# PRODUCTION OF BIODIESEL FROM CASTOR OIL: A FEASIBILITY STUDY

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**SUPERVISOR'S DECLARATION**

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scopes and quality for the award of the degree of Master of Chemical Engineering with Entrepreneurship.

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**STUDENT'S DECLARATION**

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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**Dedicated To**

*My*

*Beloved husband;*

*Parents;*

*Brothers and sisters*

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**ABSTRACT**

In this work, the requirements of a biodiesel plant and the strategic issues to be considered to assess its feasibility. This analysis is useful either when starting a new business, or identifying new opportunities for an existing business. Therefore, it will be extremely helpful for taking rational decisions about the development of a biodiesel production plant. Thus, it is important to understand the transesterification process, and optimize the variables affecting for biodiesel production from castor oil which second generation non edible oil, by acid catalysis (sulphuric and phosphoric acid) and basic catalysis (potassium methoxide and potassium hydroxide). Biodiesel was characterized by a set of parameter according to European Standard, EN 14214. The best conditions for transesterification process were 9:1 methanol/oil molar ratio, 65 ºC, and the use of potassium methoxide as catalyst with concentration 1.0 wt%. The operating cost of the process was estimated using the key information on process operation such as raw materials, utilities, and labor. A profitability analysis was carried out by examining the ROI (Return of Investment) and PP (Payback Period). It was determined that the single most important economic factor is the cost of castor oil. Consequently, a sensitivity analysis was performed to examine the effect of castor oil cost on profitability using the MATLAB code. It was determined that both ROI and PP quickly deteriorate as the cost of castor oil increase. The model bases on using two different sell prices (RM 2.30 and RM 2.60). The ROI is (about 14.48% and 42.05%) and PP is (0.64 and 0.36) respectively. Thus, it can be understood that the models developed in this study are useful tools for estimation of the sensitivity analysis of the biodiesel product from castor oil.

# ABSTRAK

Dalam kajian ini, keperluan loji biodiesel dan isu-isu strategik perlu dipertimbangkan untuk menilai kebolehlaksanaanya. Analisis ini amat berguna untuk memulakan perniagaan baharu atau mengenalpasti peluang-peluang baharu untuk perniagaan yang sedia ada. Oleh yang demikian, ianya adalah sangat membantu dalam membuat keputusan yang rasional tentang pembangunan loji pengeluaran biodiesel. Oleh itu, adalah penting untuk memahami proses transesterifikasi dan mengoptimumkan pembolehubah yang boleh mempengaruhi pengeluaran biodiesel daripada minyak castor yang merupakan generasi kedua bukan minyak makan, oleh pemangkin asid ( sulfurik dan fosforik) dan pemangkin asas (kalium metoksid dan kalium hidroksida). Biodiesel telah dicirikan oleh satu set parameter mengikut Piawai Eropah, EN 14214. Keadaan yang paling sesuai untuk proses transesterifikasi ialah 9: 1 metanol/nisbah minyak molar, 65 ºC dan penggunaan kalium metoksid sebagai pemangkin dengan kepekatan 1.0 % (berat). Kos operasi proses telah dianggarkan menggunakan maklumat penting tentang operasi proses seperti bahan mentah, utiliti dan buruh. Analisis keuntungan telah dijalankan dengan memeriksa ROI (Pulangan Pelaburan) dan PP (Tempoh Pembayaran Semula). Ia telah ditentukan bahawa faktor ekonomi yang paling penting ialah kos minyak kastor. Oleh itu, analisis sensitiviti telah dijalankan untuk mengkaji kesan kos minyak kastor ke atas keuntungan menggunakan kod MATLAB. Ia telah menentukan bahawa kedua-dua ROI dan PP cepat merosot sejajar dengan kenaikan kos minyak kastor. Model asas telah menggunakan dua harga jual yang berbeza iaitu RM 2.30 dan RM 2.60. ROI ialah kira – kira 14.48% 42.05%, manakala PP ialah 0.64 dan 0.36. Oleh yang demikian, ianya boleh difahami bahawa model yang dibangunkan dalam kajian ini adalah alat yang berguna untuk membuat anggaran analisis sensitiviti produk biodiesel daripada minyak kastor.

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| | |
|---|---|
| AFC | Annualized Fixed Cost |
| BEP | Breakeven Point |
| CCI | Calculated Cetane Index |
| CFPP | Cold Filter Plugging Point |
| CI ENGINES | Compression Ignition Engines |
| CSTR | Continuous Stirred-Tank Reactor Model |
| DCCFRR | Discounted Cash Flow Rate Of Return |
| DOE | Dept of Energy |
| EN 14214 | European Standard En 14214 |
| EPA | Environmental Protection Agency |
| FAEE | Fatty Acid Ethyl Ester |
| FAME | Fatty Acid Methyl Esters |
| FC | Fixed Costs |
| FFV | Flexible Fuel Vehicle |
| GC/MSD | Chromatography/Mass Selective Detector |
| GC-FID | Gas Chromatograph Fitted a Flame Ionization Detector |
| GHG | Effects of Greenhouse Gas |
| HPSEC | High-Performance Size-Exclusion Chromatography |
| ICCR | Interdisciplinary Centre For Comparative Research |
| IEA | International Energy Agency |
| P | Price Charged Per Unit |
| PFD | Process Flowsheet Diagram |
| PP | Payback Period |
| ROI | Return of Investment |
| TAC | Total Annual Cost |
| VC | Variable Costs of Production |

# CHAPTER 1

# INTRODUCTION

## 1.1 INTRODUCTION

In the twentieth century major research emphasis was given for the development of petroleum, coal, and natural gas based refinery to exploit the cheaply available fossil feed stock. These feedstocks are used in industry to produce multiple products such as fuel, fine chemicals, pharmaceuticals, detergents, synthetic fiber, plastics, pesticides, fertilizers, lubricants, solvent, waxes, coke, asphalt, etc. to meet the growing demand of the population (Bender, 2000 ; Demirbas, 2006). Currently, the fossil resources are not regarded as sustainable and questionable from the economic, ecology and environmental point of views (Kamm et al., 2006). The burning of fossil fuels is a big contributor to increasing the level of $CO_2$ in the atmosphere which is directly associated with global warming observed in recent decades (Shell, 2010). The adverse effects of greenhouse gas (GHG) emissions on the environment, together with declining petroleum reserves, have been realized. Therefore, the quest for sustainable and environmentally benign sources of energy for our industrial economies and consumer societies has become urgent in recent years (Mabee et al., 2005). Consequently, there is renewed interest in the production and use of fuels from plants or organic waste “Biofules”.

The biofuels produced from the renewable resources could help to minimize the fossil fuel burning and $CO_2$ production and an alternative to the depreciating fossil fuel. Biofuel produced from biomass such as plants or organic waste could help to reduce both the world's dependence on oil and $CO_2$ production. These biofuels have the potential to cut $CO_2$ emission because the plants they are made from use $CO_2$ as they grow (Osamu and Carl, 1989). Biofuels and bioproducts produced from plant biomass would mitigate globe warming. This may due to the $CO_2$ released in burning equals the $CO_2$ tied up by the plant during photosynthesis and thus does no increase the net $CO_2$ in the atmosphere. Additionally, biofuel production along with bioproducts can provide new income and employment opportunities in rural areas. Twenty one century is looking for a shift to alternate industrial feedstock and green processes to produce these chemicals from renewable biomass resources (Stevens and Verhe, 2004).

'First generation' biofuels are made largely from edible oils produced using conventional technology from feedstock like wheat, corn, sugar, palm oil and sunflower oil also can offer some $CO_2$ benefits and can help to improve domestic energy security. But concerns exist about the sourcing of feedstocks, including the impact it may have on biodiversity and land use and competition with food crops. A 'first generation' biofuel (i.e. biodiesel (bio-esters), bio-ethanol, and biogas) is characterized either by its ability to be blended with petroleum-based fuels, combusted in existing internal combustion engines, and distributed through existing infrastructure, or by the use in existing alternative vehicle technology like Flexible Fuel Vehicle (FFV) or natural gas vehicles. The production of 1st generation biofuels is commercial today, with almost 50 billion liters produced annually. There are also other niche biofuels, such as biogas which have been derived by anaerobic treatment of manure and other biomass materials. However, the volumes of biogas used for transportation are relatively small today (Shell, 2010).

However, the first generation biofuels seems to create some skepticism to scientists. There are concerns about environmental impacts and carbon balances, which sets limits in the increasing production of biofuels of first generation. The main disadvantage of first generation biofuels is the food-versus-fuel debate, one of the reasons for rising food prices is due to the increase in the production of these fuels (Laursen, 2006). Additionally it is claimed that biodiesel is not a cost efficient emission abatement technology. Furthermore, for the abatement of GHG (Greenhouse Gas), it is recommended to have more efficient alternatives based on both renewable and conventional technologies (Eisberg, 2006). Therefore, lignocelluloses feedstock can offer the potential to provide novel biofuels (bioethanol), the biofuels of the 'second generation' (Simpson et al., 2007).

'Second generation' biofuels are produced using more advanced conversion technologies that allow the use of non-edible materials derived from plants (mostly lingo-cellulosic parts, like stalks and straw, but also woodchips). Also it is produced from 'plant biomass' refers largely to lignocelluloses materials, as this makes up the majority of the cheap and abundant nonfood materials available from plants. But, at present, the production of such fuels is not cost effective because there are a number of technical barriers that need to be overcome before their potential can be realized (Eisberg, 2006). Plant biomass represents one of the most abundant and underutilized biological resources on the planet, and is seen as a promising source of material for fuels and raw materials. At its most basic, plant biomass can simply be burned in order to produce heat and electricity. However, there is great potential in the use of plant biomass to produce liquid biofuels.

On the other hand, biofuel production from agricultural by-products could only satisfy a proportion of the increasing demand for liquid fuels. This has generated great interest in making use of dedicated biomass crops as feedstock for biofuel production (Gomez et al., 2008). The production of 2nd generation biofuels is non-commercial at this time, although pilot and demonstration facilities are being developed. Therefore it is anticipated that, these 2nd generation biofuels could significantly reduce $CO_2$ production, do not compete with food crops and some types can offer better engine performance. When commercialized, the cost of second generation biofuels has the potential to be more comparable with standard petrol, diesel, and would be most cost effective route to renewable, low carbon energy for road transport (Shell, 2010).

Consequently due to many advantages and disadvantages of the 1st generation biofuels and obvious advantages of 2$^{nd}$ generation biofuels, the approaches to integral utilization of biomass for sustainable development are more reasonable, where all parts of the plant such as leaves, bark, fruits, and seeds can be utilized to useful products. The term 'Biorefinery' was initially established by NREL during 1990, for the utilization of biomass for production of fuels and other bio-products. This term refers to a facility (or group of facilities) which combines the production of materials, chemicals, or fuel products with energy production (Fernando et al., 2006).

Different feedstocks have been explored for extraction of vegetable oils in order to transform it to biodiesel. The feedstocks are Jatrophacaracas, Soya, Sunflower, Castor seeds etc. besides waste cooking oils from different restaurants and food processing industries. Considering several aspects castor oil from castor seeds seem to be an alternative promising feedstock for commercial production of biodiesel. Although from the economic point of view waste cooking oils from different sources is a better choice for biodiesel preparation compared to all other sources and vegetable oils, considering the multifarious advantages oil from castor seeds from RicinousCommunis (Palma christi)- a species from Euphorbeace family is believed to be a better option. Because castor oil is possibly the plant oil which is industry's most unappreciated asset that contains about 90% ricinolic acid as the major constituent.

The oil produced from the seed of the castor plant (Ricinuscommunis) has garnered some interest as a biofuel. The fatty acids contained within castor oil contain a hydroxyl functional group, causing castor oil to be more polar than other vegetable oils. The polarity of castor oil is sufficiently high that the oil mixes completely with methanol during the biodiesel reaction.

## 1.2 PROBLEM STATEMENT

The depression of fossil fuel and increasing in the demand of petroleum products led to increase the petrol and diesel price. This trend is expected in years to come as the resources are also depleting. Hence alternative sources of energy for running our generators, automobiles etc. are being considered worldwide. The possibility of obtaining oil from plant resources has aroused a great interest and in several countries, vegetable oil after esterification being used as “Biodiesel”. The bio- diesel can be used as 20% blend with petro diesel in existing engines without any modification. Both the edible and non edible vegetable oils can be used as the raw materials for the biodiesel. Considering the cost and demand of the edible oils the non edible oils may be preferred for the preparation of biodiesel.The utilization of vegetable oils and fats in biodiesel production causes a huge increase in the price of these edible sources and has a negative impact on the food cycle besides. Therefore, the European Union voted using the edible oils to produce the biodiesel fuel (Sani, 2009).All these motivated us to search for a second generation non edible oil source for production biodiesel which is castor oil (newly production in Malaysia). This study presents research that explores the production of biodiesel from castor oil to determine whether castor oil is a viable biodiesel feedstock. That is why it is necessary to study the potential market of biodiesel, as well as to make a feasibility analysis for the implementation of a biodiesel production plant.

## 1.3 OBJECTIVES OF THE RESEARCH

The following is the summary of the study objectives:

i. To investigative the feasibility of using castor oil as a feedstock to produce biodiesel fuel.
ii. To characterize biodiesel by a set of parameter according to European Standard, EN 14214.
iii. To develop an integrated model and simulation code exploited for calculation the business plan of the biodiesel production plant based on castor oil.

## 1.4 SCOPE OF THE STUDY

This dissertation attempts to develop model for calculation the business plan of the biodiesel production plant based on castor oil. Several points are declared herein to clarify the scope of study. These points are as follows:

i. To optimization of the variables affecting transesterification process for biodiesel production from castor oil, non edible oil, by acid catalysis (sulphuric and phosphoric acid) and basic catalysis (potassium methoxide and potassium hydroxide); and to characterize the biodiesel for its use as fuel in compression ignition motors.

ii. The studied of effect operation variables in different methanol/oil molar ratio, temperature and catalyst amount. Evolution of each process was followed by gas chromatography, determining the content of methyl esters at different reaction times.

iii. Biodiesel was characterized by a set of parameter according to European Standard, EN 14214. The best conditions for transesterification process were 9:1 methanol/oil molar ratio, 65 ºC, and the use of potassium methoxide as catalyst with concentration 1.0 wt.%.

iv. The yield of biodiesel plant production measured using break even analysis considering a fixed price for biodiesel selling.

v. The profitability analysis was estimate by determine the Return of Investment (ROI) and Payback Period (PP).

