value is beyond of DMM resistance measurement ability, more than 300 MΩ), the capacitance measurement is not affected by oil resistance. In contrast, capacitance value of methoxide is high as 13.68 μF. In the early experiments the DMM was set to use auto mode measurements, however the DMM cannot read the value because the rapid capacitance changes within the reaction. To make the DMM be able to read the capacitance value, manual mode has used in range of 10 μF, consequently, small capacitance value for oil in the early process cannot be measured, it showed zero.

Step 2 (a-b) the value of capacitance for the oil and vegetable oil mixtures climbed rapidly during first 10 minutes. During this stage the vegetable oil (mainly Triglycerides) reacts with the methanol in the presence of potassium hydroxide to form diglyceride, monoglyceride, methylesters and glycerol. Step 3 (b-c) the process continued to form methylesters and glycerol while the amount of diglyceride and monoglyceride was reduced. This stage is not rapid process as compared with step 2 (a – b), because only small amounts of monoglyceride and diglyceride are converted into methylester. From point c to point d, step 4 (c to d) the final reactions takes place and the biodiesel reaction begins to reach a state of chemical equilibrium. In this stage the capacitance value depends on the combination of different liquids that make up the final product. The final product include methyl-esters, glycerol, catalyst (KOH), excess methanol and contaminants such as water and they all contribute to the final dielectric properties and hence the capacitance detected.

### 6.4.2 Impedance measurement experiment

#### 6.4.2.1 Sensor reproducibility

Figure 6.15 shows the results of sensor measurements conducted in air and selected oils at a temperature of 24$^{o}$C. Several repeated measurements were undertaken to test sensor repeatability and sensor stability. In this study output voltage and phase were recorded and compared, the results can be seen from figure 6.17 both value of output voltage and phase. The parameters indicate the ability of the sensor to reproduce output reading when the sensor operated in the same ambient conditions. In the air the reading of phase difference averaged 49.9 mV with the variation of ± 0.085 mV.

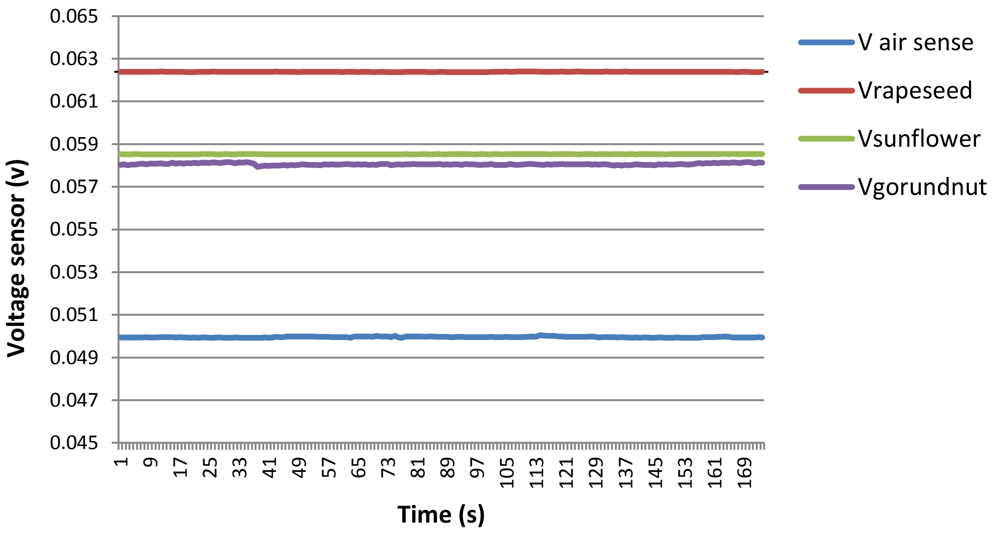


**Figure 6.17** Sensor output in air with 15 kHz excitation ±5 volt vpp and temperature 24$^{o}$C.

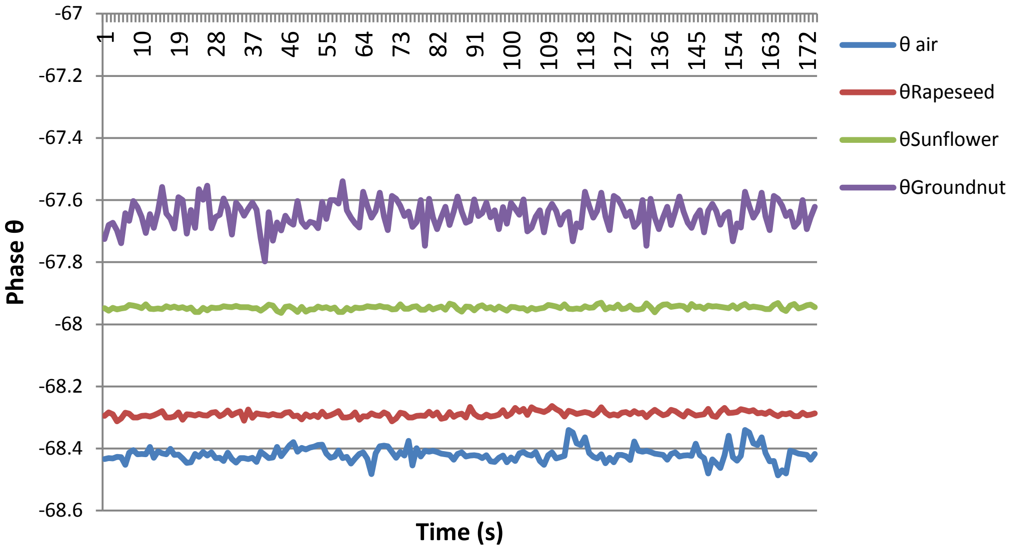


**Figure 6.17** Sensor output in air with 15 kHz excitation ±5 volt vpp and temperature 24°C.

Another experiment was undertaken in order to compare sensor readings when submerged in different materials. The ID sensor was tested using different liquids such as, vegetable oil, tap water and deionized water. The sensor with steady excitation was tested for several times to get the response.

The result showed the different response obtained from the different measured materials. In the experiment the sensor was immersed in the liquid under test for 5 minutes, and the resulting voltage and phase measurements recorded in to file. From the values of voltage and phase measured, the real component of impedance and reactance including capacitance value were calculated.

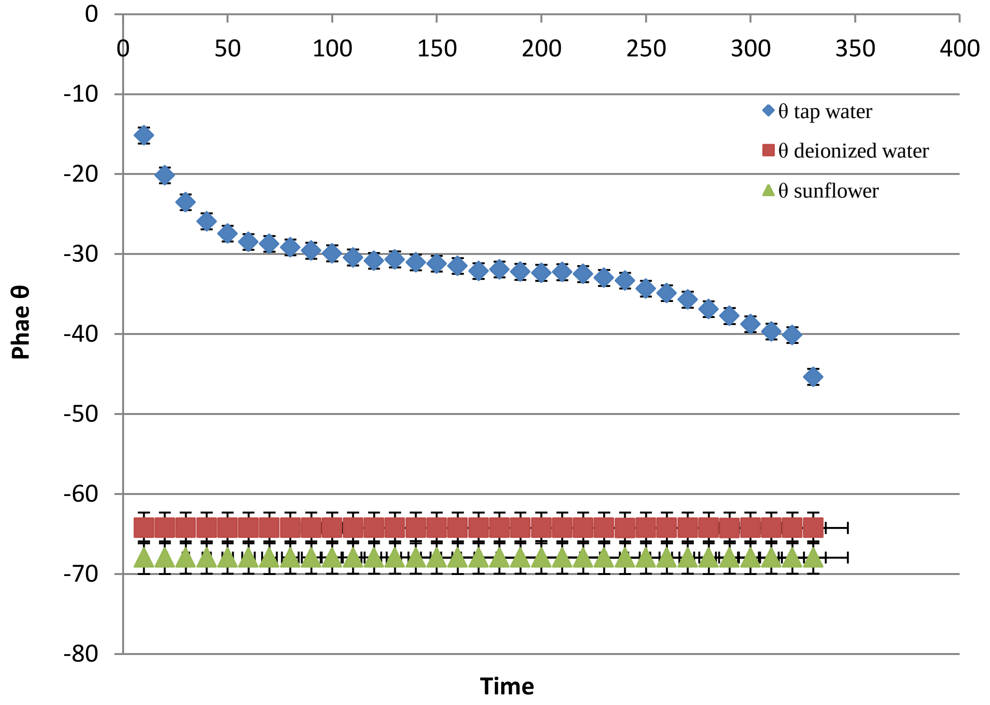


**Figure 6.18** Impedance measurements of selected liquids at room temperature (24°C).

Figure 6.18 shows impedance measurement of three kind of different liquid, deionized water, sunflower oil, and tap water, the measurement in room temperature of 24° Celsius. The results represented cover a 5 minute time period. The deionized water theoretically has fewer ions because it is already purified with mineral ions removed, the removing ions from water usually using ion exchange process or mechanical filters. The sensor output for deionized water is remaining constant for 5 minute measurement for both voltage output and phase output. The steady reading indicates the only few charge carrier present in the liquid. The sunflower oil has similar profile compare with deionized water, but has different constant value.

Tap water is usually full of ions from the soil ($Na^+$, $Ca^{2+}$), from the pipes ($Fe^{2+}$, $Cu^{2+}$), and other sources. The present of the charge carriers make the degree of polarization water change over the measurement period.

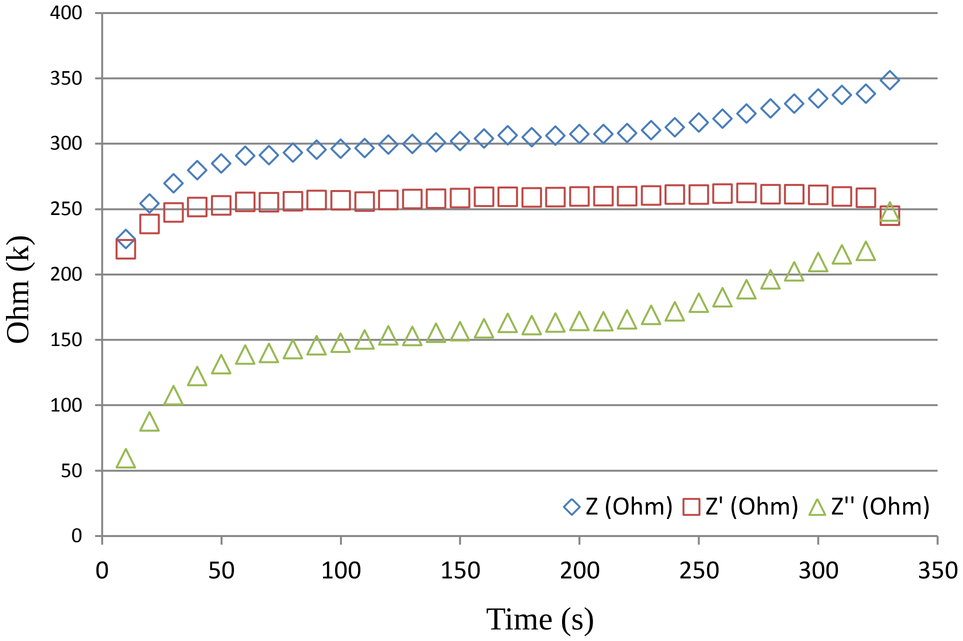


**Figure 6.19** Impedance measurement of tap water at room temperature 24$^{o}$ C, 15kHz waveform excitation and ±5 volt vpp

Figure 6.19 shows the impedance measurement of tap water subject to a 15 kHz excitation. The complex impedance is seen rise during in the first 60 seconds and then slightly stay approximately constant for 150 seconds before exhibit a very small further increase. Water impedance is mostly influenced by the imaginary component of impedance Z'' while the real component Z' has not significantly changed. Z'' is much lower compare with Z' during the first 50 seconds and continues to increase approaching the value of Z'. Sunflower oil on the other hand, the measurements were different and the imaginary component of impedance was much higher than the real component. Comparing with sunflower oil and deionized water results as indicated in figure 6.18 it can be seen that tap water exhibits higher fluctuations. This result leads to the fact that the fluctuations are due to the influence of conductivity on the measurement, a fact that ca be expected tap water has a higher conductivity.

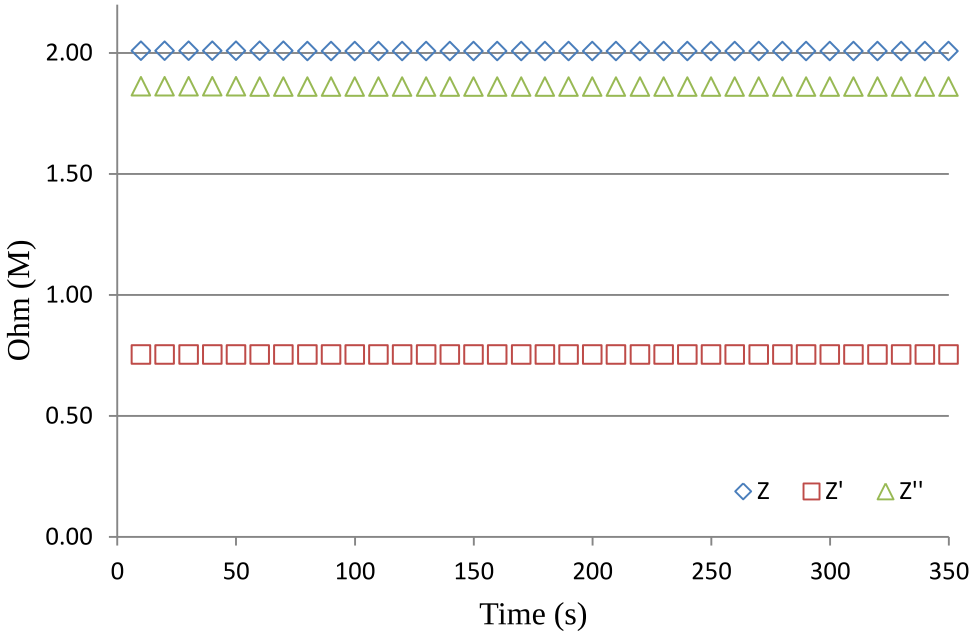


**Figure 6.20** Impedance measurement of sunflower oil at room temperature 24$^{o}$ C. 15kHz waveform excitation and ±5 volt vpp.

Figure 6.20 and figure 6.21 shows impedance measurements for sunflower oil at 24$^{o}$C, the impedance is calculated with equation 4.6. It can be seen from the graph that the impedance complex of the vegetable oil is very stable during the measurement period. Compared with both tap water and deionized water sunflower oil has higher impedance at 15 kHz. Complex impedance value is stable at 2.007 MΩ, the real part is 753.763 kΩ and imaginary parts is 1.86 M Ω.

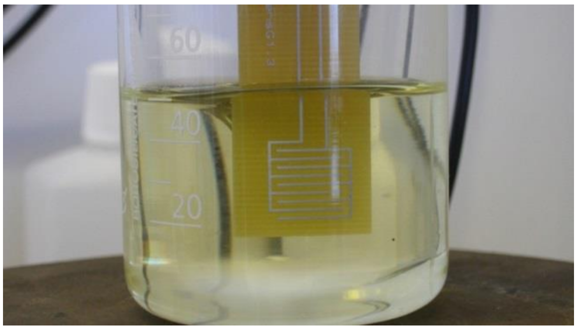


**Figure 6.21** ID sensors in vegetable oil impedance measurement

Vegetable oil consists mostly of triglycerides, vegetable oil molecules are non-polar molecules and they have very strong covalent bonds so they cannot dissociate easily, therefore ions cannot be formed, and thus electric current cannot be conducted thru the oil solution. Except, when the oil contains some impurities such as free fatty acid, water and the other conductive particles like in waste frying oils. When conductivity would be expected to be higher than the value associated with pure oil.

### 6.4.2.2 Temperature influence in static Impedance measurement.

The impedance measurement is temperature and frequency dependent, and an experiment was undertaken to measure the change of complex impedance during the heating of sunflower oil. The measurement was conducted as the temperature changed from room temperature to 70°C.

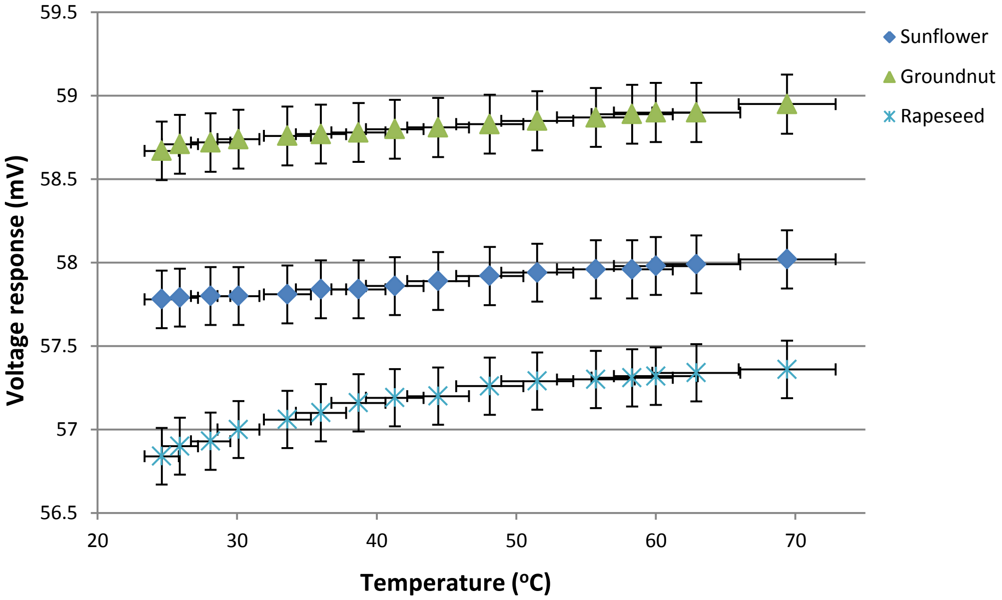


**Figure 6.22** Voltage output when heating sunflower oil from 24-69° C. 15 kHz waveform excitation and ±5 volt vpp.

It can be seen from figure 6.20 the response voltage is increase steadily from 57.78 mV to 57.99 mV, giving a difference is 0.21 mV. The increasing voltage is 0.004 mV per degree Celsius. The phase θ is changing les rapidly, it changed by 0.32 degree from 24.6 to 69.4$^o$ C, 0.0071 degree per 1$^o$ Celsius.

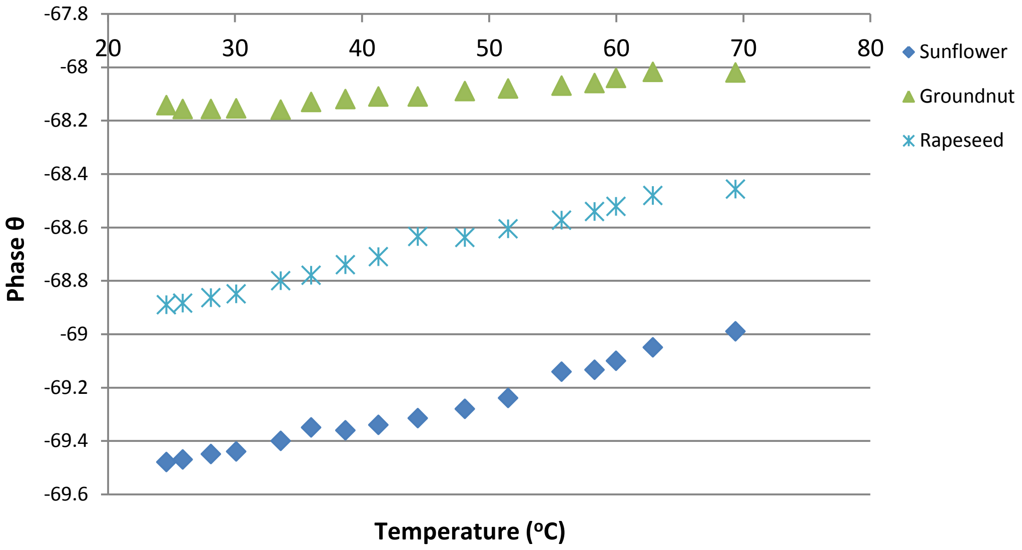


**Figure 6.23** Phase output when heating sunflower oil from 24-69$^o$ C. 15 kHz waveform excitation and ±5 volt vpp.

The results presented in figure 6.22 and figure 6.23 confirms that impedance is a function of temperature. The impedance change due to temperature change is relatively lower than the increasing voltage and phase in the biodiesel process that has been shown to occur during transesterification, therefore the value recorded during biodiesel production is considered to be caused predominantly by the reaction.

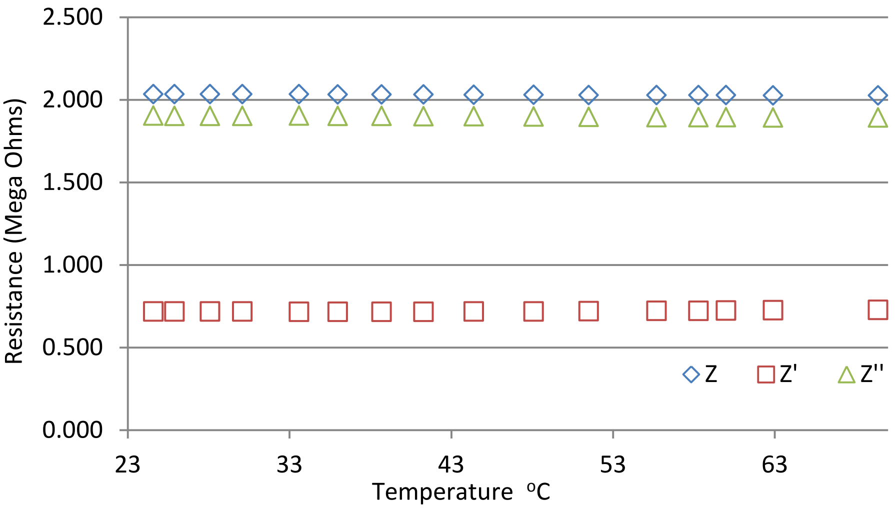


**Figure 6.24** Impedance measurement of sunflower oil heating up from 24 -69°C, 15 kHz waveform excitation and ±5 volt vpp.

Figure 6.24 also shows calculated impedance using equation 6.4 and 6.5 from heating sunflower vegetable oils. It can be seen from the graph that imaginary components has lower value than real component.

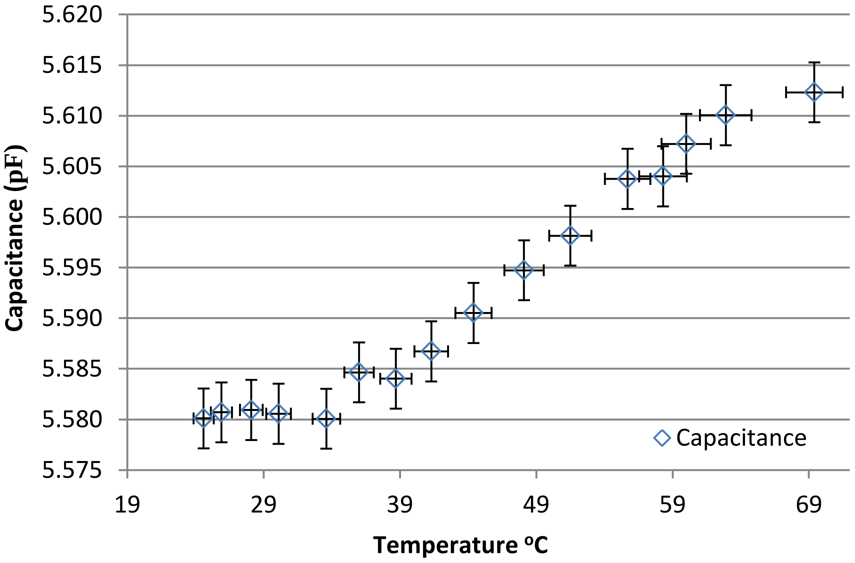


**Figure 6.25** Calculated capacitance measurement of sunflower oil heating up from 24 -69°C, 15 kHz waveform excitation and ±5 volt vpp.