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 INTRODUCTION

The depleting reserves of fossil fuel, increasing demands for diesels and uncertainty in their availability is considered to be the important trigger for many initiatives to search for the alternative source of energy, which can supplement or replace fossil fuels. One hundred years ago, Rudolf Diesel tested peanut oil as fuel for his engine for the first time on August 10, 1893 (Shay, 1993). In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, usually only in emergency. The first International conference on plant and vegetable oils as fuels was held in Fargo, North Dakota in August 1982. The primary concern discussed were the cost of fuel, the effect of vegetable oil fuels on engine performance and durability and fuel preparation specification and additives. Oil production, oil seed processing and extraction also were considered in this meeting (ASAE, 1982). Vegetable oils hold promise as alternative fuels for diesel engines (Goering et al., 1982; Bagby, 1987). But their high viscosities, low volatilities and poor cold flow properties have led to the investigation of various derivatives. Fatty acid methyl esters, known as Biodiesel, derived from triglycerides by transesterification with methanol have received the most attention (Zhang et al., 2003; Perkins and Peterson, 1991).

The name Biodiesel was introduced in the United States during 1992 by the National Soy diesel Development Board (presently national bio diesel board) which has pioneered the commercialization of Biodiesel in the United States. Biodiesel can be used in any mixture with petroleum diesel as it has very similar characteristics but it has lower exhaust emissions. Biodiesel has better properties than that of petroleum diesel such as renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens (Martini and Shell, 1998).

Ma et al., (1999) stated that Biodiesel has become more attractive recently because of its environmental benefits and fact that it is made from renewable resources. The raw materials being exploited commercially by the Biodiesel are the edible fatty oils derived from rapeseed, soybean, palm, sun flower, coconut, linseed, etc. (Ksorbitz, 1999). In recent years, research has been directed to explore plant based fuels, have bright future (Martini and Shell, 1998).

Biodiesel is a renewable fuel consisting of fatty acid alkyl esters. It is typically produced from triglyceride sources such as vegetable oil or animal fats, but it can be made from any lipid source containing fatty acids. Biodiesel is produced by replacing the acylglycerol ester linkages with small alcohols such as methanol, yielding fatty acid methyl (or alkyl) esters. This chapter focused on the source of oils, problems associated with the use of oils, production of Biodiesel from non-edible oil, Physical and chemical properties of oils and esters; advantages, disadvantages and challenges. Furthermore discusses previously published papers relevant to the production of biodiesel from castor oil. Topics to be addressed include the background and history of biodiesel production, information about the castor plant and its oil, and analytical techniques used to monitor the progress of the biodiesel reaction (Meher et al., 2006).

## 2.2 THE CURRENT STATUS OF BIODIESEL

### 2.2.1 What Is Biodiesel?

Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, called B100. A mono-alkyl ester is the product of the reaction of a straight chain alcohol, such as methanol or ethanol, with a fat or oil (triglyceride) to form glycerol (glycerine) and the esters of long chain fatty acids. Biodiesel can be used pure (B100) or as a blend (B %); this will be discussed in following chapters.

***The production process***

The manufacture process of biodiesel will be briefly described in this section. Broadly speaking, the production process starts by refining the oil, just in case the oil is not already refined. Thus, oil is refined, cleaned off impurities, and getting ready to carry out a transesterification process. The transesterification process is produced by combining the oil with a light alcohol, normally methanol. The reaction leaves glycerine as a remainder product, so that, this can be used by the cosmetic industry, among others.

The oil to be processed can come from different sources, vegetal oil and animal fat, first use or recycled. Market prices and availability are the factors that would help investors to decide which use is the most appropriate. On one hand, in terms of oil coming from seeds, EU biodiesel mainly comes from rape seed, mean US biodiesel from soybean seeds. This is related to the oil yield by hectare on different countries. On the other hand, recycled oils can be a very cheap raw material but the manufacturing process is quite expensive.

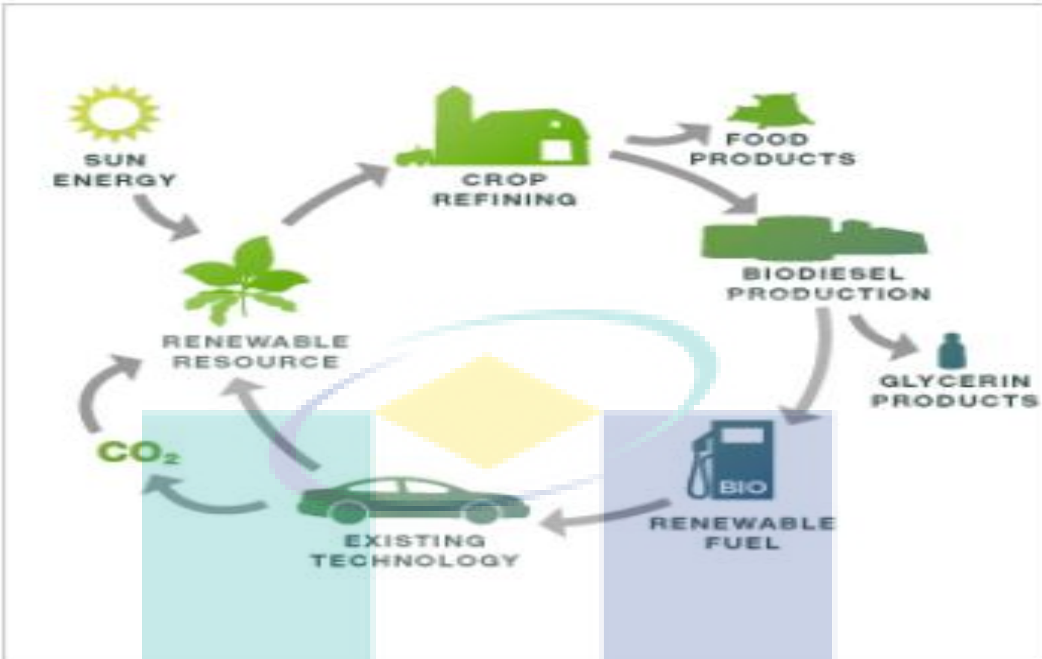



**Figure 2.1:** Biodiesel life cycle.

Source: (Propel biofuels, 2012)

***Life cycle***

The life cycle consider the environmental aspects and potential impacts associated with a product, considering the relevant energy and material inputs and environmental releases, and the environmental impacts associated with identified inputs and releases. As it is shown in the Figure 2.1, the biodiesel life cycle begins with sun energy which is transformed into energy through vegetables to be later transformed and used as a transport fuel. It is assumed than CO2 emitted on its combustion is reused by other vegetables in the photosynthesis process. So it is considered to be a CO2 emitter.

### 2.2.2 Biodiesel Compared With Other Transport Fuels

***Energy comparison***

There are different ways in which a comparison between conventional road fuels and bio-road fuels can be made. One valuable way is set on the basis of an energy balance, which is the difference between how much energy is created when producing the fuel, and how much is obtained when using the fuel (Duke, 1983). The approximation considers the energy used to make the plant grow, to produce biodiesel and to distribute it. Table 2.1 shows an energy balance of biodiesel production from soybean seeds by transesterification process.

**Table 2.1**: Energy balance of a biodiesel production from soybean seeds Source: Based on data of U.S. Dept of Energy (DOE) (DOE, 2012) and U.S. Dept of Agriculture (USDA), 1998

Source: (USDA 1998)

| **Fuel** | **Energy IN** | **Energy OUT** | **%** |
|---|---|---|---|
| Biodiesel | 1 | 3.2 | 320 |
| Ethanol | 1 | 1.34 | 134 |
| Petro-diesel | 1 | 0.84 | 84 |
| Gasoline | 1 | 0.81 | 81 |

Although the Table 2.1 shows an efficiency of 320%, different studies show different values depending on the type of raw material used, and the process carried out, thus it is widely accepted that this will be about 220% higher. The difference on figures comes by the fact that it is extremely difficult to clearly identify all steps involved.

***Property comparison***

Table 2.2 shows a comparison between biodiesel and diesel at low-sulphur content, the reason to compare those products is based on environmental and performance reasons. Note that nowadays, international efforts are being carried out to reduce emissions as well as air pollution. Therefore, then high diesel sulphur content are tried to be avoid and then extra technical obtaining process are applied on diesel production to reduce sulphur level, and thus to produce diesel at a low sulphur content.

**Table 2.2**: Biodiesel and diesel properties comparison

Source: Biofuel for transport (IEA 2004)

Biodiesel / Diesel Property Comparison

| | Biodiesel | Low-sulphur diesel |
|---|---|---|
| Cetane number | 51 to 62 | 44 to 49 |
| Lubricity | + | very low |
| Biodegradability | + | - |
| Toxicity | + | - |
| Oxygen | up to 11% | very low |
| Aromatics | 0 | 18-22% |
| Sulphur | 0 | 0-350 ppm[a] |
| Cloud point | - | + |
| Flash point | 300-400°F | 125°F |
| Effect on natural, butyl rubber | can degrade | no impact |

i. Cetane number

The cetane number measures how easily ignition occurs and the smoothness of combustion. To a point, a high number indicates good ignition, easy starting, starting at a low temperature, low ignition pressures, and smooth operation with lower knocking traits.In the EU a minimum cetaneof 49 is normally required, so low-sulphur diesel is sometimes dismissed under this value. However, in order to clearly understand the previous table, it is important to note that there is a big difference between petro diesel and biodiesel with regards to the ignition quality. That is to say, the cetane number must be used rather than the cetane index. To sort this out, the Calculated Cetane Index (CCI) is based on the historical database for the distillation curve of petroleum diesel and is not applicable to biodiesel, primarily due to the lack of a 'distillation curve' for biodiesel.

So, whereas petro-diesel is comprised of hundreds of compounds boiling at differing temperatures (determined by the petroleum refining process), biodiesel contains only a few compounds- primarily 16 to 18 carbon chain length alkyl esters (determined by the feedstock), which all boil at approximately the same temperature. Biodiesel, therefore, exhibits more of a boiling point than a distillation curve. In addition, the composition of naturally occurring oils and fats is very similar, giving a very tight boiling range for biodiesel regardless of the feedstock. The composition of biodiesel is also the reason for its high flashing point, which is an advantage in enclosed areas such as underground mines.

ii. Lubricity

Better lubricity means lower engine friction.

iii. Sulphur

One important value which is worthy to be considered is the sulphur contents, mainly because it is a basic characteristic in diesel engines, and also because of its negative effect in the environment by measures of acid rain. Thus, in the US and in Europe, legislation tries to take the diesel oil sulphur content, at levels close to zero. Meanwhile no sulphur emissions are produced with the use of biodiesel.Reducing the sulphur contents also reduces fuel lubricity. That is reason of oil companies must add to diesel some chemical and synthetic additives to mitigate that anomaly. Blending biodiesel can help, since it does not contain sulphur and helps improve lubricity. For example, in France all diesels sold have been added with Biodiesel to 2%, due to the fact that biodiesel is a good lubricant. On the other hand, blending only small quantities of biodiesel with conventional diesel does not bring the average sulphur contents down appreciatively. To reduce 350 ppm sulphur diesel down to 50 ppm, for example, requires a blend of more than 85% biodiesel. At current biodiesel production costs, refiners will likely prefer to cut the sulphur content of conventional diesel at the refinery.

***Emissions***

By using biodiesel instead of petroleum diesel, a contribution to reduce greenhouse gas emissions can be made by nearly 80 per cent, according to the Environmental Protection Agency’s 2002 report.

1. Biodiesel also substantially reduces particle emissions and PAH air toxins (including benzene) which are hazardous to human health.
2. The use and the production of biodiesel exhibit a closed-loop carbon cycle. Unlike petrodiesel, which releases greenhouse gases contained (or sequestered) deep beneath the earth, the emissions released by using biodiesel are equivalent to the amount absorbed by the plant while growing.
3. Biodiesel is the first and only alternative fuel to have a complete evaluation of emission results and potential health effects submitted to the U.S. Environmental Protection Agency (EPA) under the Clean Air Act.

Then, although emissions vary with engine design, vehicle condition, and fuel quality, the US EPA (EPA, 2002b) Figure 2.2 found that, with the exception of $NO_x$, potential reductions from biodiesel blends are considerable relative to conventional diesel, and they increase nearly linearly with increasing blend levels. Reductions in toxic emissions are similarly large.

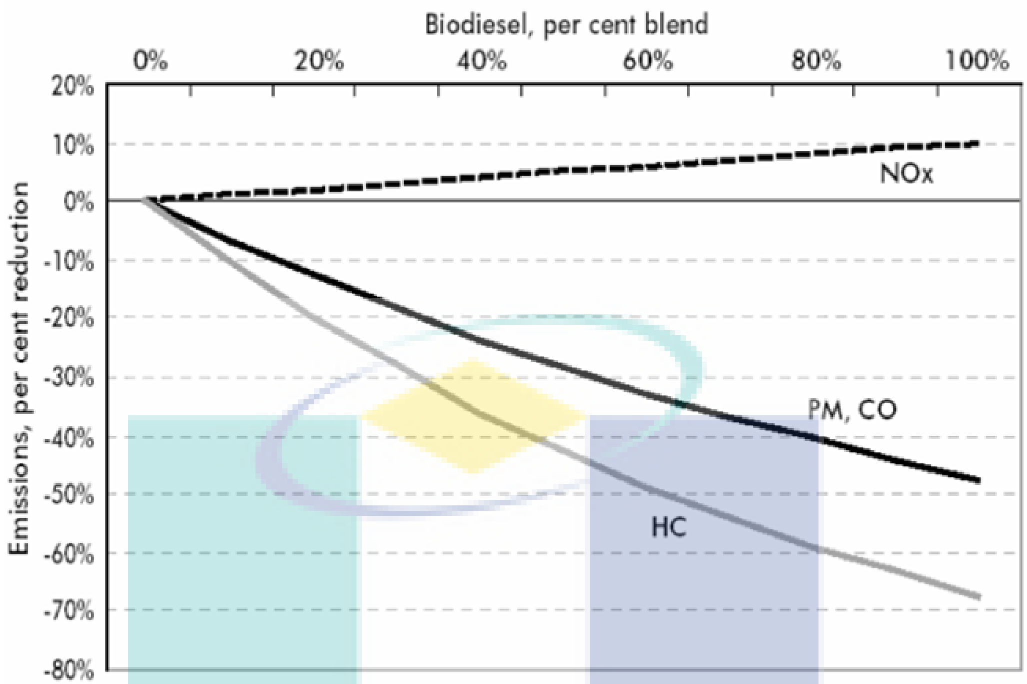



**Figure 2.2:** Potential Emissions Reductions from biodiesel blends.

Source:(EPA 2012).