Temperature increase is well understood to cause increased electrical conductivity as shown in figure 6.25, and the influence of the conductivity by temperature can be expressed (Judendorfer, *et al*, 2011):

$$\sigma = \sigma_0 . e^{\frac{w}{k.T}} \qquad 6.7$$

Where σ is conductivity of the material, k is the Boltzman constant and T is the temperature, w is the activation energy and $\sigma_0$ is conductivity at room temperature . An increase in liquid temperature will cause the liquids viscosity to decrease and this leads to increase in the ions mobility in liquid. Also elevated temperatures may cause an increase in the number of charge carrier available in the liquid due to dissociation of molecules. Since conductivity in liquid is dependent factor as in equation 6.7, increasing liquid temperature lead to increasing liquid conductivity subsequently (Bartnikas, 1994).

It can be seen that capacitance has steady value at lower temperatures and has slight increase at higher temperatures. The slight increase in capacitance value shown figure 5 is caused by increasing liquid dielectric constant. Both real part and the imaginary parts increase slightly with temperature, resulting increasing capacitance values. Furthermore, increasing conductivity values due to temperature make the value of dielectric loss increase respectively. This result agrees with other measurement (Romano & Sorichetti, 2011).

### 6.4.2.3 Measuring different oil with different frequency

The following graph shows the experiment conducted in some oils with different sensor excitation frequencies. The experiments were carried out using three vegetable oils with frequency range from 400 Hz to 40 kHz.

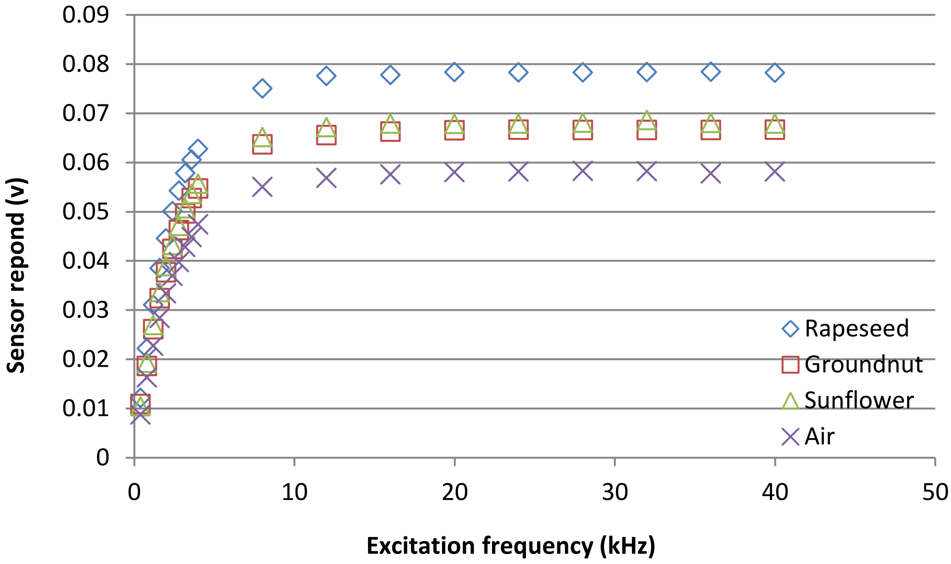


**Figure 6.26** Sensor output in selected vegetable oil, in different excitation frequency up to 40 kHz ±5 volt vpp and temperature 24$^{o}$C

The measurement shows the output of the sensor is low from 400 Hz to 10 kHz. Above 10 kHz sensor output has optimum output. The sensor output differs between the type oils due to variation in triglyceride bonds.

### 6.4.2.4 Impedance measurements on transesterification biodiesel process

The virgin vegetable oil used for the work described is a predominately non-polar fluid with a low ion concentration. On the other hand, the methoxide is a polar fluid with a high ion concentration (Zhou & Boocock, 2006). These differences give rise to different electrical properties (conductivity and permittivity) and each individual fluid would be expected generate a significantly different response from the ID sensor.

As both fluids are immiscible then there is a need to mix the reactants together before the reaction may proceed. Without mixing there is a high mass transfer resistance between the fluids and the transesterification reaction would only proceed as a very slow rate. During mixing it is normal to inject the methoxide into the raw oil and hence the initial sensor response will be based on the electrical properties of the raw oil. With further mixing the sensor response will change to reflect the increased conductivity due to the increased ion concentration associated with the methoxide.

Therefore, based on mass transport phenomena theory, mass transfer resistance exists between two fluids. The progress of mass transfer can be detected by measuring ion transport throughout the oil. The measurement may be conducted from triglyceride phase which has high resistance or methanol phase with high conductivity. The influence of mass transfer resistance is clearly feasible at low temperatures compare with high temperature (Stamenkovic *et. al.*,2008 ). As the vegetable oil has high viscosity at lower temperatures, heating the oil during the transesterification process will do a favour to speed up the process by shortening mass transfer control region time.

**Table 6.1** Permittivity value some vegetable oils and methanol at 25°C (Romano & Sorichetti, 2011).

| Material | Permittivity ε |
|---|---|
| Rapeseed | 3.08 |
| Sunflower | 3.09 |
| Soybean | 3.04 |
| Corn | 3.13 |
| Methyl ester | 3.32 |
| Methanol | 32.6 |
| Glycerol | 42.5 |

Recent hypothesis about transesterification process on batch reactor stated the mechanism reaction of transesterification process consist an early stage of mass transfer controlled region followed by kinetically controlled region. Chemical reaction between triglyceride with methanol will occurred after mass transfer start. During the reaction long chain of triglyceride hydrocarbon molecule will break out become smaller chain diglyceride, monoglyceride and glycerol. The change in molecule composition will be affected how the mixture adsorbs the applied electromagnetic.

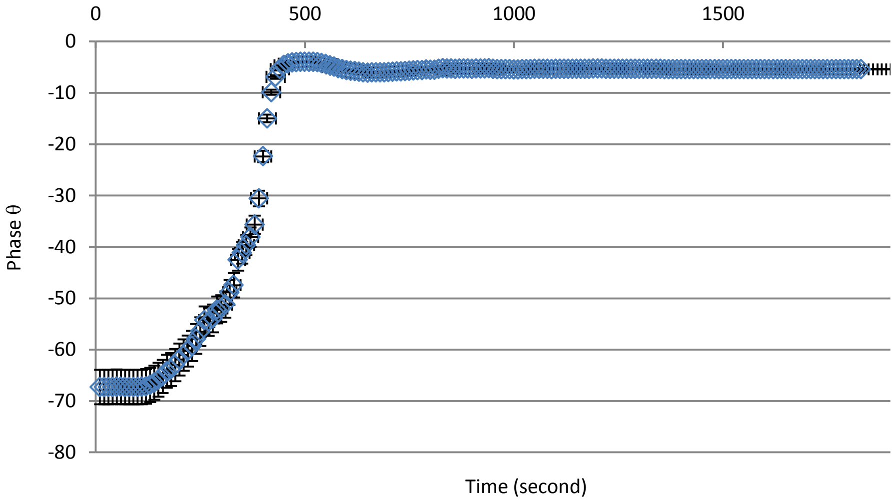


**Figure 6.27** Phase shift measurement of transesterification process at 40°C

Figure 6.27 and Figure 6.28 shows the phase difference and voltage response measured during a sunflower biodiesel transesterification process carried out at 40°C. Data values were recorded at one second intervals and averaged over a 10 second period to reduce noise. θ phase angle is seen to remain unchanged during 60 seconds following introduction of methoxides. The signal is then observed to rapidly increase during the next 300 – 400 seconds. The rapid changes in phase angle (θ) may have been caused by a combination of changes in conductivity (σ) and/or changes in material permittivity (ϵ).

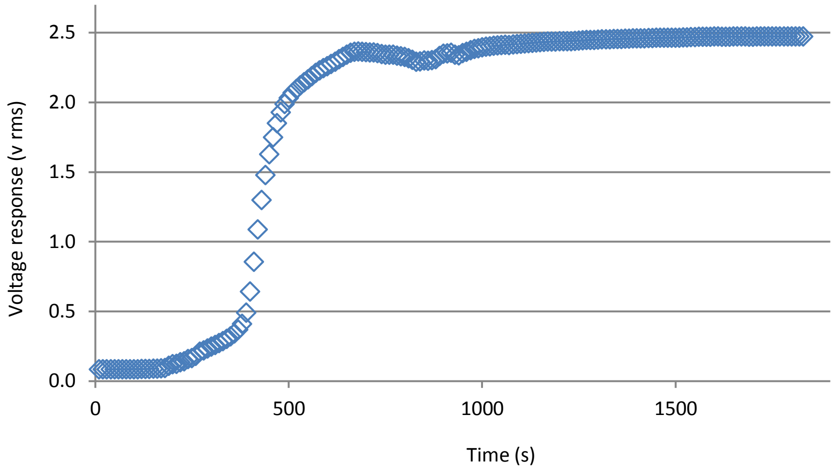


**Figure 6.28** Voltage response of transesterification process at 40$^{o}$C

Figure 6.29 illustrate the change in impedance during the reaction. In the early stage of the process the reactance if of higher magnitude than the real component, by a factor of two. This is caused by the permittivity of triglycerides, and vegetable oil having a small value. When the methoxide was introduced with by continuous injection at rate of 300 ml/minute and over 90 seconds period, the reactance can be seen to drop rapidly. Since the fluid was then a mixture of vegetable oils and methoxide, the permittivity which sensed by sensor is reduced by the presence of the methoxide.

Figure 6.29 shows that real part of the impedance is lower compare with the imaginary part. Precision shunt resistor value used has significant influence in moving phase impedance. A shunt resistor 40.2K Ω 0.1% tolerance, was selected so as to increase sensitivity on imaginary part of total impedance (Mukhopadyay, 2005), more over it is used to suppress highly conductance sensitivity during introduction of methanol into the vegetable oil.

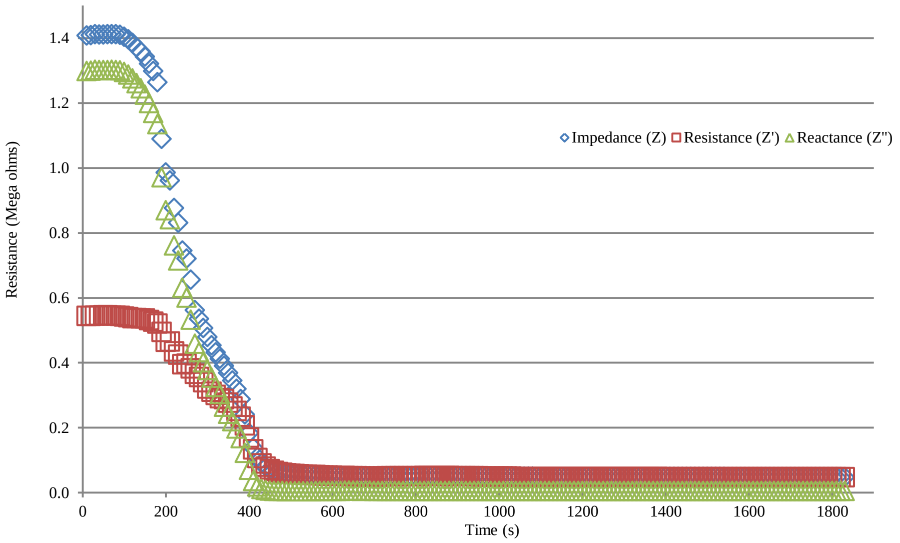


**Figure 6.29** Impedance measurement of trasesterification process

Figure 6.29 represent simultaneous measurement of resistance (real component of impedance) and capacitance (derived from the imaginary component) during the sunflower oil transesterification process. The resistance results are measure of ion transport within the mixture, and in this case sense disperse of the methanol into the vegetable oil. Furthermore the resistance curve ($\frac{dR}{dt}$) represents the rate of change of ion distribution and hence results gives a visualization of the mass transfer process occurring during the mixing phase of the reaction. This gradient is highly affected by the droplet size of the dispersed metoxide and it reduces rapidly with progress of transesterification reaction

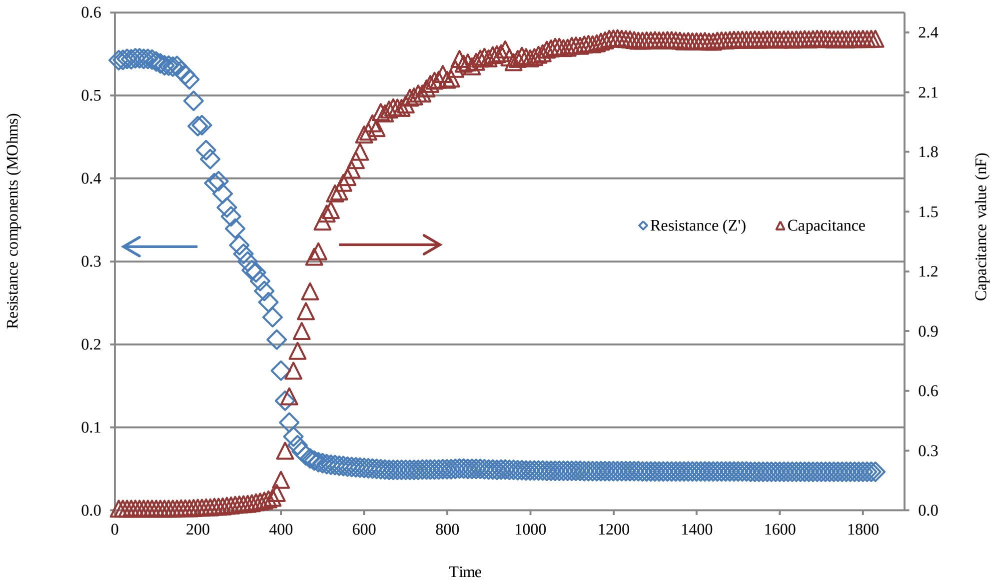


**Figure 6.30** Resistance and Capacitance measurement during the transesterification process

The mass transfer resistance is caused by the initially small availability of active specific catalyst surface area, which is mainly covered by adsorbed molecules of methanol (Veljkovic *et al.*, 2009). It is generally accepted that the progress of mass transfer exhibits sigmoid shaped process kinetics which have a slow slope in the early stage, a rapid change in the middle and a slowing down period before it steady state conditions are attained.

From the result presented (figure 6.30) it can be seen that when the ion distribution (mass transfer) has nearly reached steady state the capacitance value start has increase. The increase in capacitance is initially rapid and then reduces before reaching a steady state. During the early stages of the transesterification process, the reactance is the two forms the triglyceride phase and the methanol phase. As the two phases are immiscible poor diffusion between the phases has resulted in a low reaction rate. When methyl esters are formed, they will become a mutual solvent for reactants (Veljkovic *et al.,* 2008), and boost the reaction rate as seen by the steep increase in capacitance value.

The measured capacitance of vegetable oil at the beginnings of the process was very low approximately 8.18 pF, and the value increased when the chemical reaction began. The measured capacitance value is depends on the permittivity of the reactants. Since the permittivity is determined by how the molecules of the chemical compounds respond to the applied electromagnetic field, it means changes in the molecular composition of the reactants will give rise to changes in measured permittivity.

### 6.4.2.5 Mass transfer and conductivity

In the early stages of the transesterification process the methanol is ineffective and the reaction rate is limited by the interface *mass transfer resistance* (Kai, *et al*, 2010). The speed and the successfulness of the chemical reaction controlled region is very likely controlled by first step of the process, the mass transfer control region. If this is so, then it will be beneficial to monitor the progress of mass transfer processes and use this data for feedback into the process control system. The impedance measurement process presented offers the potential to monitor the initial mass transport controlled portion of the reaction for process control purposes. The mass transfer rates of methanol to the oil phase via the oil-methanol interface will increase with increased interfacial area (Furukawa, *et. Al.,* 2010). Therefore agitation of the reactants during the initial stages of the reaction is an important limiting process. It has been confirmed that catalyzed transesterification of the vegetable oils is not a homogeneous reaction, but is characterised by slow reaction rates at both initial and final reaction stages. The initial slow reaction rate is due to the immiscible nature of the reactants. The slow reaction rate at the final stage is because catalyst is extracted by glycerol and becomes separated from the reactants to the immiscible and dense glycerol phase (Boocock, *et al.*, 1996). Consequently, the reaction slows down to the point of being impractical for a commercial one step process. It is evident that degree of contact or solubility of polar methanol or glycerol and a non-polar oil phases strongly affect the reaction rate. In other words, mass transfer between two phases plays a critical role during transesterification. In order to enhance the contact between the two phases, several techniques such as mechanical mixing, ultrasonic cavitation and hydrodynamic cavitation, extra inert co-solvent, and catalyst free transesterification under super critical methanol condition have been investigated (Zhang, *et al*., 2009). In general, mass transfer intensification has the purpose of reducing mass transfer resistance to gain the fastest transesterification process or to increase energy efficiency in the transesterification process.

Methanol and vegetable oils are immiscible and this reduces the interface surface area, hence stirring (mechanical mixing/agitation) is required to develop conditions favourable for mass transfer to occur between the methanol phase (methoxide) and triglyceride phase (oil).

For this reaction the catalyst resides exclusively in the polar methanol phase. Previous work (Ataya, *et, al*., 2007) has shown that at low temperatures the mass transfer between phases is limited and influenced by the time taken for methoxide addition and that the immiscibility from both reagents leads to mass transfer resistant (Guan, et. Al., 2009). As a result ion distribution within the triglyceride phase will follow the mass transfer process, i.e. enhanced mixing will increase interface area and this will result in higher transport of ions into the triglyceride phase. It would be expected that the initial rate of mass transfer would be low, increase during methoxide addition and then reduce when mixing was complete. The mass transfer limitation in the beginning of the process on batch reactor is influenced by power given to the process through mechanical agitation. The expected sigmoidal curve of methanolysis has been observed by several authors.

Figure 6.31 illustrates the change in measured conductance throughout the transesterification at the temperatures considered. In the early stages of the process, methoxide was introduced into the reaction vessel at a controlled rate. Initially the sensor was exposed only to the non-polar triglyceride phase, as a result the measured conductance was low. With introduction of methoxide and the subsequent mixing of the phases, the current flow through the resistor increased gradually in response to more mobile charge carriers being present in the triglyceride phase.

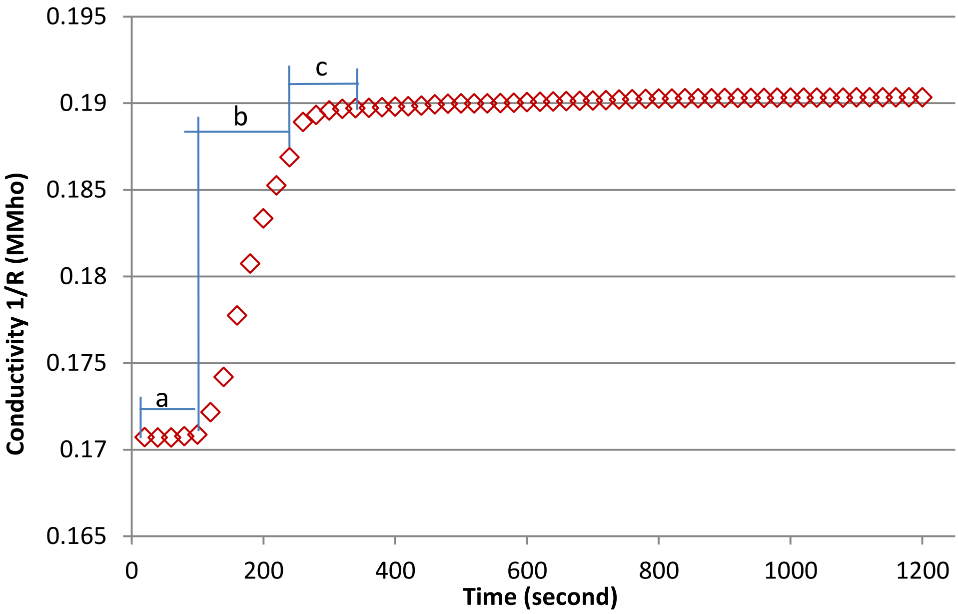


**Figure 6.31** Conductance measurement for biodiesel transesterification process at 40°C, 15kHz, 5 Vpp signal excitation.

In figure 6.31 there are stages or sctions can be identified:

*Section a*. In the early stages of the experiment the initial rate of mass transfer was very slow due to the heterogeneous reaction mixtures caused by the immiscibility of both fluids.

*Section b***.** The increase in conductance indicates an increased concentration of methoxide within the triglyceride phase. During this period of the reaction the sensor will be exposed to a mixture containing two phases, a methoxide phase with a high ion concentration and a triglyceride phase with increasing ion concentration. Passage of distinct regions of fluid of differing ion concentration over the sensor gave rise to a noisy signal. The results presented in Figure 6.31 do not exhibit this as they were filtered using a 10 second moving average so as to represent the mean state of the system.

During the process fatty acid methyl esters are formed and act as cosolvent or mutual solvent for the reagents. During the process surface active compounds such as monoglycerids, diglycerids and soaps are also formed. As a result the reaction mixture becomes pseudo homogenous (Vicente, *et al.*, 2004), and therefore ion distribution during this stage increases rapidly.

*Section c*. This period represents a period of reduced ion mass transport. This period is followed by the last stage of biodiesel process before the process reaches a steady state condition. Depletion of reactants and dominant reverse reactions act to slow down the process before it reaches plateau state (Stamenkovic, *et al*., 2008). The mass transfer limitations that are exhibited by the low temperature reaction are reduced considerably when the reaction is carried out at a higher temperature. This effect has been reported and it is related to the drop size of the dispersed methanol, the rate of drop size reduction and is faster when the process temperature is higher (Stamenkovic, *et al*., 2008).

The experimental results presented show that the IDC based monitoring technique detects the dispersal of methoxide throughout the reacting mixture. The sigmoid graphs presented show clearly the three stages of the transesterification process and are consistent with the findings of other researchers. The proposed sensor is very simple to fabricate, has no moving parts and requires relatively simple electronics. The resulting measurement data are very useful for the control of early stages of the transesterification process and the detection of steady state conditions. It may be possible to use the sensor to save energy during the process by reducing the speed of the mechanical agitation in batch reactor after complete mixing has been achieved.

## 6.5 Summary

In this chapter experimental result has been presented, the summary as follow:

- An ID sensor has been developed using photolithography and the shunt resistor is used to measured circuit current. I-V method has been used to measure unknown impedance Z. The sensor has been tested in different liquids, the results shows that the reading is very stable in virgin oil compare to conductive liquids (tap water).
- Phase angle and voltage changes were sensed during the heating of sunflower oil and and the sensitivity to temperature change determined to be: 0.004 mV/°C and for phase angle 0.0071°/°C. These results confirm that the impedance change due to temperature change is significantly lower than the changes observed during the biodiesel production process.

- Process monitoring using impedance measurement reveals simultaneous changing of the real and imaginary components of impedance. The resistance curve represents the rate of ion distribution and the change in capacitance confirms the change in permittivity that occurs during the conversion process.
- The capacitance data observed during the biodiesel process can be used to develop an algorithm for process estimation. In the next chapter Black Box identification with time delay is used to develop a system model using step input data (u1) from injection methoxide and output data (y1) determined from in-process capacitance measurement.