According to the Figure 2.2, by using biodiesel B20, carbon monoxide can be reduced on 13%, hydrocarbons on 11%, particles on 18%. Also by using biodiesel B100, carbon monoxide can be reduced on 43%, hydrocarbons on 56%, particles on 55%. It is considered that total air toxics can be reduced by 0.3% by using B20 or by 1.5% by using B100.

### 2.2.3 Importanceof Biodiesel

The biodiesel have advantages and disadvantages can summarize it as follows:

***Advantages***

Biodiesel is an ecological fuel which has the following characteristics:

1. It is obtained from renewable resources. Biodiesel can be produced from vegetal, animal and recycled oils. Among vegetables, although there are more than three hundred types of oil, the most common one in biodiesel production is soybean, rape, sunflower and palm oil.
2. During its combustion it consume smaller amount of $CO_2$ than the one absorbed on their growth, so that the final balance of $CO_2$ emissions is positive. In fact, it is considered as a $CO_2$ neutral emissary. Therefore, the combustion of biodiesel does not contribute to the greenhouse effect; it is neutral and it aids to fulfil the protocol of Kyoto. This is extremely important. In detail, according to the European Environment Agency, BAFF, changes (%) in EU greenhouse gas emissions by sector (1990-99) has increased around 20% in the transport sector, so by using biodiesel this value could be decreased.
3. Do contain neither benzene nor other carcinogenic aromatic substances, such as aromatic hydrocarbons.
4. It is easily biodegradable, and in case of spill and/or accident, it do not put in danger neither the ground nor underground waters. Biodiesel is biodegradable in approximately 21 days. The absence of a chemical and synthetic compound makes it innocuous with our environment.
5. Is not dangerous merchandise, the flash point is over 110º C. Biodiesel flash point is over 110ºC, for that reason it is not classified as non hazardous merchandise, which helps on safe storage and safe manipulation.

***Disadvantages***

1. At low temperatures, it can begin to solidify and to form crystals that can obstruct the conducts of the fuel. Due to its solvent properties, it can soften and degrade certain materials, such as natural rubber and polyurethane foam.
2. Production costs still can be higher than the cost of diesel itself. It all basically depends on the oil source which has been used.

## 2.3 BIODIESEL FROM VEGETABLE OIL

The transesterification of the soybean oil, degumming soybean oil, and castor oil was a study by De Oliveira et al., (2005) , which he chooses to use ethanol as the alcohol substrate because the large ethanol industry in their home country of Brazil. Like methanol, ethanol is wholly miscible with castor oil. The authors used a gas chromatograph fitted with flame ionization detector (GC-FID) to determine the fatty acid compositions of the several oils. The samples of Fatty acid ethyl ester (FAEE) were analyzed thru a gas chromatography/mass selective detector (GC/MSD). Where he referred that the use various fatty acid ethyl esters as internal criteria, but didn't afford details of exactly how the peak area was correlative to reaction conversion.

The paper does not destine whether the values of Reaction conversion and the measured response variable were in a mass or molar basis, where the values were given as a percentage for each set of reaction conditions. According to the maximum conversion were attained as 96%, 94%, and 93% for castor oil, refined soybean oil, and degummed soybean oil, respectively, but no calculations were applied. Besides the analysis was not executed for reaction intermediates, such as mono- or diglycerides; thus, no kinetic analysis was conducted.

A response surface model of conversion versus the reaction variables was developed for each vegetable oil based on the experimental data. According to the authors' analysis, the catalyst concentration had a negative effect on reaction conversion, whereas temperature and reaction time had a positive effect on conversion. Also, the oil to ethanol ratio had no significant effect on conversion for the castor oil system and only a slight positive effect for the two soybean oil systems. According to the model, the optimal conditions for castor oil conversion were achieved at a 70 °C reaction temperature, a catalyst amount of 0.5 wt%, an ethanol to oil ratio of 3:1, and a three-hour reaction time. The experimental conversion at these levels was 96.2%, and the predicted value was 95.4%. No explanation was given as to why sodium hydroxide concentration had a negative effect on yield, but one possible explanation is that there is an inhibiting effect caused by the water created when mixing the sodium hydroxide with the ethanol.

Da Silva et al., (2006) discussed the transesterification of castor oil with ethanol using sodium ethoxide as the alkaline catalyst. The studied variables were reaction temperature (30 – 80 °C), ethanol to castor oil molar ratio (12:1– 20:1), and sodium ethoxide catalyst concentration (0.5 – 1.5 wt %). The agitation level (600 rpm) and reaction time (30 min) were kept constant. Cooling and dilution with tetrahydrofuran quenched the reaction.

High-performance size-exclusion chromatography (HPSEC) was used to determine the amount of monoglycerides, diglycerides, triglycerides, FAEEs, and glycerol present in the reaction mixture. This method, also called gel-permeation 11 chromatography, selectively retains the molecules based on size. Each of the five groups of compounds mentioned above appeared as a single peak on the chromatograms. Rather than using any external standard to quantify the various peak groups mentioned above, the authors calculated the reaction conversion as the area of the ethyl ester peak divided by the sum of the peak areas representing the four components that contain fatty acids: triglyceride, diglyceride, monoglyceride, and ethyl ester. The type of detector is not mentioned in the paper, but the cited paper for the HPSEC method used a refract meter detector (Fillières et al., 1995).

The interpretation of the results was ambiguous, but the authors concluded that temperature was not a significant factor in determining the reaction conversion. They posited that the increased solubility of the castor oil in ethanol eliminated the need for elevated temperatures. It was determined that conversion increased when either catalyst concentration or the alcohol to oil ratio was increased, with catalyst concentration being a more significant factor.

Another paper compared using ethanol and methanol in the production of biodiesel from castor oil (Meneghetti et al., 2006). Reaction yield was measured by GC-FID as percent mass of FAMEs or FAEEs present in a sample from the biodiesel reaction, with tricaprylin as an internal standard. In this study, a variety ofalkaline (KOH, NaOH, KOCH3, and NaOCH3) and acidic (H2SO4, HCl) catalysts were used to drive the transesterification reaction. In each case, the alcohol/oil/catalyst molar ratio remained at 60:10:2. The paper did not address whether the reaction continued while the reaction mixture underwent distillation prior to neutralization. The authors stated that their efforts to use a separatory funnel to separate the phases of the resulting mixture proved to be difficult because of the polar nature of the castor oil. Before analyzing the samples via gas chromatography, the mixture was dried with MgSO4 and centrifuged. The authors reported that the best yields were usually achieved with the methoxide ion as the catalyst. The authors explain that the alkoxide ion (methoxide or ethoxide) was the active species in all the alkaline reactions, but the conversion of the hydroxide ion to the active species forms water, which could reduce the yield. Despite the slightly higher yields achieved by the alkaline reactions, a number of factors could have diminished the conversion. The presence of free fatty acids in the castor oil may have neutralized some of the catalyst, decreasing the amount of catalyst available for catalysis. This side reaction would produce soaps, which could cause further difficulty in separating the biodiesel from the reaction mixture. AlsoMeneghetti et al. Hypothesizedthat the distinctive hydroxyl group at C-12 of ricinoleic acid may be deprotonated by the base, again reducing the amount of alkoxide available for catalysis.

As mentioned previously, the transesterification reactions were also performed with acid catalysis. Meneghetti et al., (2006) pointed out previously published data that indicates acid-catalyzed reactions take place at rates approximately 4000 times more slowly than similar base-catalyzed reactions; however, the results reported in this paper show that the conversion of castor oil via the acid-catalyzed transesterification behaved similarly to that 13 of the base-catalyzed reactions. The given explanation suggested that the discrepancy was due to the castor oil's distinctively high content of hydroxyl fatty acid derivatives, although no mechanism to explain this phenomenon was stated. Additionally, because of the ability of acidic catalysts to simultaneously esterify free fatty acids while transesterifying the glycerol-bound fatty acids, the authors argue that industrial-scale acid-catalyzed biodiesel production from castor oil may be economical.

On the topic of comparing the use of methanol and ethanol as the transesterification substrate, the authors concluded that using either is feasible, although methanol seemed to be superior in terms of conversion and reaction time, regardless of the choice of catalyst. Additionally, since both reactions were conducted near the boiling point of the chosen alcohol, the methanol reaction requires a lower energy contribution. The maximum yields reported for methanolysis and ethanolysis were 90% and 80%, respectively. These yields were achieved in one hour with methanol and five hours with ethanol.

## 2.4 PRESENT AND FUTURE OF BIODIESEL

At the present time, recent researches indicate that the use of biodiesel has moved to a world-wide scale market, emerging from countries like Brazil, the US, EU or China. However, there are some barriers to this development; most of which have to do with cost reasons. Nowadays, international present policies for the introduction of biodiesel especially in the transport sector, are improving this situation thus helping the biodiesel market. According to the Interdisciplinary Centre for Comparative Research in the Social Sciences- ICCR, 98% of the energy consumed in the transport sector comes from fossil fuels. Due to this, it is evident that non petroleum producing countries all over the world should be worried about the reduction of their strong dependency on these fuels. It is also obvious that the transport sector becomes most directly affected by this petroleum dependency. For that reason, the European Union has established in the directive EU 30/2003, some strategies to reduce petroleum dependency, specially focusing attention on the sector transport (EUW, 2012). Also, with respect to the polluting emissions, the transport sector is responsible for 87% of the CO emissions, 66% of the NOx, 60% of CO2 and 5% of SO2.

## 2.5 POTENTIAL OF CASTOR OIL FOR BIODIESEL PRODUCTION

### 2.5.1 Castor Oil Description

Castor seed, Ricinuscommunis L., is a member of the tropical spurge family, Euphorbiaceae, and can nowadays be found naturalized and cultivated in all temperate countries of the world. Castor is amongst the plants with the highest oil yield potential because of its high yield of seeds and the high oil content of its seeds. It may be possible to obtain a maximum of 2000 kgoil·ha-1 (Scholz and Silva, 2008). Whereas rapeseed produces about 1000 kgoil·ha-1 and soybean only produces about 500 kgoil·ha-1 (Balat and Balat, 2010). Therefore, castor oil is a promising source to produce biodiesel, with less in cultivated land.

The composition of castor oil is 80-90 % ricinoleic acid, 3-6 % linoleic acid, 2-4 % oleic acid and 1-5 % saturated fatty acids (Scholz and Silva, 2008). Ricinoleic acid is the main fatty acid found in castor oil; this fatty acid possesses 18 carbons with three highly reactive functional groups: the carbonyl group in $1^{st}$ carbon, the double linking or instauration in $9^{th}$ carbon and the hydroxyl group in $12^{th}$ carbon. This feature causes castor oil properties are different from other vegetable oils (Conceição et al., 2007). The high content of ricinoleic acid, with a hydroxyl group, is the reason for castor oil has especially high viscosity and density. Castor oil is also characterized by its high stability, high hygroscopicity and its solubility in alcohol, which affects the transesterification reaction (Scholz and Silva, 2008; Conceiçao et al., 2005; Ogunniyi, 2006).

Castor oil is soluble in methanol; hence, this oil favors the transesterification reaction. Biodiesel production from castor oil has been studied by several researchers. Response surface methodology was used to optimize the transesterification reaction in traditional conditions. The results showed that reaction temperature affected the reaction slightly, however catalyst amount affected especially (Da Silva et al., 2009; Jeong and Park, 2009). The reaction using co-solvent was also studied as well as a kinetic study has been carried out (Peña et al., 2009; Ramezani et al., 2010).

### 2.5.2 Status As An Energy Crop

Castor is currently considered experimental as a biofuel feedstock and mainly a crop of interest for small scale farmers in areas with challenging agro-climatic conditions. Under mechanized high-input farming other energy crops are likely to be more profitable. Castor oil fetches a higher price on the world market than other vegetable oils and is therefore not attractive as a raw material for biofuel production. Tax incentives such as the ones provided in Brazil can change this situation (Da Silva César and OtávioBatalha, 2010). In dry and isolated areas where biofuel is produced and consumed locally it is sometimes one of the only options for oil crops and it may be competitive due to the low transport costs involved compared to importing oil. The Brazilian government supports Castor as a biofuel crop for small farmers in the North-East of the country. In India and elsewhere it is being inter-cropped with other types of crops sometimes with Jatropha as a biofuel crop.

### 2.5.3 Centre Of Origin And Current Distribution

Castor probably originated in North-East Africa from where it spread thousands of years ago to the Mediterranean, the Middle East and India. Today Castor is cultivated and growing in the wild throughout the drier tropical, warm-temperate and subtropical regions between 40° South to 52° North. It is found at altitudes from sea level to about 3,000 m in areas where there is no or only slight frost.

### 2.5.4Yields and Conversion In To Biodiesel

Yields under small holder conditions without irrigation are typically 300-400 kg/ha. Irrigation can double the yield. In India the average yield is 560 kg/ha, in Brazil 900 kg/ha and worldwide 1100 kg/ha. Under mechanized high-input farming up to 5000 kg/ha/year can be achieved (Jeong and Park, 2009).

**Table 2.3:** Castor oil production worldwide 2008 (Panwar et al., 2009)

| Country | Tons |
|---|---|
| India | 1,123,000 |
| China | 220,000 |
| Brazil | 120,499 |
| Mozambique | 52,071 |
| Thailand | 11,330 |
| Paraguay | 10,500 |
| Ethiopia | 7,000 |
| Viet Nam | 5,000 |
| South Africa | 4,900 |
| Pakistan | 4,023 |
| Angola | 3,500 |

### 2.5.5 World Market for Castor Oil

The share of castor seed is less than 0.15% of total world trade of oil seeds. At present, the annual world yield of castor seeds is about 1.3 million tones, which corresponds to about 0.55 million tones of castor oil. Since the beginning of the 1970's, castor oil seed production increased continuously but, in some cases, subjected to yearly fluctuations of 20%, especially due to storm damage in the main producing regions. About half of all the castor oil produced in the world is exported, with India dominating the market with a share of 80%. Presently, India produces over 90% of the castor oil in the entire world as shown in Table 2.3 (Volkhard and Jadir, 2008).