# Chapter 7

# Batch Reactor Biodiesel Transesterification System Identification

In the field of system control the term system identification refers to methods that maybe implemented to build mathematical models of dynamic systems based on observed and measured input and output data from the identified system. The mathematical model describes the behaviour of the process, and its formulation is often the first step undertaken in the design of a controller. Identification techniques for the estimation of dynamic transfer function models from experimental data are essential for model based controller design. It is often the derivation of precise and accurate models that is difficult because of the complexity of chemical process reactions. Therefore, system identification method is a valuable tool to identify low order models, based on input and output data for controller design (Ramakrishnan & Chidambaram, 2003). Ljung stated that its generally accepted concept that system identification for control system in industrial setting often means a simple process model with usually three parameters is fitted to real time data (Ljung, 2002).

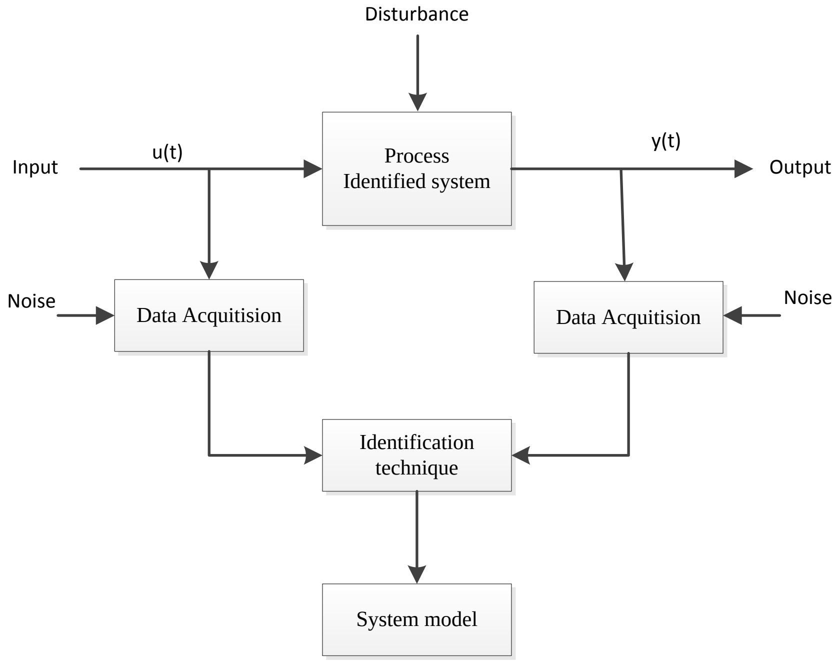


**Figure 7.1** System identification

## 7.1 Classification of the system identification problem

Classification of system identification is depending on the degree a priori knowledge of the system. The modelling of a system may be classified in three different categories as black box, grey box and white box identification.

White box identification models constructed based on the laws of physics behind the process. The system parameters are already known hence all the priori information about the system dynamics is used to derive the model. The main advantage of the white box identification is that the values of the model parameters have a physical meaning that can be compared by tabled values for those quantities.

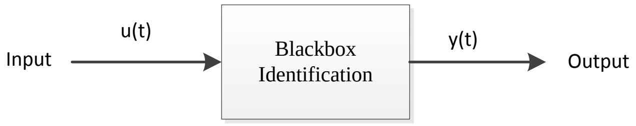


**Figure 7.2** Blackbox identification

For black-box identification on the contrary, there is no priori knowledge is applied to develop a system model. Figure 7.2 shows black box identification diagram, black box identification is strictly based on the collected input-output system data. The main advantage of blackbox technique in most cases is simple and low complexity. However, obtaining blackbox identification has a drawback which is not clear connection amongst obtained parameter values and involved physical entities in the process.

The gray-box identification method is a compromise between black-box and white-box identification. Grey-box technique is used if a priori information available and can be used to estimate unknown parameters resulting semi-physical models (Ljung, 2010).

Whatever the system identification to be selected white-box, black-box or grey-box is used to develop a certain system model, the model should be formulated in discrete time. Discrete time models or difference equations are commonly used to describe events which are natural to regard at fixed (discrete) intervals. On the contrary, continuous time models provide a description of the continuous time system. This might be of interest for nonlinear system since most nonlinear control theory is based on continuous time models (Khalil, 2002).

In some cases it is an advantage to have a model of the system available online while the system is in operation. Then the model can be based on the observation until the current time in other words the estimated parameters of the model algorithms are updated every time a new observation of the system available. The new estimated parameters are equal to the previous estimate plus a correction which depend on the prediction error. It is called recursive identification methods where the parameter estimates are computed recursively over time. Recursive identification method is very useful when the system dynamics are time-varying, moreover this method requires low memory allocation in computational since not all data stored. Batch identification is counterpart to recursive method in which all the observations data are used simultaneously to estimate the model (Ljung, 2010).

Parametric identification methods can be defined as mapping from the recorded data to a finite-dimensional estimated parameter vector. Prediction error methods and subspace methods are examples for parametric methods.

Nonparametric methods might provide models in the forms of curves, tables or functions that do not result from a finite dimensional parameter vector. Examples of nonparametric models including impulse responses, frequency response function or series expansions through kernels such as Volterra and Wiener series expansions S (Söderström, & Stoica, 2001).

## 7.2 Time domain modelling

The dynamics of a system may be obtained from the response of the process to deterministic signals such as pulses, steps and ramps. In principle the dynamics of a linear system may be determined from the result of a transient response experiment. To use this approach requires a system that is at rest or steady before the input is applied, and relays on their minimal measurement errors. However in real applications it is relatively difficult to make sure that a system is at rest. There will be measurement errors due to parasitic signals or the other disturbances, so the transient response method in practice is limited to simple models. However, the models determined from a transient response experiment are often adequate for simple controller tuning like PID controller, moreover the methods are also very simple to apply (Astrom & Hagglund, 1995).

A static process model contribute the steady state relationship between the input and output signals. During the transient state periods of a process a dynamic model will give the relationships between the input and output signals. Such models also can be used to explain the behaviour of a systems where there are some deviations from equilibrium. In Linear Time Invariant (or LTI) system, a linearity means if the input u1 gives the output y1 and the input u2 it then follows the output y2 that the input au1+ bu2 gives the output ay1 + by2. There are some common signals can be utilized to describe a systems response such as its response to a step function or sine wave. The response of a system in the time domain can be used to determine the best fit of an assumed process model.

### 7.3 Step response identification

There are many methods based on step response identification which can be categorized as a deterministic method due to input signal is deterministic. Simple transfer function models can be obtained graphically from step response. A plot of the output response of a process to step change in input is sometimes referred to as a process reaction curve. The results of a step identification process often take the form of an equation:

$$A(p)y(t) = B(p)u(t - td) \tag{7.1}$$

Where A and B the coefficient of the polynomials, p = d/dt is the differentiation operator and td is time delay. The purpose on this method has aim at first estimates to the process and provides information about an approximate process gain, time constant and time delay.

The input signal in step identification used is step change of one of the process inputs when all other inputs are held constant. It is important that controlled process is in a steady state before application of the step change. The measured signal from process response is a real step response which needs to be normalised for unit step change and for zero initial conditions.

## 7.4 Time delay

Time delays may appear in many processes in industry or the others fields such as economical and biological systems. Figure 7.3 shows time delays, time delays can be caused by various phenomena including a) time needed to transport mass or energy b) the accumulation of time lags in a great number of low order systems connected in series and c). the processing time for sensors analysers, controllers that need some time to implement a complicated control algorithm or process (Normey & Camacho, 2007).

**Figure 7.3** Time delay

$q_i$ is input to dead time element and $q_0$ output of dead time element.

$$q_0(t) = q_i(t - \tau_{DT}).u(t - \tau_{DT}) \qquad 7.2$$

and

$u\ (t - \tau_{DT}) = 1$ for $t \geq \tau_{DT}$ 7.3

$u\ (t - \tau_{DT}) = 0$ fot $t < \tau_{DT}$ 7.4

The easiest way to determine time delay is by graphically methods or by taking the first two term of Taylor series expansion of the Laplace transfer function of time delay element $\tau_{DT.}$(figure 7.4).

L [f(t - $\tau_{DT}$) u (t - $\tau_{DT}$)] = $e^{\tau_{DT}S}$F(s) 7.5

$\frac{q_0}{q_i} = e^{\tau_{DT}S} \approx 1 - \tau_{DT}S$ 7.6

$q_0(t) \approx q_i(t) - \tau_{DT}\frac{dq_i}{dt}$ 7.7

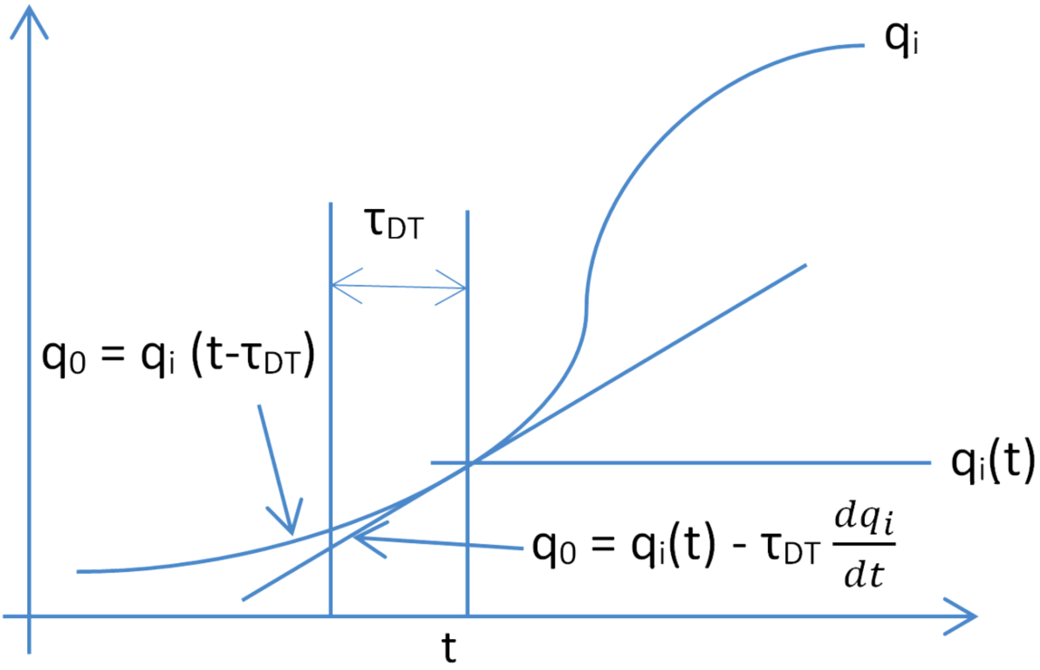


**Figure 7.4** Graphical time delay approximation

The approximation accuracy depends on the time delay being sufficiently small relative to the rate of change of the slope of $q_i(t)$. If $q_i(t)$ has a constant slope, the approximation would be perfect for any value of $\tau_{DT}$. When the slope of $q_i(t)$ varies rapidly, only small $\tau_{DT}$ will give a good approximation.

## 7.5 Linear polynomial model structure

In black-box modelling it is common to use a trial and error process, where the estimation of parameters comes from some candidate model structures and the results are compared (It is common to start from the simple linear model structure and proceed towards to more complex model structures). A common simple linear black-box model structure is the ARX (Auto Regressive Exogenous Input) model which is has simplest input-output polynomial model. A common polynomial model using a generalized notion of transfer function is used to describe relationship between the input u(t), the output y(t) and the noise e(t).

### 7.5.1 Box Jenkins (BJ)

Box Jenkins model provides independent parameterization for the dynamic process and the noise using polynomial functions. If a model has the noise does not enter the input but it comes up from a measurement disturbance then BJ model is suitable for such processes, also the BJ structure has flexibility to model the noise (Mathworks, Inc., 2013)

$$A(q)y(t) = \sum_{i=1}^{nu} \frac{B_i(q)}{F_i(q)} u_i(t - nk_i) + \frac{C_{(q)}}{D_{(q)}}\, e(t) \qquad 7.8$$

Figure 7.5 shows signal flow of a box Jenkins model, the variables A, B, C, D and F are polynomials expressed in the time-shift operator $q^{-1}$. *ui* is the *i*th input, *nu* is the total number of inputs and *nki* is the *i*th input delay that represent the time delay and the white noise is *e(t)*.