## 2.6 MARKETING OF BIODIESEL

The global biodiesel production increased from2001 to 2007, where edible-grade vegetable oils (soy, rapeseed, sun flower and palm) are currently the major biodiesel feedstock's (Scholz and Da Silva, 2008). This intensive production and commercialization of biodiesel have raised some critical environmental concerns. Its large-scale production can lead to imbalance in the global food market by drastically increasing consumption oil prices, which mainly affect developing countries. Land availability, and in particular competition for acreage with food crops, is also considered a core limitation (Bindraban et al., 2009). In order to mitigate these environmental consequences, unconventional oilseeds are being investigated as alternative feedstocks.

Biodiesel has received much attention in Brazil as of lately. It was first introduced in the Brazilian energy grid in 2007 as an option, but in 2008, it became compulsory. Since then, the biodiesel sector has been rapidly developing (Gui et al., 2008). A federal program called National Program for Production and Use of Biodiesel (PNPB in Portuguese) and its corresponding legislation have created a substantial demand for biodiesel Furthermore, the PNPB began to stimulate not only its production from various types of oil but also its social inclusion (ANP, 2009; IEA, 2007; Pousa et al., 2007). Despite the real and potential growth of the Brazilian biodiesel market, it is surrounded by many uncertainties, especially with regard to its long term sustainability and economic viability (Garcez and Vianna, 2009; IEA, 2007; Pousa et al., 2007).

Among the various oilseeds, castor bean (Ricinuscommunis) was identified as the ideal one to promote social development in the Brazilian northeastern region (Ce´sar and Batalha, 2007). Its low implementation and production cost and its relative resistance to hydric stress, have enabled this oil plant to develop under adverse climate and soil conditions, which are the characteristics of the semi-arid region in Brazil (IICA, 2007).

In present study the biodiesel derived from castor seed oil has been used. It is a triglyceride derived from ricinoleic acid, which constitutes 90% of fatty acids present in the molecule and 10% non-hydroxylated fatty acids, mainly by oleic and linoleic acids. Due to this particular chemical composition castor oil becomes highly valuable for industrial purposes (Soares et al., 2001; Ogunniyi, 2006). The demand of renewable combustible fuel derived from vegetable oils has increased in the last years, and has led to the development of a number of processes for transesterification of oils with methanol or ethanol, involving acidic (Lotero et al., 2005; Serio et al., 2005) or basic catalysis (Vicente et al., 2005; Marchetti et al., 2007)

# CHAPTER 3

# METHODOLOGY

## 3.1 THE PROCESS TECHNOLOGY SELECTION:

Biodiesel from fatty acids can be produced by a variety of esteritification technologies. The production of biodiesel, or methyl esters, by esteritification is a well-known chemical process that has been used for decades in the soap and detergent industry. First the oil is filtered and pre-processed to remove water and contaminants. If free fatty acids are present, they can be removed or transformed into biodiesel using pre-treatment technologies. The pre-treated oils and fats are then mixed with an alcohol (usually methanol) and a catalyst (usually sodium or potassium hydroxide). The oil molecules (triglycerides) are broken apart and reformed into esters and glycerol, which are then separated from each other and purified. The resulting esters are biodiesel.

By this time, there are three basic chemical routes to produce methyl esters from renewable oils and fats:

1. Base catalyzed transesterification of oil with methanol.
2. Direct acid catalyzed esterification of oil with methanol.
3. Conversion of the oil to fatty acids, and then to methyl esters with acid catalysis.

The selection of these chemical routes will determine the technology process to be used, and must be taken extremely carefully. This can be carried out basing on the following aspects:

1. Batch vs. Continuous Technology.
2. Existing vs. Developing Technology.
3. Capital and Operating Cost Differences.
4. Product Yields and Quality from Various Feedstock's.

Nowadays, most of the methyl ester producers use the base-catalyzed reaction called transesterification, in a batch process. This is mainly for economical and operational reasons whose justification is based on the fact that it is easier to handle variations in raw material quality in a discontinuous process.

The main characteristics of the transesterification process in comparison to others, according to Biodiesel Production Technology report of January 2004, are the following:

1. Low temperature about 71-82 ºC.
2. Low pressure about 103 Pascal to 206 Pascal.
3. High yields conversion around 98% with minimal side reactions when low free fatty acid feed stocks are used.
4. No exotic materials are required for construction.

## 3.2. THE TRANSESTERIFICATION

### 3.2.1 Chemical Reaction

Transesterification is a base-catalyzed chemical reaction process. Almost all the biodiesel is produced by using a base-catalyzed transesterification process, as it is the most economical process for it only requires low temperatures and pressures. In the reaction, 100 parts of a fat or oil is reacted with 10 parts of methanol in the presence of a base catalyst to produce 10 parts of glycerine and 100 parts of methyl esters (biodiesel). Normally, the methanol is charged in excess to assist in quick conversion and the excess is recovered for reuse. The catalyst is usually sodium or potassium hydroxide that has already been mixed with the methanol. Figure 3.1 shows a typical transesterification reaction, a triglyceride reacts with methanol through a base catalyst to produce biodiesel methyl ester and glycerine (Da Silva et al., 2006).

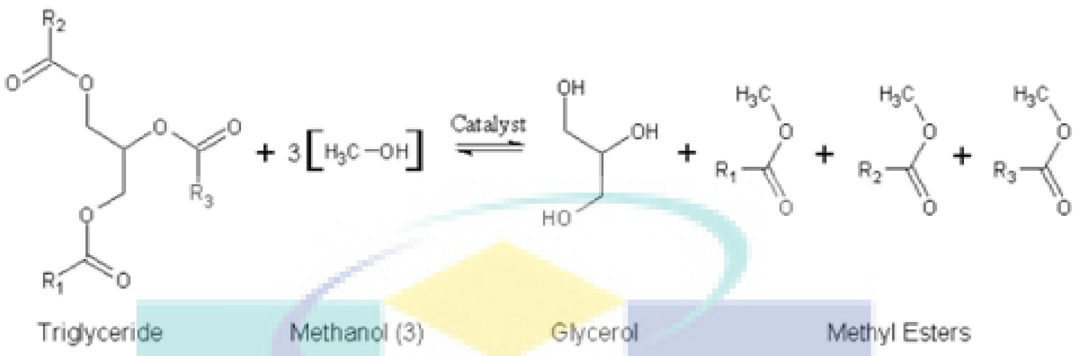



**Figure 3.1:** The transesterification reaction. Source: Technology Information, Forecasting.

### 3.2.2 Production Process

The chemical reaction for base catalyzed bio-diesel production is depicted generic reaction in Figure 3.2. One hundred pound of fat or oil are reacted with 10 pounds of short chain alcohol in presence of a catalysts to produce 10 pounds of glycerin and 100 pounds of bio-diesel. The short chain alcohol, signified by ROH (usually methanol, but sometimes ethanol) is charged in excess to assist in quick conversion.

The base catalyzed production of bio-diesel generally occurs using the following steps:

1. Mixing of alcohol and catalyst - It is dissolved in the alcohol (methanol) using a standard agitator and mixer.

2. Reaction – The alcohol/ catalyst mix is then charged into a closed reaction vessel prevents loss of alcohol and the castor oil added. The reaction mix is kept just above the boiling point of the alcohol (around 67.4$^{o}$C) to speed up the reaction. Recommended reaction time varies from 1 to 8 hours, and some systems recommended the reaction take place at the room temperature. Excess alcohol is normally used to ensure total conversion of the oil to its esters. Care

must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream.

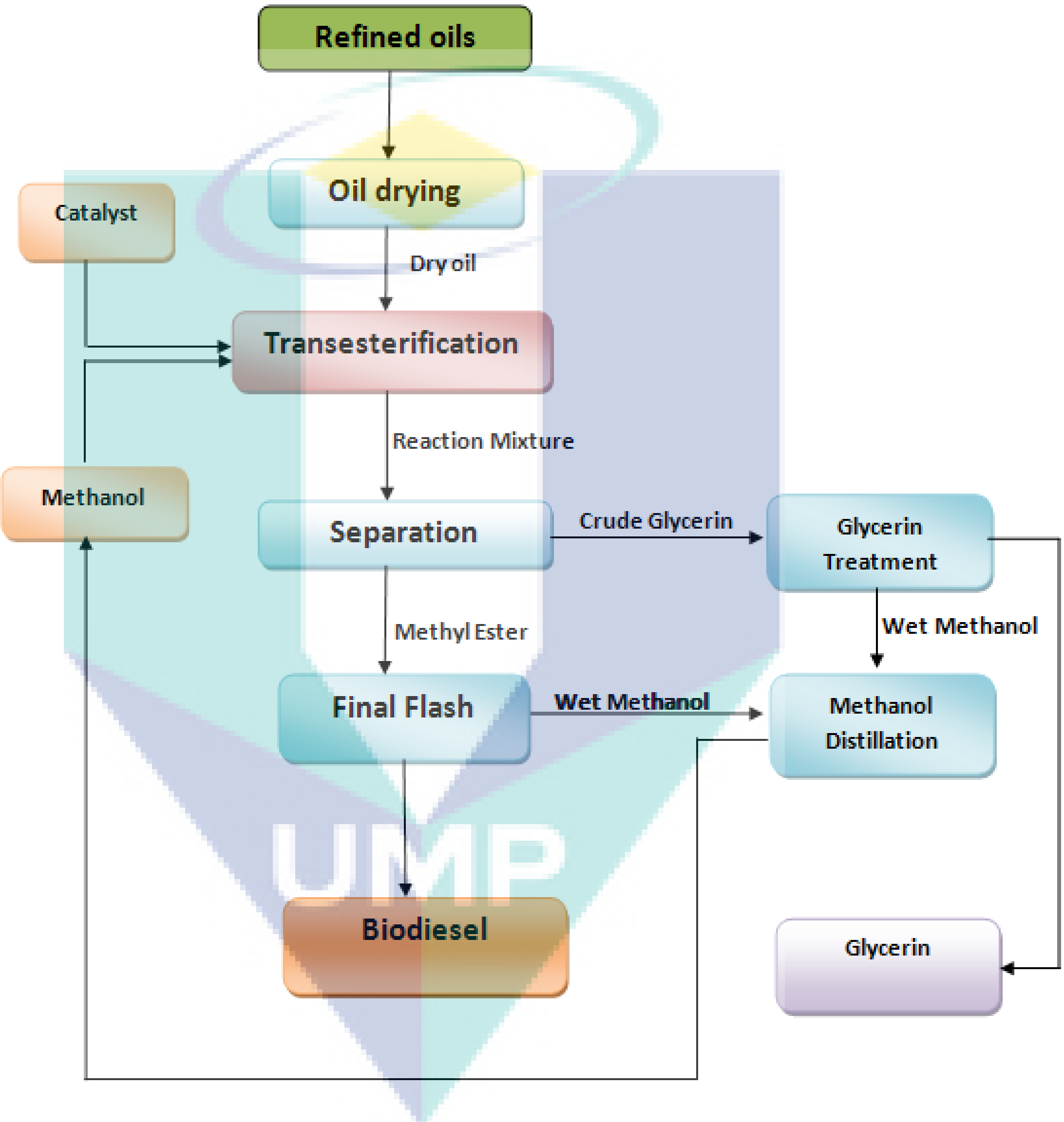



**Figure 3.2:** Biodiesel Production Process

3. Separation – Once the reaction is complete, two major products exist: glycerin and bio-diesel. Each has a substantial amount of the excess methanol that used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than bio-diesel phase and the two can be gravity separated with the glycerin simply drawn off the bottom of the

settling vessel. In some cases, a centrifuge is used to separate the two materials faster.

4. Alcohol Removal – Once the glycerin and bio-diesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In others systems, the alcohol is removed the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

5. Glycerin Neutralization – The glycerin by-product contains unused catalyst and soaps that are neutralized with and acid and sent to storage as crude glycerin. In some cases the salt formed during this phase is recovered for use as fertilizer. In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 80 -88% pure glycerin that is ready to sold as crude glycerin. In more sophisticated operations, the glycerin is distilled to 99% or higher purity and sold into the cosmetic and pharmaceutical markets.

6. Methyl Ester Wash – Once separated from glycerin, the bio-diesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried and sent to storage. In some processes this step is unnecessary. This is normally the end of the production process resulting in a clear amber-yellow liquid with viscosity similar to petro-diesel. In some systems the bio-diesel is distilled in an additional step to remove small amounts of color bodies to produce colorless bio-diesel.

7. Product Quality – Prior to use as a commercial fuel, the finished bio-diesel must be analyzed using sophisticated analytical equipment to ensure it follows the Standard EN 14214 specifications.

## 3.3 MATERIALS AND METHODS

### 3.3.1 Transesterification Reaction

Flowing the description of one of transesterification reaction where the castor oil was obtained in our laboratory in a mechanical press and then refined. Table 3.1 presents castor oil properties. Methanol (99.6%), potassium methoxide, potassium hydroxide, and sulphuric and phosphoric acids were purchased from Panreac. Methyl esters of ricinoleic, palmitic, stearic, oleic, linoleic, linolenic and erucic acids, employed as standards in the chromatographic determination, were supplied by Sigma-Aldrich.

**Table 3.1:** Characterization of biodiesel obtained from castor oil transesterification

| | |
|---|---|
| Density at 15 °C | 961.20 $kg.m^{-3}$ |
| Viscosity at 40 °C | 258.01 cSt |
| Water content | 0.20% |
| Saponification value | 180.33 $mg_{KOH} \cdot g_{sample}^{-1}$ |
| Iodine Value | 84.19 $gI_2 \cdot g_{sample}^{-1}$ |
| Acid Value | 1.09 $mg_{KOH} \cdot g_{sample}^{-1}$ |
| Acid Number | 0.55 |
| Molecular Weight | 918.12 $g \cdot mol^{-1}$ |

Transesterification reaction was carried out in a 1000 mL spherical reactor, provided with thermostat, mechanical stirring, sampling outlet, and condensation systems. This installation was consistent with that utilized in previous works (Encinar, et al., 2005; Encinar, et al., 2007)and it showed in Figure 3.3. The procedure followed is described next. The reactor was preheated to 65 ºC to eliminate moisture, and then 500 g of castor oil was added. When the reactor reached its established temperature, the methanol and the catalyst were added, amounts calculated for each experiment, and the stirring system was connected, taking this moment as time zero of the reaction.