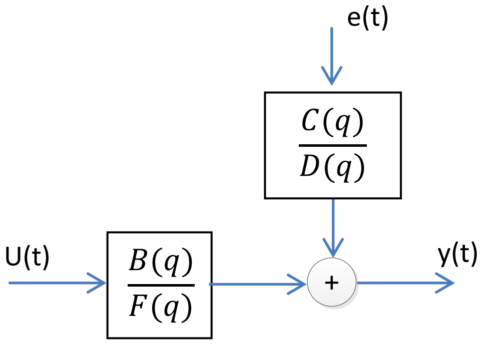


**Figure 7.5** Signal flow of a Box-Jenkins model

Where,

$$B(q^{-1}) = 1 + b_1 q^{-1} + \cdots + b_{n_b} q^{-n_b+1} \qquad 7.9$$

$$C(q^{-1}) = 1 + c_1 q^{-1} + \cdots + c_{n_c} q^{-n_c} \qquad 7.10$$

$$D(q^{-1}) = 1 + d_1 q^{-1} + \cdots + d_{n_d} q^{-n_d} \qquad 7.11$$

$$F(q^{-1}) = 1 + f_1 q^{-1} + \cdots + f_{n_f} q^{-n_f} \qquad 7.12$$

Polynomial parameters are $i, j, k$ and $l$, where $i = 1, \ldots, n_b$; $j = 1, \ldots, n_c$; k = 1, …, $n_d$; $l = 1, \ldots, nf$.

### 7.5.2 Auto regressive moving average with exogenous input ARMAX model

In polynomial ARMAX model structure the disturbance is included in the model. This structure as shows in figure 7.6 is very useful for the process which has large disturbance early in the process.

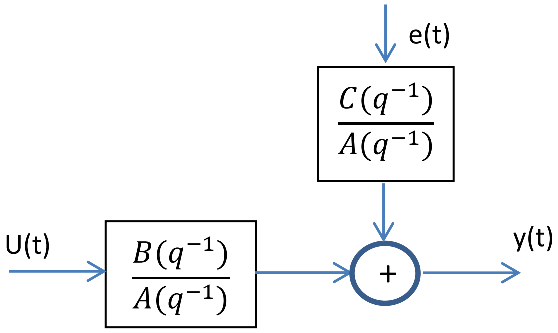


**Figure 7.6** Signal flow of a ARMAX model

$$A(q^{-1})y(t) = B(q^{-1})u(t - n_k) + C(q^{-1})e(t) \quad 7.13$$

$$y(t) = \frac{B(q^{-1})}{A(q^{-1})} u(t - n_k) + \frac{C(q^{-1})}{A(q^{-1})} e(t) \quad 7.14$$

Where the polynomials ARMAX are :

$$\mathrm{A}(q^{-1}) = 1 + a_1 q^{-1} + \cdots + a_{n_b} q^{-n_a} \quad 7.15$$

$$\mathrm{B}(q^{-1}) = 1 + b_1 q^{-1} + \cdots + b_{n_b} q^{-n_b+1} \quad 7.16$$

$$\mathrm{C}(q^{-1}) = 1 + c_1 q^{-1} + \cdots + c_{n_c} q^{-n_c} \quad 7.17$$

Then $i$, $j$ and $k$ are the polynomials parameters for $I$ = 1, …, $a_n$; $j$ = 1,…,$b_n$ and order of each polynomials described by $n_a$, $n_b$ and $n_c$.

### 7.5.3 Auto regressive exogeneous input (ARX) model

ARX model may be the simplest model of the generalised polynomial linear (figure 7.7). C*($q^{-1}$)* for disturbance channel is simplified to 1, it means the disturbances are become parts of the system dynamics.

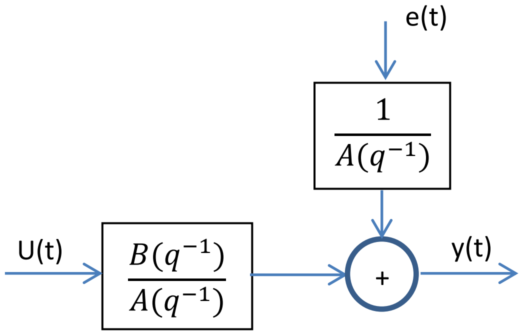


**Figure 7.7** Signal flow of a ARX model

$$A(q^{-1})y(t) = B(q^{-1})u(t - n_k) + e(t) \qquad 7.18$$

$$y(t) = \frac{B(q^{-1})}{A(q^{-1})} u(t - n_k) + \frac{1}{A(q^{-1})} e(t) \qquad 7.19$$

*i* and *j* are polynomial parameters $i = 1,\ldots, n_a$ ; $j = 1, \ldots, n_b$

### 7.6 Goodness of fit statistics

Goodness of fit is to describe how close the fitted curve is to the actual data points. After fitted curve displayed in curve fitting application a visual examination can be conducted. Commonly, it can do by comparing between a plot of model output and actual data points for the same sequence of inputs. The measurement of fit statistics can be used to explain the difference in the degree of goodness in fitting achieved by different model structures.

$$R = \sqrt{1 - \frac{\sigma_e^2}{\sigma_y^2}} \qquad 7.20$$

$\sigma_e$ is defined as variance of the residuals and $\sigma_y$ is the variance of the output data. The fitting value of R can take value between 0 and 1, with a value closer to 1 indicating better model fit. If the value of R reach 1 that's mean the value of variance of the residual approaching 0, then a perfect model fit can be obtained.

### 7.7 Model validation

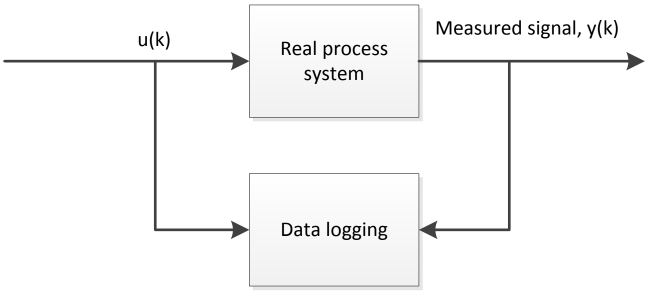
Residuals are differences between the one-step-predicted output from the model and the measured output from the validation data set. Thus, residuals represent the portion of the validation data not explained by the model. An analysis of residual $\epsilon$ can be very useful to assess a dynamic system affected by white (Gaussian) noise or disturbance (Söderström & Stoica, 2001). A good residual will be near zero-mean, also it is independent of all past and future inputs if the model adequately represents the system dynamics and the system is open loop.

Residual analysis consists of two tests: the whiteness test and the independence test. According to the *whiteness test* criteria, a good model has the residual autocorrelation function inside the confidence interval of the corresponding estimates, indicating that the residuals are uncorrelated. According to the *independence test* criteria, a good model has residuals uncorrelated with past inputs. Evidence of correlation indicates that the model does not describe how part of the output relates to the corresponding input. For example, a peak outside the confidence interval for lag *k* means that the output *y(t)* that originates from the input *u(t-k)* is not properly described by the model. The confidence interval corresponds to the range of residual values with a specific probability of being statistically insignificant for the system. The toolbox uses the estimated uncertainty in the model parameters to calculate confidence intervals and assumes the estimates have a Gaussian distribution.

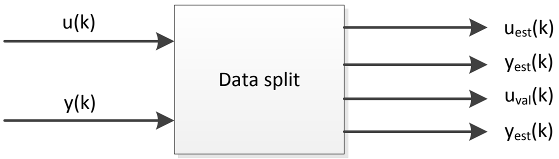
## 7.8 System identification of biodiesel transesterification process.

In order to develop a mathematical representation of the biodiesel trasesterification process measurement data, Matlab System Identification tool box was used. The software provides a user friendly environment for ease of computations and allows for multiple iterations enabling users to determine the best model that best fits the measured data. In this system identification different steps have used including:

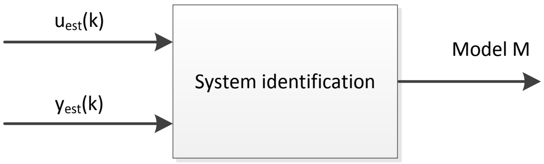
1. Data logging, data output signals impedance from the biodiesel transesterification process was logged and this data is used to system identification analysis.



2. Batch reactor system identification transesterification process is not continuous process,



3. Model estimation, the model or model parameters will find out using system identification methods which is using system identification toolbox.



4. Model validation, to confirm the mathematical model or model parameters.

The data from the (figure 7.8) experiment was used as the output signal y(t), the step input signal u(t) was not directly measured but synthesised from the known injection time of Methoxide. As other process variables such as temperature, agitation speed, assumes did not change during the reaction. They were no used in the system identification process.

## 7.9 Process Models estimation using System Identification Matlab Toolbox.

Figure 7.8 shows the input and output signals for system identification. The input signal (u1) represents timed injection of methoxide into vegetable oil and the output signal (y1) representing capacitance measured during the mass transfer process and subsequent chemical reaction. Other parameters like temperature, stirrer speed are assumed to be steady and they were not changed during the experimental process.

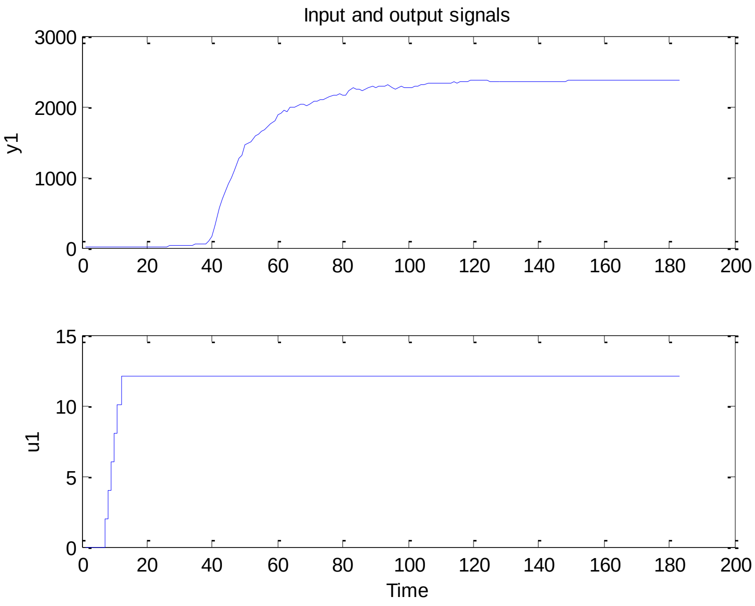


**Figure 7.8** Input (u1) and output signal (y1) biodiesel transesterification process

There are some options to calculate the model, in this case polynomial model structure selected from the available options and the performance of three model approximation technique are investigated ARX, ARMAX and Box Jenkins. The three techniques were optimised to give the best fit between model and measured data on the basis of residual analysis.

### 7.9.1 ARX Estimation

To enable fitting of the ARX model order and delay parameters, manual adjustment of A(q) and B(q) was required. Various combination of A(q) and B(q) were tested in order to determine the combination that produced the best fit with measured data. Figure 7.8 is graphical representation of measured and estimated model output from optimal fit resulting from different A(q) and B(q) polynomial orders.