At evenly spaced intervals, 1.5$cm^3$ of samples withdraws for later chromatographic analysis. In each experiment the reaction time was 3h, and thus the conversion to esters was practically complete. After cooling, the two phases formed (upper phase consisted of methyl esters, and the lower phase contained the glycerol, the excess methanol and the remaining catalyst) were separated by sedimentation. The methyl esters were purified by distilling the residual methanol at 80ºC, the remaining catalyst was extracted by successive rinses with distilled water, and, finally, the present water was eliminated by heating at 110ºC.

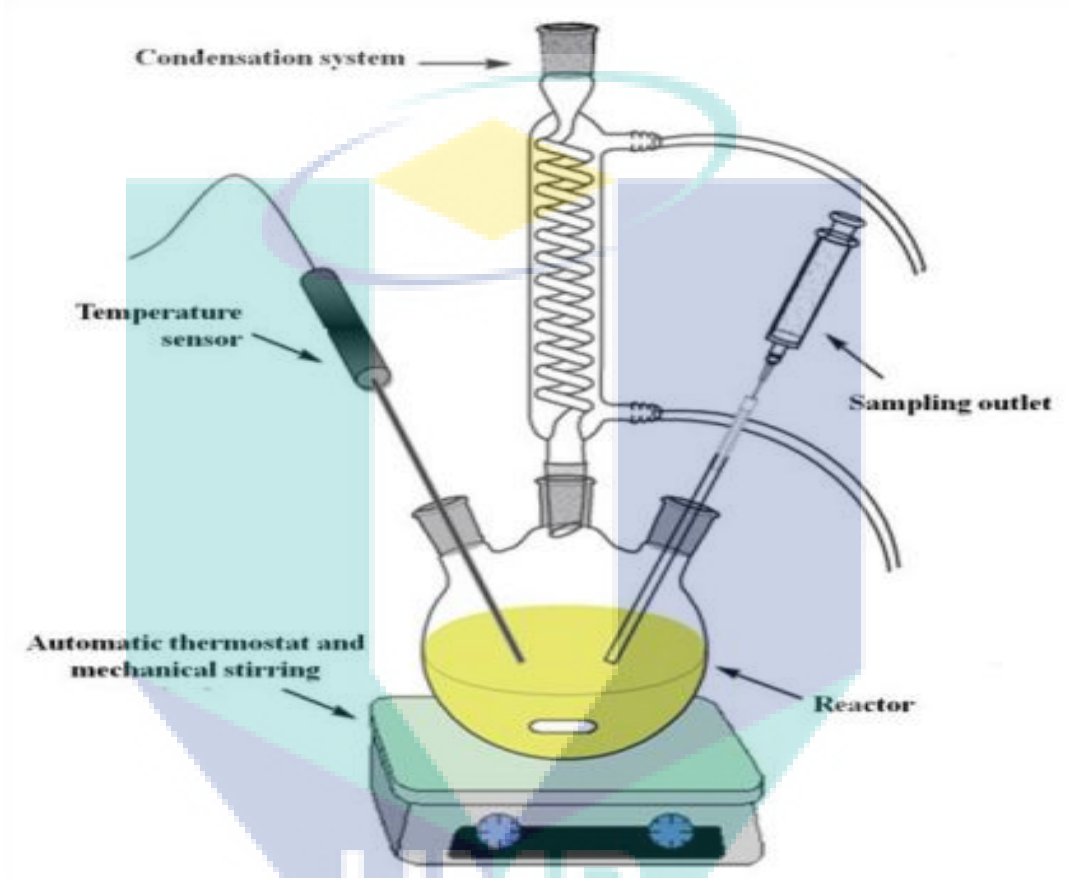



**Figure 3.3:** Schematic diagram of Batch Reactor Apparatus.

### 3.3.2 Product Analysis

The analytical methods used to determine the characteristics of biodiesel were basically those recommended by the European Organization for Normalization (CEN)(Heinrich, 2002). This organization specifies the criteria that should be satisfied by biodiesel of high quality, or diesel and biodiesel mixtures, for its use in motor vehicles (Heinrich, 2002). Methyl ester content was assayed by gas chromatography in a VARIAN 3900 chromatograph, provided with a FID, employing a silica capillary column of 30 m length, 0.32 mm ID, and 0.25 µm film thickness. Heptane was used as solvent, and the carrier gas was helium at a flow rate of 0.7 mL/min. The injector temperature was kept at 270 ºC, and the detector temperature, 300 ºC. Temperature ramp starts with 200 ºC, then 20 ºC/min up to 220 ºC.

The following properties of the final biodiesel product were determined: density (pycnometry), kinematic viscosity (Cannon-Fenske routine viscosimeter, size 100), distillation characteristics (ISO 3405 norm), cetane index (UNE 51-119-84), cold filter plugging point, CFPP (EN-116), flash and combustion point (EN-116), water content (Karl Fisher), and saponification and iodine values.

## 3.4 THE IMPLEMENTATION

### 3.4.1 Schedule

As usual, all projects need to be clearly planned. The success on the execution of the project directly depends on the plan and therefore on the execution of it. As it is shown in the following graph, the key project phases and major activities are mainly: a feasibility study, a conceptual idea, a project definition, the design, the construction, and finally starting it all up. Obviously, the duration of each phase will depend on how many resources and efforts are assigned to each phase.

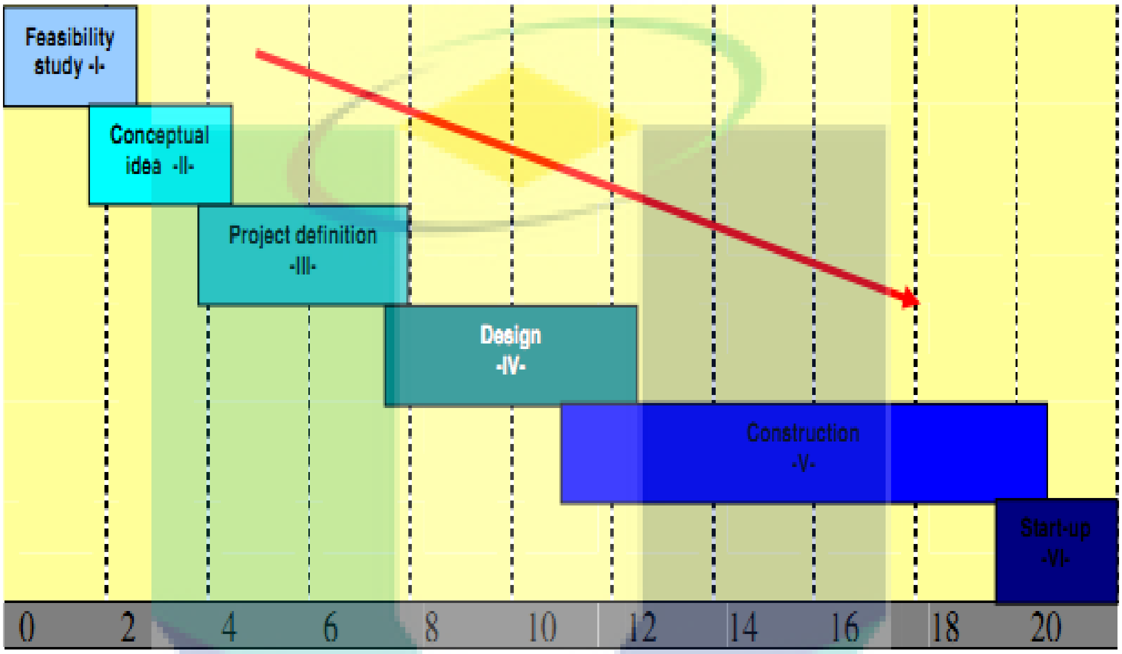
***Feasibility study***

In this part of the project the technical and economical feasibility is analysed. This phase must take into account:

1. To initiate the feasibility study by defining the opportunity.
2. To develop and evaluate different technology options and select the right one.
3. To develop different supply chain options including products and sub-products.
4. To develop execution alternatives.

5. To develop basis for business.
6. To define funding strategy.
7. To study the marketing and its competition.

**Table3.2:** Project duration in months..




Project duration (months)

***Conceptual idea***

To accomplish the business objective, the best approach to the conceptual idea must be considered. This phase must take into account:

1. To make an effort on defining the conceptual business idea.
2. To clearly define the technology option, the operation method and the supply chain which are going to be used.
3. To evaluate costs.
4. To put down an execution plan on schedule and to define milestones.

***Project definition***

The basis for the design that will be used by the engineering contractor will be developed on the project definition. The details of the plan to be executed will also bedefined. The project definition will set the basis to build the plant, so it is required to develop a detailed guideline for the design process. To reach this, it is important:

1. To develop a detailed scope.
2. To create the Project Execution Plan according to the PFD.
3. To prepare the basis for the design.

***Design***

Clearly, the project execution begins here. In this phase, the engineers from the Contractor Company start to design the details of the execution phase, then the team starts to build according to the design. To reach this, it is important:

1. To use resources on design management.
2. To define installations based on safety considerations. Due to the flammability of methyl and ethyl alcohol, and to the corrosive nature of the acids and bases, biodiesel plants are considered hazardous chemicals plants. A good Hazard and Operability (HASOP) study should be done.
3. To access the equipment to build and to test.

***Construction***

The project executions mainly take place in this phase. So, engineers from the contractor company execute the plan following the detailed project design. To reach this, it is important:

1. To use resources on construction management.
2. To develop a detailed Start-Up plan, including a training plan.

***Start-Up***

The execution project finally ends in this phase. To reach this, it is important:

1. To allocate a Start-Up team.
2. To train the Start-Up team.
3. To evaluate the final implantation of the detailed instructions.
4. To evaluate the final operation performance of the plant and final capacity reached.

**3.4.2. Site Location Study**

For the election of the site location, it must be taken into consideration mainly:

1. The feedstock supply.
2. The biodiesel distribution.

***Feedstock Supply***

The plant preferred located near of raw marital source to minimize the cost therefore the plant location in Industrial Estate, Kuching, Sarawak which is strategic and is within close proximity to the Kuching Port and it has castor oil refinery Figure 3.4. The location chosen is partly due to the close proximity to the port to save on logistics costs and the availability of crude castor oil and other raw materials to produce biodiesel.

***Biodiesel Distribution***

Biodiesel will be sold through distributor under the following strategy:

1. Produces pure biodiesel for sale to petroleum retailers/distributors.
2. Bulk biodiesel is shipped with tank trucks or tanker ships to petroleum retailers/distributors.

3. Blending is conducted by petroleum distributors' loading racks.
4. Biodiesel product is distributed to end users via pump stations.

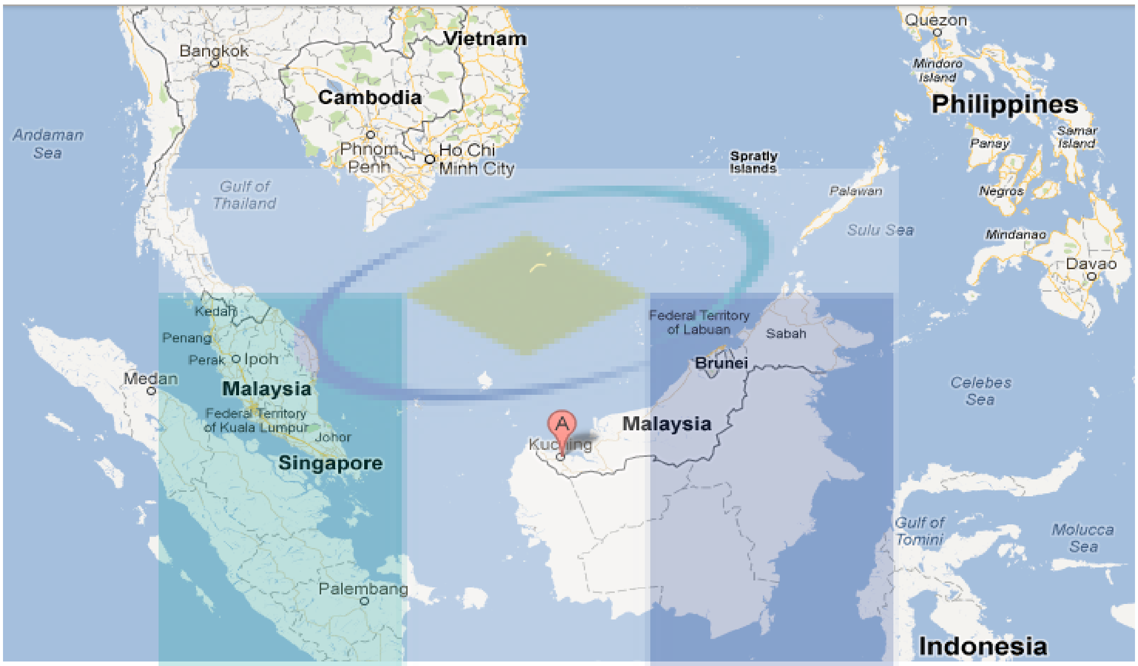



**Figure 3.4:** Biodiesel plantlocation

### 3.4.3 Plant Components

Based on the process flow sheet shown in Figure 3.5 the main equipment of biodiesel production are as following:

***Reactors***

In chemistry, following an English dictionary, "a Reactor is a large container for processes in which the substances involved undergo a chemical reaction. Due to this, the reactor is the only place where a chemical conversion occurs in a biodiesel plant". The Reactor must be designed to maximize net present value for the given reaction, and then designers must make sure that the reaction proceeds with the highest efficiency towards the desired output, at the time of producing the highest yield of product while requiring the least amount of money to purchase and operate with them.