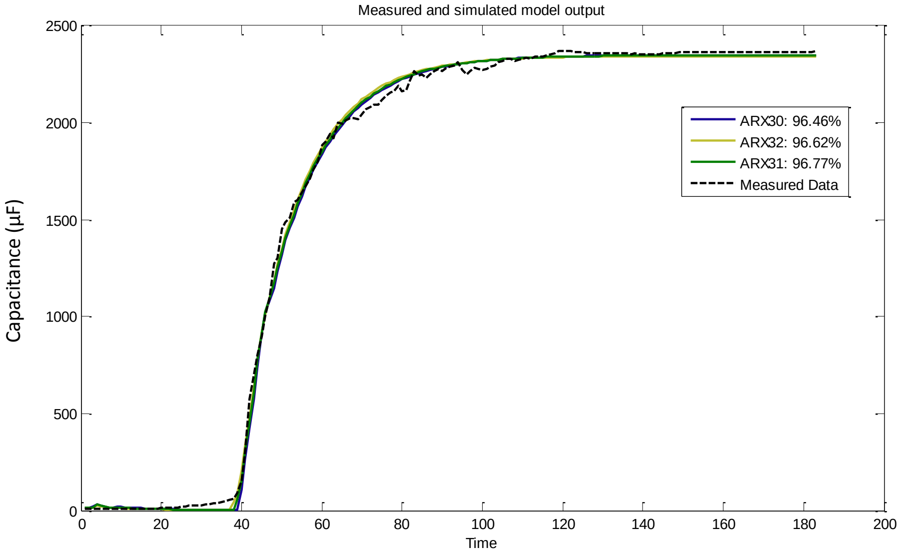


**Figure 7.9** Fitting of estimated ARX models and the measured data process data

The ARX model did not estimate the delay time and thus had to be manually identified and input into the simulation process. On the simulation panels delay was set to 30s for all model comparison. The best estimation for ARX model delivered R 96.77% fit as shows on Figure 7.9. The estimated ARX model equation from A(q) and B (q) polynomials are as follows,

$A(q) = 1 – 0.77q^{-1} – 0.146q^{-2}$

$B(q) = 25.89q^{-1} + 9.42q^{-2}$

Polynomial orders na = 2 ;nb = 2 ;nk = 1

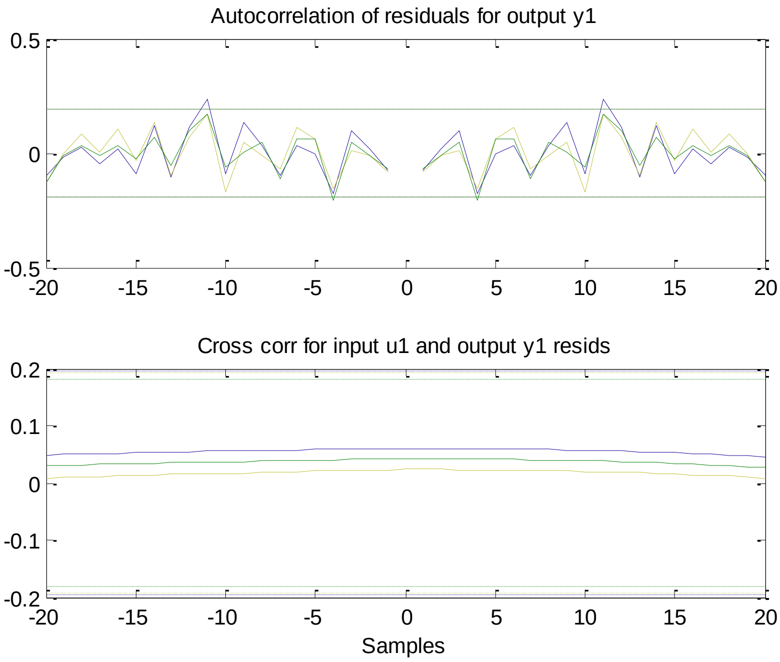


**Figure 7.10** Auto-correlation and Cross correlation of estimated ARX model

Model validation test is evaluated by observing autocorrelation and cross correlation residual analysis. Figure 7.10 shows the model evaluation under residual testing. Residual analysis quantities the error between the predicted outputs of the estimated model and measured outputs from data set. In residual analysis tests include both whiteness and independence tests to check whether the residual has good confidence level also that the data are not correlated and are independent from past input. It can be seen from the figure 7.10 the residual have a confident range between from 0.2 to - 0.2. Only one model of 96.46% fit has one residual stand outside confident range of ARX model.

### 7.9.2 ARMAX estimation

In the ARMAX model, the noise model structure C(q) polynomial is important to identify along with A(q) and B(q) model polynomials. Figure 7.11

shows various combination of best possible ARMAX model for measured and estimated output at different A(q), B(q) and C(q) polynomials.

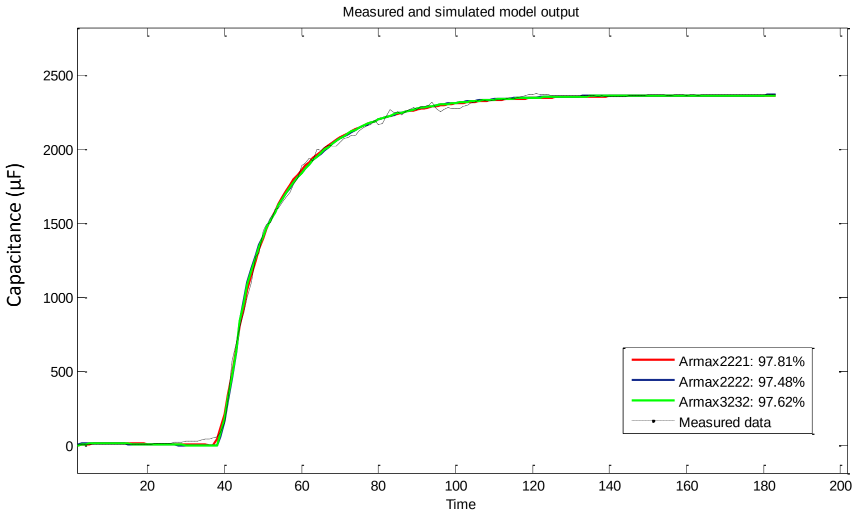


**Figure 7.11** Fitting of some estimated ARMAX models and measured data

In ARMAX models the best fit was achieved for a combination of polynomials of order 2 2 2 1, the other combinations resulted in poorer fits. The estimated ARMAX model equation from A(q) and B (q) polynomials were as follows,

$A(q)y(t) = B(q)u(t) + C(q)e(t)$

$A(q) = 1 – 1.78q^{-1} + 0.7884q^{-2}$

$B(q) = 18.98q^{-1} – 17.26q^{-2}$

$C(q) = 1 – 1.097q^{-1} + 0.097q^{-2}$

Polynomial orders na = 2 ;nb = 2 ;nc = 2 ;nk = 1

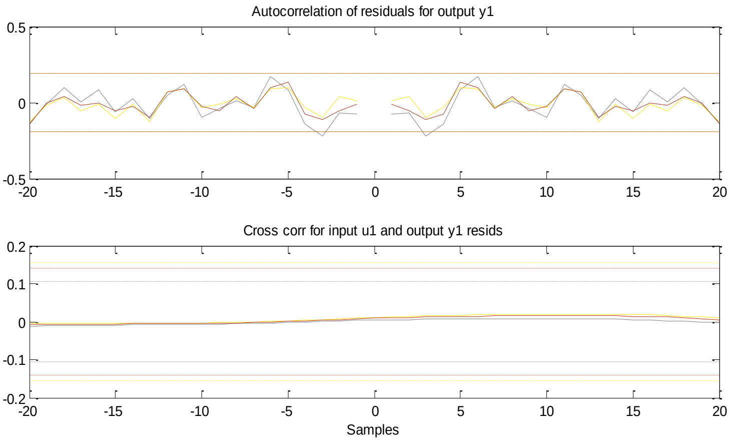


**Figure 7.12** Auto-correlation and Cross correlation of estimated ARMAX model

Figure 7.12 Shows autocorrelation and cross correlation for ARMAX model, similar to ARX model validation, the residual reside the confident range from 0.2 to -0.2, also for desired polynomial order, the residuals are not correlated and independent from past input.

### 7.9.3 Box Jenkins model estimation

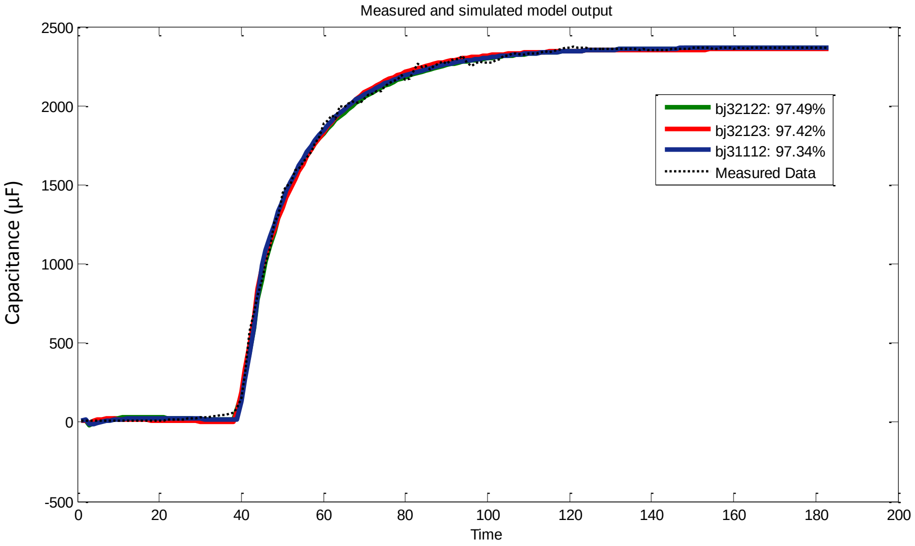


**Figure 7.13** Fitting of estimated Box-Jenkins models and the process measured data

The highest estimated Box-Jenkins has R = 97.49%, and the resulting model equation from A(q) and B (q) polynomials as follows,

$y(t) = [B(d)/F(d)]u(t) + [C(d)/D(z)e(t)]$

$B(d) = 33.46d^{-2} – 46.11d^{-3} + 14.19^{-4}$

$C(d) = 1 + 0.5015d^{-1} + 0.2264d^{-2}$

$D(d) = 1 + 0.002875d^{-1}$

$F(d) = 1 – 1.792d^{-1} + 0.7994d^{-2}$

Polynomial orders nb=3 ;nc=2 ;nd=1 ;nf=2 ;nk=2

Figure 7.13 shows the comparison of Box Jenkins models with various combinations of polynomial orders. The highest fitting value has achieved after choosing the combination of polynomials orders nb=3 ;nc=2 ;nd=1 ;nf=2 ;nk=2.

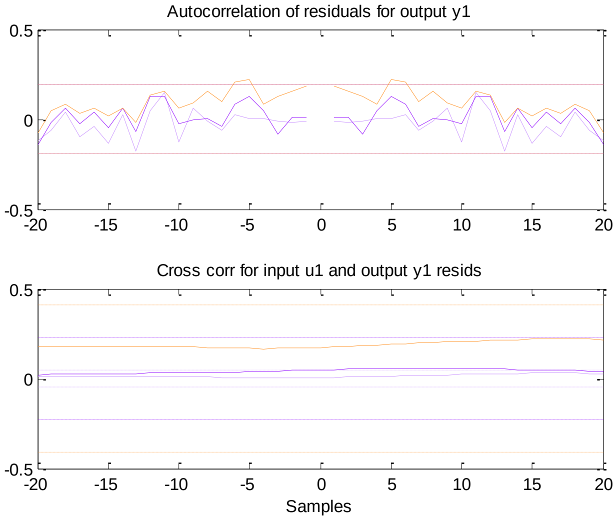


**Figure 7.14** Auto-correlation and Cross correlation of estimated BJ model

Figure 7.14 illustrates the Box Jenkins auto-correlation and cross-correlation of model residual. It can be seen that all data plot inside confident region area of 0.2 to -0.2. The tolerance of the data validation is within ± 0.5%. The validation tests confirm that the data passes both whiteness and independence tests, the tests confirm that residuals are not correlated and are independent from past input.

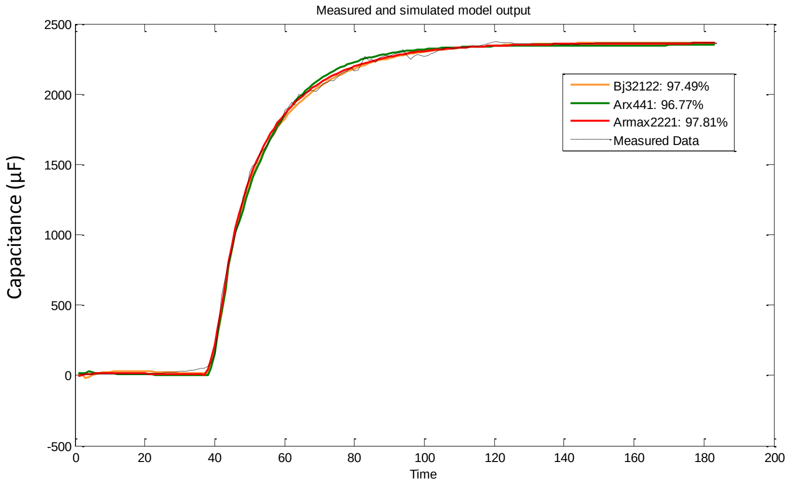


**Figure 7.15** Fitting comparison of estimated models ARX, ARMAX, Box-Jenkins and measured data.

Figure 7.15 depicts a comparison between ARX, ARMAX and Box-Jenkins models. The comparison between third models shows that ARMAX model has highest fitting, with goodness fit of 97.81%, whereas ARX and BJ method has achieved the best fit up to 96.77% and 97.49% respectively. ARMAX models appear to be best model for step response of first order biodiesel transesterification proses. It also observed all model structures pass model validation test using residual analysis within the range of confidence.

## 7.10 Identified Model

Three model structures ARX, ARMAX and BJ are compared using system identification technique. The difference of fit R amongst them is not notably high, however the model complexity is increases compare with ARMAX and BJ due to increase in system order. Since the transesterification biodiesel conversion is a simple process, most likely the measurement noise is come from measurement equipment rather than come from process dynamic. Therefore, the reasonable reason for choosing the ARX model structure for simple proses is considered suitable for this application.

The ARX model structure can be written by equation 7.27, the equation can be rearranged to give the transfer function form shown in equation 7.28.

$$A(z)y(t) = B(z)u(t) + e(t) \tag{7.27}$$

$$y(t) = \frac{B(z)}{A(z)}u(t) + \frac{1}{A(z)}e(t) \tag{7.28}$$

The ARX model selection has yielded on the following A(z) and B(z) polynomials with statistical fitting 96.77%. The identified polynomials can be written in equation 7.29 and 7.30.

$$A(z) = 1 + a_1 z^{-1} + a_2 z^{-2} + a_3 z^{-3} \tag{7.29}$$

$$B(z) = b_1 z^{-1} + b_2 z^{-2} \tag{7.30}$$

The identified model parameters from Matlab system identification toolbox are shown in table 7.1

Table 7.1 Model parameters

| A(z) | Value | B(z) | Value |
|---|---|---|---|
| $a_1$ | 1 | $b_1$ | 26.3 |
| $a_2$ | – 0.77 | $b_2$ | 9.42 |
| $a_3$ | -0.146 | | |

The system model discrète time transfer function are show in an equation as follows :

$$G(z) = \frac{B(z)}{A(z)} = \frac{26.3z - 9.42}{z^2 - \ 0.77z - 0.146} \qquad 7.31$$

And continuous transfer function :

$$\mathrm{Y(s)} \ = \frac{-22s^2+2.32s+0.4158}{s^2+0.2823s+0.002069} \qquad 7.32$$

The yielded transfer function plot for step response shows in figure 7.16. The time response of a first order systems consist of two parts: the transient response and steady state response. The transient response is defined as the part of the time response which goes from the initial state to the final state and reduces to zero as time becomes very large.

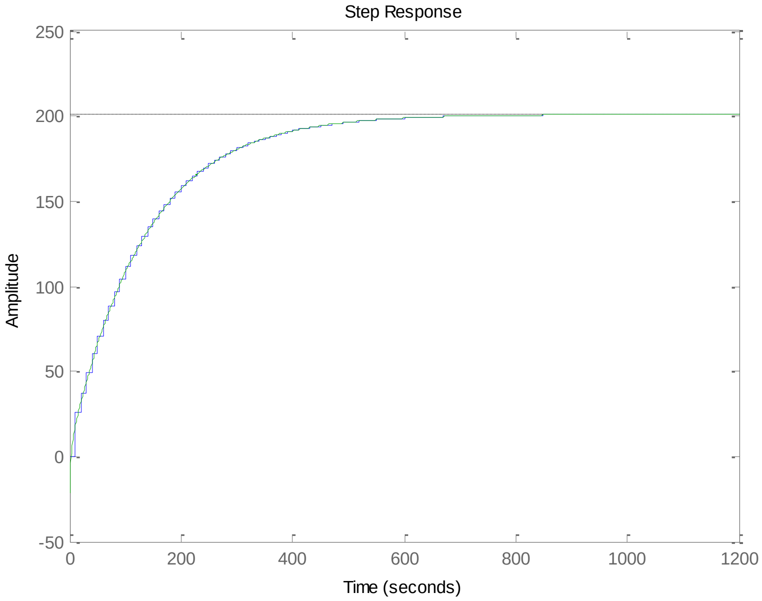


Figure 7.16 Step function of discrète time transfer function without time delay.

The steady state response is defined as the behaviour of the system as t approaches infinity after the transients have died out. Thus the system response y(t) can be written as :

$$y(t) = y_t(t) + y_s(t) \qquad 7.32$$

Where $y_t(t)$ denotes the transient response and $y_s(t)$ denotes the steady states. In first order process T is called time constant and its time it takes for the step response to rise 63.2% of its final value. The settling time $T_s$ is the response of the system within 2% of the final value and the rise time $T_r$ is defined as the time for the waveform to go form 10% to 90% of its final value. The process time summary shows in the table 7.2

**Table 7.2** Time process in First order transesterification biodiesel process

| Time | Capacitance value | Time (s) |
|---|---|---|
| Time constant T | 1491 | 510 |
| The settling time $T_s$ | 2312 | 1040 |
| Rise time $T_r$ | 1888 | 410 |

Capacitance and resistance measurement on biodiesel measurement can be plot as shown on figure 7.19. Resistance measurement can be used as indicator when the mass transfer taking place during the reaction. When the resistance (indicate mass transfer) reach the final value, the capacitance start to rise.

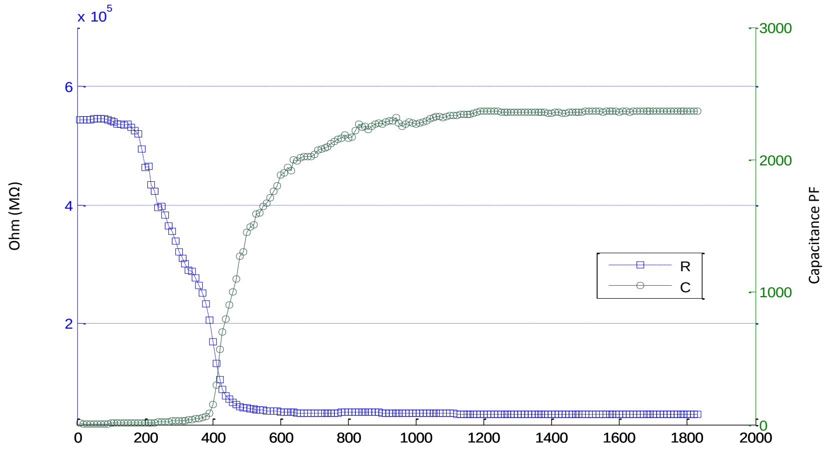


Figure 7.19 Resistance and Capacitance measurement during the transesterification process.

Capacitance measurement in transesterification can be considered as first order system, as common first order response the unit step response of a system can be determined and for steady state detection depend on the desired accuracy. Final value of capacitance measurement is 2.36 nF, time constant T was achieve in 510 s and settling time was 1040s, within this time the reaction is consider in equilibrium state.

## 7.11 Summary

In this chapter system identification has been discussed and chapter 7 summary as follows:

- The comparison of three models shows a good fitting with the highest fitting is ARMAX models and the different fitting is not significant. However increasing polynomials model is significantly adding complexity in calculation. Therefore, ARX is suitable for biodiesel process monitoring.

- All model structures pass model validation using autocorrelation and cross correlation within the range of confident.
- From identified model structures can be determine the state of transesterification process.

# *Chapter 8*

# *Conclusions and recommendation for further work*

The research conducted in this thesis was to perform an investigation on the alternative monitoring of biodiesel transesterification conversion process. Low cost inter digital sensor was designed and manufactured. The designed sensor was used to monitor the biodiesel conversion process. The conclusion are made related to the conducted research.

## 8.1 Conclusion

- A batch transesterification reaction of vegetable oils consist two important stages, mass transfer controlled region and kinetically controlled region. Mass transfer stages is important part of the process because overall transesterification process speed is depend on how fast this stage.  Slow biodiesel process lead in energy and time inefficiency.
- The design of low cost Interdigitated sensor and measurement method has been proposed to monitor the process on the biodiesel process. In this thesis the sensor is employ to measure of both value of capacitance and conductance simultaneously. Single frequency impedance measurement has been used with National instruments hardware and software to detect phase different between excitation and sensing waveform.
- Measurement of biodiesel transesterification monitoring process by means of impedance measurement has been presented. The suggested impedance measurement technique shows promise of being useful for process monitoring as feedback to determine the progress of the biodiesel reaction. Simultaneous measurement of the resistant and reactant has represent the two stages of transesterification biodiesel reaction which is contain mass transfer control region and kinetically controlled region. The monitoring technique detects the

dispersal of methoxide throughout the reacting mixture and changing in permittivity of reactants during the reaction. The graphs shows the process of reducing resistance which is depict the mass transfer following by increasing capacitance and permittivity which is represent the chemical reaction during the reaction, this is consistent with the findings of other researches.

- The proposed sensor is very simple to fabricate, has no moving parts and requires relatively simple electronics. The resulting measurement data is very useful for the control of early stages of the transesterification process and the detection of steady state conditions. It may be possible to use the sensor to detect the process steady state and save energy during the process by reducing the speed of the mechanical agitation after complete mixing has been achieved
- The real parts or resistant from the measurement has been proposed as a mass transfer in transesterification process due to it is measure the mixing of high concentration ion liquids (methoxide) and low ion concentration liquids (vegetable oil). The imaginary parts of the impedance measurement are representing of capacitance value which is dominantly by changing in imaginary parts of permittivity. The changing in the value of capacitance is proposed as represent of chemical reaction. It can be prove between resistant value and capacitance value in time domain measurement experiment, have different time scale which are the resistant is decrease in earlier the process following the rising of the capacitance value. The permittivity value in this measurement is changing during the reaction, both imaginary component and real component.

- National Instrument Hardware and software has been used to measure impedance changing in transesterification process. The digital signal processing accompany with NI hardware offer the degree of simple programming to produce real-time waveform, manipulating and logging the data value. The measurement equipment is less sophisticated compared with analog measurement therefore it easy to applied using embedded system to measure the process independently or combined with control system.
- System identification method has been used to evaluate step response from transesterification process. Black box system identification is used to characterize the unknown system parameters using input and output signal. the step input from methoxide injection is used, and measured impedance has been used as output signal. Those input and output result was used to create process reaction curve (prc). System identification Matlab tool box is used to develop the model. Auto regressive with exogenous structure (ARMAX) model has good fitting with 97.81%, and the data set was pass using residual analysis within the range of confident.

## 8.2 Recommendation for further work

- The measurement of the both mass transfer and chemical reaction will enable to develop on both control strategies and plant design. Control design may detect the steady state reaction and make further action like turn off the stirrer or reduce the speed of the agitator. This optimisation can make further enhancement to reduce energy during the conversion process.

- Single frequency measurement is frequency and temperature dependant; it is very useful to mapping the process for various temperature conversions.

- Further design for interdigital capacitance sensor might be based on cylindrical design, to improve robustness and can be easily attached on biodiesel plant. Also further calibration can be conducted to assess relationship between a complete biodiesel reaction with the impedance value, both resistant and capacitance.

- Extended for this single frequency measurement can be further investigate to develop a useful portable of handheld equipment base on Romano and Sorichetii method. The measurement method in this work not only for detecting the process of biodiesl conversion but also it can be used to monitoring quality vegetable oil before process and biodiesel after the process.

- It is possible to use this measurement to embedded system, with FPGA development module. Low frequency measurement in this experiment is relatively simple and low cost to implement through FPGA technology.

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