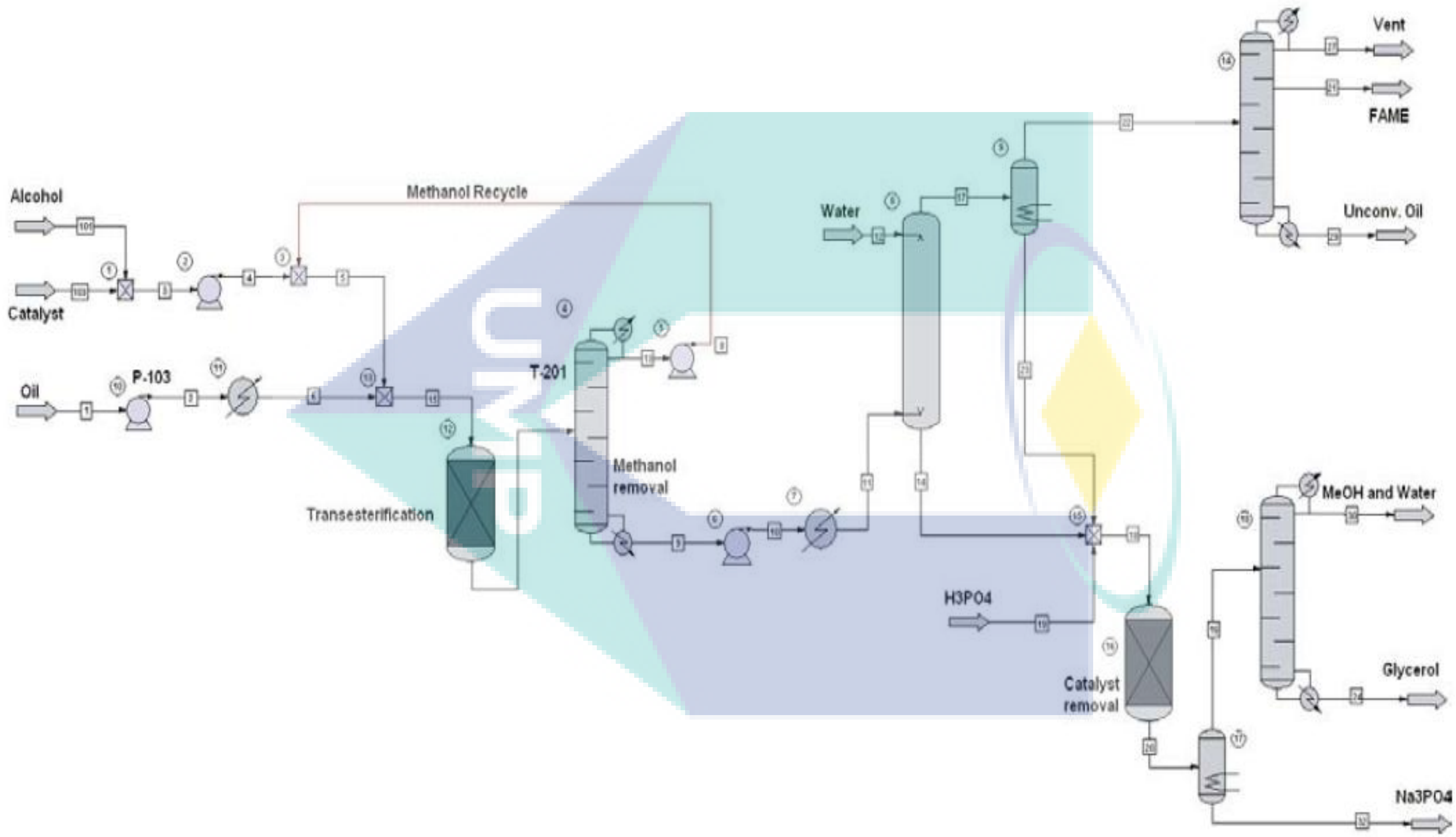



**Figure 3.5:** Process flow sheet for biodiesel production.

There are three main basic models used as reactors; Batch reactor model, Continuous stirred-tank reactor model (CSTR) and Plug flow reactor model (PFR). Batch reactors are discontinuous process reactor, in which all the reactants are loaded at once. It is preferred because by leaving the reactant in the reactor for long periods of time, it is possible to get high conversion levels. However, it conveys the disadvantages of high labor costs per batch and also the difficulty of large scale production. It is necessary to use external agitation to mix separate feeds initially and to enhance heat transfer, and so the reaction takes place. Batch reactors are widely used by chemicals industries, because they have good flexibility in regards to reaction time and due to the types and quantities of reactions that can be performed. As a summary, the characteristics of a batch reactor include the total mass of each batch being fixed, each batch being a closed system, and the reaction time for all elements of fluid being the same.

Generally speaking, the most important aspects to be taken into account in a reactor are the conversion, which is the extent of reaction of the reactants; and the selectivity, which is the selectivity of the reaction of the desired products. Current batch reactors have many positive features that are mixing characteristics, relative ease of handling homogeneous catalysts, and good flexibility with respect to reaction time. Due to this, as it was discussed earlier in the previous chapters, the reactor which is currently most used in biodiesel plants is the batch reactor. Note that batch reactors can be turned into a continuous mode by using multiple reaction vessels sequenced.

In the transesterification process, it must be taken into account that methanol, due to the fact that it is an alcohol that can easily become gas, and at the reaction it is in a liquid phase step, the pressure in the reactor must be maintained at a level that should keep the methanol in the liquid phase. To achieve this, as the reaction temperature is increased, the pressure must also be increased. Besides, it must be taken into consideration that to increase the conversion in a reactor is necessary to increase the time of the reaction; therefore for a given temperature, conversion is going to increase as the reaction time increases.

***Pumps***

According to an English dictionary, “a pump is an apparatus or machine for raising, driving, exhausting, or compressing fluids or gases by means of a piston, plunger, or a set of rotating vanes”.

Nowadays, in the chemical industry, the most common type of pump which is being used is a centrifugal one. It is basically built by a deterioration dynamic pump that uses a rotating impeller to increase the pressure of a fluid. Therefore, the fluid enters the pump impeller along or near the rotating axis and it is accelerated by the impeller. So, the fluid is flowing radially outwards into a diffuser, from where it exits into the downstream piping system. Due to this, centrifugal pumps are commonly used to move liquids through a piping system. However, in biodiesel plants, the shear created by a centrifugal pump can create emulsion problems for the product stream from the biodiesel reactor. To sort this out, by using a positive displacement pump it is possible to reduce the amount of fluid shear imparted by the pump.

***Centrifuges***

According to an English dictionary, “a centrifuge is an apparatus consisting essentially of a compartment spun about a central axis to separate contained materials of different specific gravities, or to separate colloidal particles suspended in a liquid”.

Centrifuges are typically used to separate solids and liquids, but they can also be used to separate immiscible liquids of different densities, so this will be helpful in a biodiesel process. However the separation can also be made by a settling tank. Centrifuges work using the sedimentation principle, where the centripetal acceleration is used to separate substances of greater and less density. Therefore the performance of a centrifuge depends on the characteristics of the mixture to be separated, but product quality specifications must be taken into consideration, in order not to damage the fluid by selecting wrong centrifugation speed. Besides, the centrifuge size has some important implications, e.g. higher viscosity fluids are more difficulty to handle.

***Distillation***

According to an English dictionary, “distillation is the purification or concentration of a substance, the obtaining of the essence or volatile properties contained in it, or the separation of one substance from another, by such a process”.

This is another way to separate chemicals in a fluid mixture, by exploiting the differences in boiling points between the chemicals. Therefore, this is useful in a biodiesel plant for sub-products recovery such as it happens with water and biodiesel according to what was described in previous. Distillation can be done by applications including both batch and continuous fractional, vacuum, azeotropic, extractive, and steam distillation. The degree of the separation that can be achieved depends on the relative volatilities of the chemicals to be separated, and also on the number of trays or the height of the packing, and finally on the reflux ratio.

## 3.5 EVALUATION OF OPERATING PLANT ISSUES

### 3.5.1 Method of Operating the Plant

To determine the method of operating the plant, the following factors must be taken into consideration: capacity of production, shift works, number of employees, and maintenance and several inspections.

***Production capacity***

Initially, the production volume should match the initial demand, but the capacity must be designed to make it easily possible in case a future expansion of the aforementioned capacity is needed due to an increase in the demand. For such a reason, it is important to design a process that could be easily expanded in order to accomplish higher demands, and also to produce for the current demand at good economic production rates. As it was previously discussed the discontinuous batch process matches these requirements.

***Shift works***

The production capacity depends on the operating schedule. Current biodiesel plants work by using a variable production schedule in order to match the plant production capacity to the demand. By using a discontinuous process, factories can be run on a 1, 2, or 3 shift or a 7 day-production schedule, depending on the demands.

***Number of employees***

In much business all over the world, employee costs represent the highest annual costs in the final business administration annual audition. Due to this, it is necessary to evaluate the possibility of using a high technology process so highly automated plants that it requires as few employees as possible, always searching for higher skilled operators and mechanics; a low technology process which require complex operations, but lower skilled people so less cost salary can also be considered. Eventually a decision between the two models must be made. Holidays and seasonal weather changes must also be taken into consideration.

***Maintenance and several inspections***

In addition to the whole production process, maintenance as a routine must be done to keep the equipment in optimum conditions. Besides, safety inspections on personal, standards and equipments are required in order to match local regulations and health, safety and security standards.

**3.5.2 Start-Up**

It is important to consider the following aspects:

***Employee Training***

Training is an important issue to be dealt with a successful result. Therefore, the training responsibility should be established early in the project and a training

Coordinator must coordinate trainers and trainees to allocate them on time for the training processes in order to run the factory in a satisfactory way. Training will be different depending on different positions and works. e.g vendors, labors, engineers… It is highly important that the start-up team is involved in engineering training, due to the advanced technical knowledge required for engineering works and controls.

***Sales and Marketing Team***

Nowadays, the sales and marketing staff is becoming perhaps the most important part on the biodiesel operation, because they are responsible to sell the output from the factory and to tell the production staff about next demands. These days, some companies are hiring their own staff, while others are using existing biodiesel marketing companies to sell their fuel. In both cases, the success of the factory hardly depends on their performance.

***Safety***

The current legislation force factories to have a high standard quality process in terms of Health, safety and security stands. Due to this, it is compulsory to select someone in charge for the adherence to process and personnel safety. This role must be identified and must be involved from the beginning of the project. Besides, due to the hazardous chemical materials involved in a biodiesel plant, some procedures are compulsory:

1. Analysis of all the systems and procedures must be completed under the Safety point of view. Safety training must be established to all workers prior to start-up HAZOP.
2. All training process must include some safety aspects integrated in to specific programs.
3. Extreme precautions in the start-up process must be taken because of the fact that new equipment is being used.

***Quality Assurance***

The current market forces factories to have a high standard quality process in terms of biodiesel quality stands. Due to this, it is compulsory to select someone in charge of making sure that all the process need to guarantee quality. This role must be identified and must be involved from the beginning of the project.

Moreover, this role must identify the needs on training people to work on factory, and also of those responsible for the test quality according to local regulations and standards test methods as seen in previous chapters, e.g. European Biodiesel Standards EN 14214 test methods. It must also identify which analytical procedures will be performed by their own staff and which must be done by certified standard laboratories, e.g. Cetane Number.

## 3.6 ESTIMATION OF FINANCIAL PLANT

The traditional methods of producing biodiesel are analyze and compare to those employed in modern technologies worldwide. In this work, the criteria used to determine the economic viability of castor oil for biodiesel production include the total capital cost, the total production cost, profitability and sensitivity assessments. There are currently no tax credits or subsidies for renewable energy production and so no consideration of it in this work.

### 3.6.1 Total Capital Investment

This is the amount of money that must be supplied or required to finance the purchasing of equipments as well as its auxiliary parts, spare parts, construction of the plant and the acquisition of items necessary for plant operation. The total capital investment comprises the fixed capital, i.e. investment needed to supply all production facilities as well as supply of construction overheads and plant components that are directly or indirectly related the biodiesel process from castor; and the working capital, i.e. the amount of money needed to start the project. This is normally estimated as

0.15times the Fixed Capital Investment (Sinnot, 1986). Total capital cost may include costs of land, equipment and installations, building and construction costs.

### 3.6.2 Total Production Investment

The total production investment involves the cost needed to run the project including marketing of the product. This generally consists of the variable cost, fixed costs and general expenses. Variable cost consists of direct and indirect costs. Generally, variable cost may include costs of raw materials, utilities, miscellaneous materials, shipping and packaging which are negligible in this work because the biodiesel processor is fabricated locally. Fixed costs also include the cost of maintenance, operating labor, supervision, plant overheads, capital charges, Insurance rates and Royalties (Sinnot, 1986). General expenses are made up of administrative costs, engineering and legal costs, office maintenance and communications, distribution and selling cost (Peters and Timmerhaus, 1981).

### 3.6.3 Profitability Analysis

The methods used in estimating the profitability of the project are Rate of Return on Investment (ROI), payback period (PP), breakeven point (BEP), discounted Cash Flow Rate of Return (DCCFRR) and the net present/future value (Achten, et al., 2008).

### 3.6.4 Sensitivity Assessment

Sensitivity analysis is a way of examining the effects of uncertainties in the forecast on the viability of a project. This is achieved by the most probable values for various factors which establish the base case for the analysis. The cash flows and criteria of performance used are calculated assuming a range of error for each of the factors in turn (Sinnot, 1986).

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 INTRODUCTION

In order to final out which is the most profitable biodiesel production procedure were reviewed, different operational variable these were catalyst type (acid catalysis: sulphuric and phosphoric acids; basic catalysis: potassium hydroxide and potassium methoxide), catalyst concentrations (2, 3 and 4 wt.% in acid catalysts; 0.5, 1.0 and 1.5 wt.% in basic catalysts), methanol/oil molar ratio (3:1, 6:1, 9:1 and 12:1) and temperature (25, 35, 45, 55 and 65ºC). Finally reaction time (3 h) and agitation rate (700 rpm) were fixed as common parameters in all experiments. However, just to consider biodiesel price is not a reasonable way to measure biodiesel benefits. In fact, by increasing the use of Biofuels the global energy supply security can be improved, the greenhouse gas and pollutant emissions can be reduced, and also the rural economy can be improved. An estimate on production costs can be made based on the technology and the type of the raw material used in the following paragraphs a deep analysis of biodiesel costs will be shown.

## 4.2 INFLUENCE OF THE TYPES AND CONCENTRATIONS OF CATALYST

Table 4.1 shows the results for the catalysts studied. With regard to the two acid catalysts tested, we see that the effectiveness of sulfuric acid was much higher than phosphoric acid, for the same concentration of catalyst Moreover, as expected, with methoxide used a high product was achieved than with hydroxide (Peña, et al., 2009;

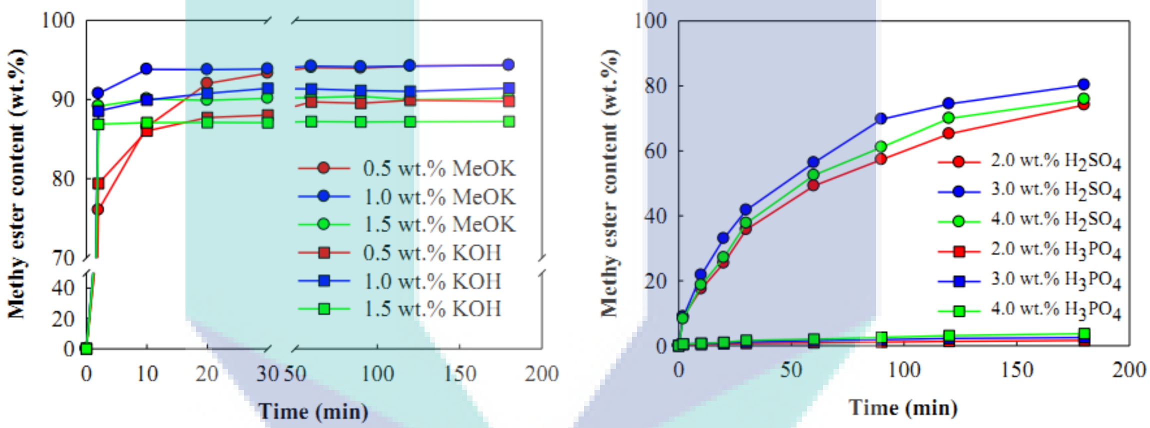
Vicente, et al., 2004) .This is because dissolving the hydroxide in methanol, a small amount of water is formed. This fact is against the transesterification reaction (Ramezani, et al., 2010).

Finally, it was found that the transesterification reaction of castor oil under study was more favorable with basic catalyst. This oil has low content of free fatty acids and therefore the use of acid catalysts did not result in any improvement to the process. In general, as the catalyst concentration increased, the conversion of triglycerides also increased. This is because an insufficient amount of catalyst results in an incomplete conversion of triglycerides into fatty acid esters (Leung, et al., 2010). In basic catalyst, a slight decrease in ester content was observed in the experiments with 1.5 wt.% of catalyst, with regard to the experiments with 1 wt%. This is because the addition of excess alkaline catalysts caused more triglycerides participation in the saponification reaction, resulting in increased production of soap and the reduction of the esters yield (Eevera, et al., 2009).

**Table 4.1:** Methyl ester content, as function of catalyst type and concentration. Reaction conditions: methanol/oil molar ratio, 9:1; temperature, 65 ºC; reaction time, 3h.

| Type catalyst | Concentration catalyst, wt.% | Methyl Ester content, w/w% |
|---|---|---|
| $H_2SO_4$ | 2 | 74.09 |
| | 3 | 80.34 |
| | 4 | 75.62 |
| $H_3PO4$ | 2 | 1.54 |
| | 3 | 2.61 |
| | 4 | 3.68 |
| KOH | 0.5 | 90.04 |
| | 1.0 | 91.01 |
| | 1.5 | 87.16 |
| $CH_3OK$ | 0.5 | 94.38 |
| | 1.0 | **94.66** |
| | 1.5 | 90.26 |

Figure 4.1 shows the formation of the esters content over time, depending on used concentrations of each catalyst (Figure 4.1a for basic catalysis and Figure 4.1b for acid catalysis). With sulfuric acid, the formation was slow for all concentrations, typical of acid catalysts. In the initial stages, the increase was somewhat faster but became slower when approaching the equilibrium conditions. It is not possible to ensure that steady state was reached after three hours of reaction, although the slopes of the curves indicate that this state should be close. For phosphoric acid, cannot see anything except an increasing trend over time, given that the conversion was negligible. In basic catalysis, both catalysts gave rise to high concentrations of esters in short reaction times.




(a) Basic catalysts (b) Acid catalysts

**Figure 4.1:** Methyl ester content, as function of catalyst amount for basic catalysts (a) and acid catalysts (b). Reaction conditions: methanol/oil molar ratio, 9:1; temperature, 65 ºC.

The difference between the experiments lies in the rate to reach steady state. The rate was higher when the catalyst concentration was increased. In any case, the differences between these experiments were not significant because only in the experiment with 0.5 wt% of catalyst, there was a growing area before reaching the asymptote. These trends confirm that the reaction rate is enhanced with basic catalysis compared to the acid, such as in the production of biodiesel from other oils (Dos Santos, et al., 2008; César and Batalha, 2010).

## 4.3 INFLUENCE OF METHANOL/OIL MOLAR RATIO

As mentioned, the transesterification activity also depends on the molar concentrations of methanol to oil. Large excess of methanol is required to shift the equilibrium favorably during transesterification for better yields of biodiesel (Sree, et al., 2009). Methanol/oil molar ratio is associated with the type of catalyst used. In general, acid catalysis requires a methanol/oil molar ratio higher than basic catalysis (Ma and Hanna, 1999).

To evaluate methanol/oil molar ratio influence the most effective catalysts for acidic and basic catalysis have been chosen. Table 4.2 shows experimental conditions and obtained results. In acid catalysis, when methanol/oil molar ratio was increased from 3:1 to 9:1, methyl esters content increased, while from 9:1 to 12:1 there were not significant changes. In basic catalyst similar situation was achieved, except that a slight decrease of methyl esters content was produced by increasing methanol/oil molar ratio from 9:1 to 12:1.

**Table 4.2:** Methanol/oil molar ratio influence, Reactor conditions: temperature, 65ºC; time, 3h.

| Methanol/oil ratio, mol:mol | Catalyst | Methyl Ester content, w/w% |
|---|---|---|
| 3:1 | $H_2SO_4$, | 64.70 |
| 6:1 | 3 wt.% | 69.55 |
| 9:1 | | 80.34 |
| 12:1 | | 80.78 |
| 3:1 | $CH_3OK$, | 74.29 |
| 6:1 | 1 wt.% | 80.48 |
| 9:1 | | **94.66** |
| 12:1 | | 91.60 |

The higher alcohol molar ratio interferes with the separation of glycerol because there is an increase in solubility. In addition, an excess of alcohol seems to favor conversion of di- to monoglycerides, but there also is a slight recombination of esters and glycerol to monoglycerides because their concentration keeps increasing during the course of the reaction, in contrast to reactions conducted with low molar ratios (Encinar, et al., 2005). In basic reactions conducted with low molar ratios (Encinar, et al., 2005). In basic catalysis, this effect can be observed because the reaction is fast, whereas in acid catalysis the effect is not apparent, probably due to the low rate of the reaction.

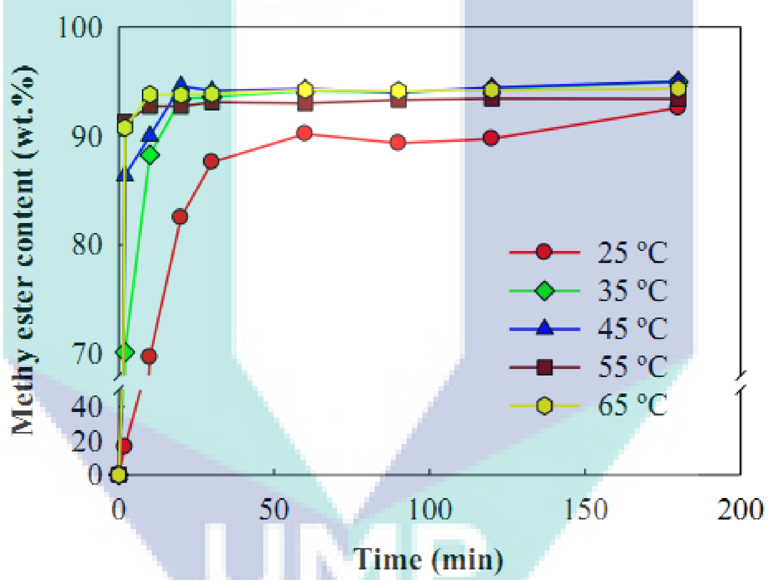



**Figure 4.2:** Influence of the reaction temperature on the methyl ester content. Reaction conditions: catalyst, CH3OK; catalyst amount, 1 wt%; methanol/oil molar ratio, 9:1.

**4.4 TEMPERATURE INFLUENCE**

The transesterification of castor oil with methanol was carried out at 25, 35, 45, 55 and 65 ° C, in order to determine the temperature influence on the methyl esters Production. Figure 4.2 shows how the methyl ester yield was almost constant with all studied temperatures after 30 min of reaction. When the temperature decreased, the reaction rate decreased, but it did so very slight, just noticeable in the first minutes of reaction. From 55 ° C, the influence of temperature on reaction rate was not noticeable, reaching the maximum methyl esters content from the first minutes of reaction.

## 4.5 BIODIESEL SPECIFICATIONS

Table 4.3 shows the specification of biodiesel with higher methyl esters content (other properties depend on esters content (Refaat, 2009). This biodiesel was obtained with the following reaction conditions: 1 wt% of potassium methoxide as catalyst, a methanol/oil molar ratio 9:1, 65 ºC and 700 rpm. By way of comparison, castor oil properties and limits set by European Biodiesel Standards EN 14214(European Standard EN 14214, 2002) are also shown in Table 4.3.

**Table 4.3:** Biodiesel specification, Reaction conditions: CH3OK as catalyst, 1 wt%; methanol/oil, 9:1; 65 ºC; 3 h; 700 rpm

| Specification | Biodiesel | EN 14214 | |
|---|---|---|---|
| | | Min. | Max. |
| Methyl Ester content, w/w% | 94.66 | 96.5 | - |
| Density at 15 °C, kg m$^{-3}$ | 917.16 | 860 | 900 |
| Viscosity at 40 °C, cSt | 14.85 | 3.50 | 5.00 |
| Water content, mg kg$^{-1}$ | 600 | - | 500 |
| 50% Distillation, °C | 321 | - | - |
| Cetane index | 36.91 | 51.0 | - |
| Flash point, °C | 205 | 120 | - |
| Combustion point, °C | 215 | - | - |
| Cold filter plugging point, °C | 17 | -20 | 5 |
| Iodine value, $gI_2(100g)^{-1}$ | 82.49 | - | - |
| Saponification value, $mg_{KOH}\ g^{-1}$ | 182.40 | - | - |

Density is a key fuel property, which directly affects the engine performance characteristic. It affects the mass of fuel injected into the combustion chamber and thus, the air-fuel ratio. This is because fuel injection pumps meter fuel by volume not by mass and a denser fuel contains a greater mass in the same volume. Thus, the changes in the fuel density will influence engine output power due to a different mass of fuel injected

(Alptekin and Canakci, 2008). It is known that biodiesel density mainly depends on its esters content and the remained quantity of alcohol; hence this property is influenced primarily by the choice of vegetable oil (Predojevic, 2008).

The density of castor oil used in this work is 961.20 kg·m-3 and density of biodiesel obtained in better operating conditions was 917.16 kg·m-3. Although the reduction achieved (4.58%) is similar to that of biodiesel made from other oils (Predojevic, 2008; Encinar et al., 2010), this density value is not within the limits of the standard values. It made from other oils, this density value is not within the limits of the standard values. It would therefore be necessary to improve this property with mixtures. Kinematic viscosity is a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another. Its value affects the atomization of a fuel upon injection into the combustion chamber and thereby, ultimately, the formation of engine deposits. The tendency of the fuel to cause such problems is higher when the viscosity is greater. The kinematic viscosity of biodiesel is about an order of magnitude lower than that of the parent oil (Knothe, et al., 2005). As already mentioned, castor oil has a kinematic viscosity higher than usual caused by the presence of the hydroxyl group (Knothe and Steidley, 2005). Castor oil employed has a viscosity of 258.01, and the more favorable viscosity achieved with transesterification process was of 14.85. This represents a viscosity reduction of 94.2 %, however, EN 14214 sets the kinematic viscosity limits between 3.5 and 5.0 cst. As with the density, castor biodiesel breach this rule, the viscosity should be corrected by mixing with other methyl esters or mineral diesel.

Water in the biodiesel can promote microbial growth, lead to tank corrosion, participate in the formation of emulsions, as well as cause hydrolysis or hydrolytic oxidation (Prakash, 1998). Water content of obtained biodiesel is similar to the established maximum. Temperature of 50 % of distillated was determined by aim to calculate cetane index. It is a relative measure of the interval between the injection of the fuel into the cylinder and the onset of auto-ignition, i.e. the ignition delay time. The higher cetane number, meaning the shorter the ignition delay time (Refaat, 2009). As with the mentioned properties, the cetane number of obtained biodiesel did not meet the requirements of the standard.

Flash and combustion points are parameters to consider in the handling, storage, and safety of biodiesel. Minimum flash point established is 120 ºC, biodiesel obtained in this research has a value higher than the limit. One of the major problems associated with the use of biodiesel is poor low temperature flow properties (Knothe, 2005). Cold filter plugging point (CFPP) is defined as the highest temperature at which the fuel, when cooled under defined conditions, does not flow through a filter wire mesh within a certain time. This parameter is related to the cold engine start, and should be sufficiently low, as if the biodiesel freezes, the engine will not start (Encinar et al., 2005). The cold-flow problems are caused by the presence of high amounts of saturated fatty acid esters (Knothe, 2010). Castor oil biodiesel has a high CFPP despite having a lower content of saturated fatty acids. This limitation is mainly caused by its viscosity, which increases as the temperature decreases and, therefore, flows more slowly. The filter does not get clogged, but biodiesel does not flow in the time required for analysis.

Iodine number is a measure of total instauration within a mixture of fatty material. Its value only depends on the origin of the vegetable oil, the biodiesel obtained from the same oil should have similar iodine values (Encinar et al., 2005). In Table (8) it is possible observer that iodine index is within the limits. Saponification value is related to the average molecular weight of the sample. When de molecular weight decreases, the saponification value increases. Saponification values increased with the yield of methyl ester (Encinar et al., 2005). European Biodiesel Standard EN 14214 does not specify any saponification value.

## 4.6 FINANCIAL ANALYSIS

Based on contemporary production processes and using current best values for reagent, equipment, and supply costs, a computer model of a biodiesel production facility was designed, and employed to estimate the biodiesel sell price and production costs for the synthesis of fuel grade biodiesel from castor oil. This model is relatively preliminary in regard to the level of its detail. It is not meant to replace the thorough engineering analysis that is required in the final design and construction of such a plant, but rather is meant for use as a tool in estimating sell price and operating costs. The model is flexible, and is meant for use in assessing the effects on estimated biodiesel production costs of changes in feedstock, in feedstock and glycerol prices, in chemical or process technology employed, or in equipment specified for the facility.

**Table 4.4:** Finance required

| **Start Table -up Expenses** | **Cost** |
|---|---|
| Total Start-up Expense | RM9,600 |
| **Start-up Assets Needed** | |
| Cash Requirements | RM5,440,000 |
| Total Short-term Assets | RM5,440,000 |
| Total Assets | RM5,440,000 |
| Total Start-up Requirements: | RM5,449,600 |
| ***Start-up Funding Plan*** | |
| Founder | RM160,000 |
| Investor | RM5,289,600 |
| Total investment | RM5,449,600 |
| Loss at Start-up | RM9,600 |
| Total Capital | RM5,440,000 |
| Total Capital and Liabilities | RM5,440,000 |

Based on the process flow diagram capital and production costs were calculated. Capital costs are summarized in Table 4.4 (Details of the facility specifications are available from the authors). The estimated total capital cost was approximately (RM5,440,000). Furthermore, the equipment cost for production biodiesel shown in Table 4.5.

**Table 4.5:** Biodiesel production equipment

| N | Name | Quantity | Cost, RM |
|---|---|---|---|
| 1 | Esterification unit 5000 t/year | 1 | 2,873,600 |
| 2 | Catalyst preparation unit | 1 | 588,800 |
| 3 | Reservoirs, 60 ton | 7 | 96,000 |
| 4 | Reservoirs, 10 ton | 4 | 32,000 |
| 5 | Pipes, pumps | | 16,000 |
| 5 | Compressor | 1 | 16,000 |
| 6 | Boiler | 1 | 32,000 |
| 7 | Fire prevention equipment | | 32,000 |

**4.7 COST OF RAW MARITAL**

The projected annual operating costs for the modeled biodiesel production facility are shown in Tables 4.6a and 4.6b. This analysis calculates a final biodiesel production cost of 2.1RM/Liter. Raw materials costs constitute the greatest component of overall production costs, and of these the cost of the castor oil feedstock is the biggest contributing factor, itself constituting 88% of the overall production cost.

Capacity of plant –5000 Ton/Yr

**Table 4.6.a:** Chemicals and energy cost.

| N | Name | Quantity required kg per ton | Price RM/Kg | Total quantity required Kg/yr | Cost per year RM |
|---|---|---|---|---|---|
| 1 | Methanol 99.9% | 120 | 1.12 | 600,000 | 672,000 |
| 2 | CaO - Calcium oxide | 7 kg | 12.6 | 35000 | 441,000 |
| | Total chemicals | | | | 1,113,000 |

**Table 4.6b:** Castor oil cost (DOVE, 2002)

| Variable costs per hectare | Cost per hectare |
|---|---|
| castor seed oil production per hectare | 900 Kg castor oil |
| castor seed oil production per hectare | 990 Liters |
| castor oil cost per kg including crushing | € 0.13 per Liter = 0.52 RM/Liter |
| castor oil production costs | € 0.38 per Liter= 1.52 RM/Liter |
| To produce 5000 ton of biodiesel | 7,600,000 Liter castor oil |

**Table 4.7:** Annual Operating Cost

| Operating Cost RM | |
|---|---|
| Raw Materials Cost | 8,713,000 |
| Operating Labor Cost | 500,000 |
| Maintenance Cost | 20,000 |
| Electricity | 20,000 |
| Utilities Cost | 35,200 |
| Total | 9,288,200 |

This substantial price differential, and the large contribution of feedstock cost to the cost of biodiesel, highlights the potential value of low cost alternatives to vegetable oils in improving the economic viability of biodiesel. The annual operating cost is shown in Table 4.7.

## 4.8 CALCULATION OF TOTAL ANNUALIZED COST

Based on the following assumptions and the estimates annual operating cost Tables 4.8 and 4.9, which helped for modeling the cost of biodiesel production. In finance the total annual cost (TAC) is the cost per year of owning and operating an asset over its entire lifespan. TAC is often used as a decision making tool in capital budgeting when comparing investment projects of unequal lifespan.

Total Annualized Cost (TAC) = Annualized Fixed Cost + Annual Operating Cost

**Table 4.8:** Calculation of Total Annualized Cost (TAC)

| Description | Cost | Unit |
|---|---|---|
| Annualized Fixed Cost (AFC) | 1,424,052 | RM/Yr |
| Annual Operating Cost | 9,288,200 | RM/Yr |
| Total Annualized Cost (TAC) | 10,712,252 | RM/Yr |

**Table 4.9:** Calculation of Production Cost

| Description | Cost | Unit |
|---|---|---|
| Total Annualized Cost (TAC) | 10,712,252 | RM/Yr |
| Actual Production Rate | 5000 | Ton /Yr |
| Production Cost | 2.14 | RM/Liter |

**Table 4.10:** Calculation of Annual Gross Profit

| **Annual Gross Profit = Annual Production Income - TAC** | | | |
|---|---|---|---|
| | 2.30 | 2.60 | RM/Liter |
| Annual Production Income | 11,500,000 | 13,000,000 | RM/Yr |
| TAC | 10,712,252 | 10,712,252 | RM/Yr |
| Annual Goss Profit | 787,748 | 2,287,748 | RM/Yr |

Depending on calculation of total annual cost which is almost 10,712,252 RM/Yr can found the biodiesel production cost around 2.14 RM per litter as shown in Table 4.10. For this study MATLAB program used to simulate different prices of biodiesel then estimate cost production, return of investment, and payback period. Table 4.11 shows the comparison of castor oil prices and their impact on Return of Investment (ROI) percentage which is one way of considering profits in relation to capital invested by calculating the annual gross profit Table

**Table 4.11:** Calculation of ROI

| **ROI = [Annual Gross Profit/Capital Investment] x 100** | | | |
|---|---|---|---|
| | 2.30 | 2.60 | RM/Liter |
| Annual Goss Profit | 787,748 | 3,037,748 | RM/Yr |
| Capital Investment | 5,440,000 | 5,440,000 | RM/Yr |
| ROI | 14.48 | 42.05 | % |

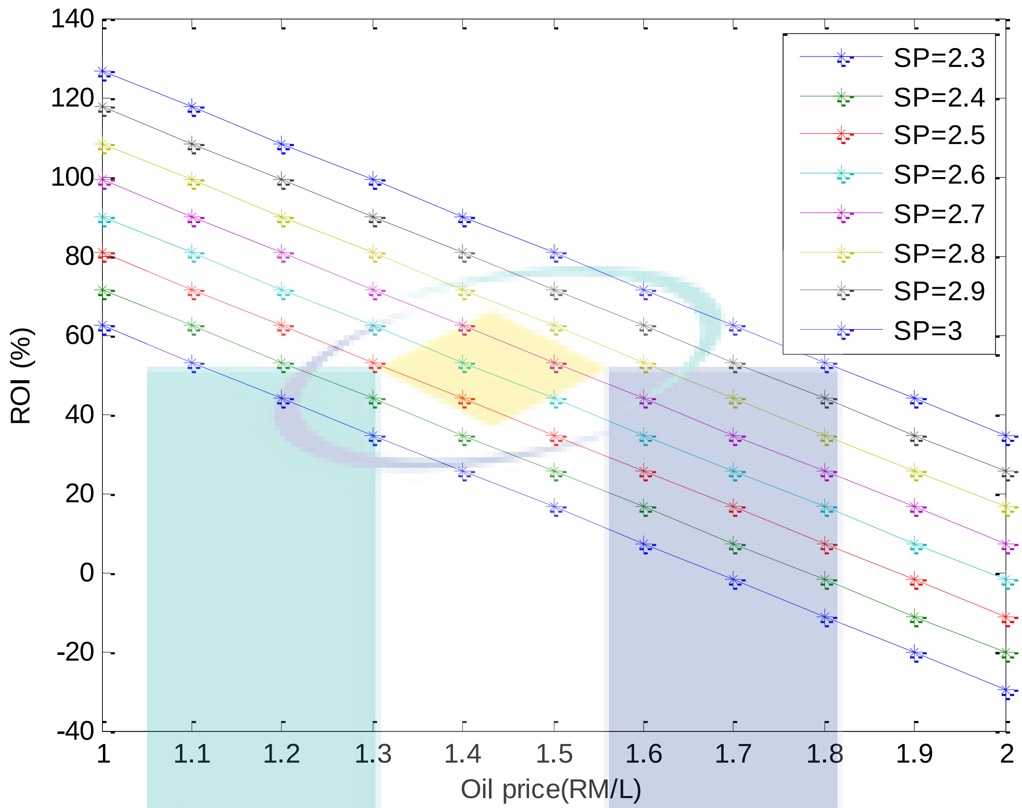



**Figure 4.3:** Sensitivity Analysis of ROI

Figure 4.3 illustrates the effect of oil price on ROI percentage. It can be seen that the ROI has linearly decreased with the increased in the price of castor oil. In this study two sell price have been taken, first price 2.3 RM for the producing biodiesel fuel with 1.52RM as a castor oil price, While, the second price 2.6 RM at same castor oil price. Therefore, the ROI was about 14.48% and 42.05% respectively. Meanwhile, the return of investment can cover as soon as possible when increasing biodiesel sell price and fixed castor oil price but this way is not practical because biodiesel price should follow marketing situation which almost steady therefore, fixing biodiesel sell price and change castor oil price more logical.

**Table 4.12:** Calculation of Pay Back Period (PP)

| **Payback period (yrs) = Fixed Capital Investment/(Annual income - Annual operating cost)** | | | |
|---|---|---|---|
| Description | 2.30 | 2.60 | RM/Liter |
| Fixed Capital Investment | 1,424,052 | 1,424,052 | RM/Yr |
| Annual Income | 11,500,000 | 13,000,000 | RM/Yr |
| Annual Operating Cost | 9,288,200 | 9,288,200 | RM/Yr |
| Payback Period | 0.64 | 0.36 | |

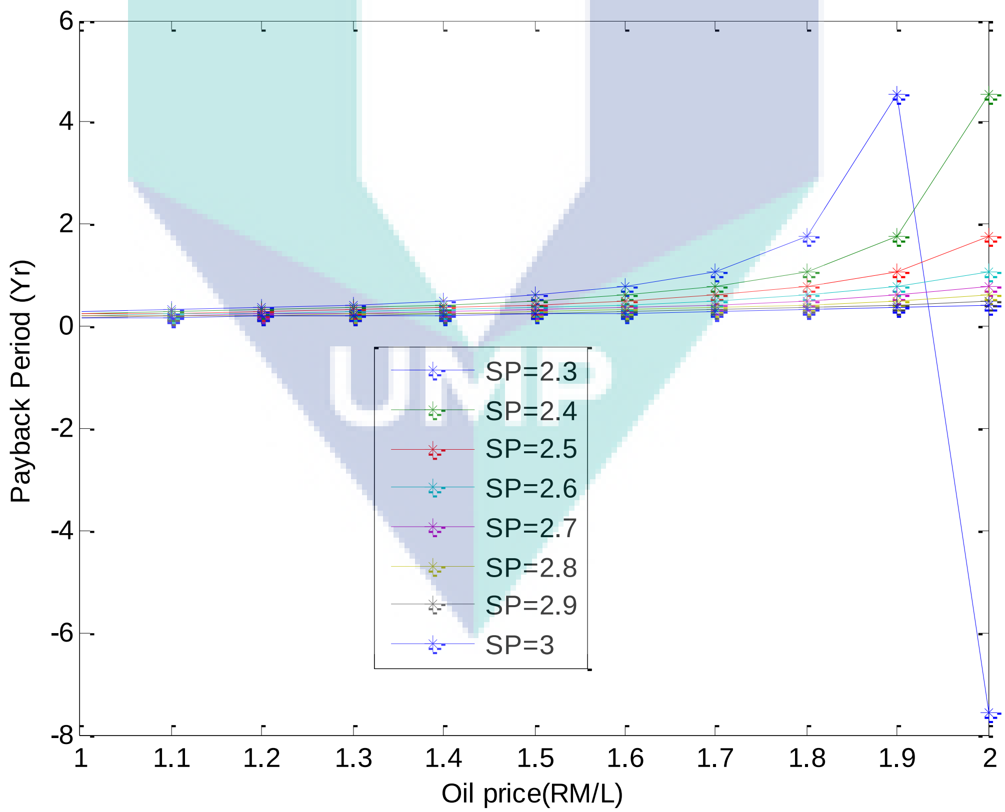



**Figure 4.4:** Sensitivity Analysis of PP

The calculation of pay Back period (PP) is shown in the Table 2.12. Meanwhile, Figure 4.4 shows the effect of castor oil price on the payback period which is the last refers to the period of time required for the return on an investment to repay the sum of the original investment. It can be seen that the payback period increased when the oil price increase except in case when oil price more than 1.9 RM per liter and take 2.3 RM as a sell price the payback period experiencing a sharp decline because sell price don't cover production cost .

## 4.9 BREAK-EVEN ANALYSIS

The break-even point is one of the simplest yet least used analytical tools in management. It helps to provide a dynamic view of the relationships between sales, costs and profits. Break Even quantity (BEQ) is the formula that is used to determine the break-even point. This formula is as follows:

BEQ= FC/P-VC

Where:

FC= Fixed Costs.

P= Price Charged per unit.

VC= Variable Costs of production.

- Production quantity: 5,000 tons.
- Unit sales price:
-

At sale price1 = 2.30 RM/L the Price Charged per unit 1= 2,300 RM/ton

At sale price2 = 2.60 RM/L the Price Charged per unit 2= 2,600RM/ton

Variable costs can include operation cost (Table 12). These variable costs are:

Raw Materials Cost =8,713,000;
Maintenance Cost =20,000;

Electricity= 20,000;
Utilities Cost=35,200
and 8,788,200 as a total

Labor is not regarded as a variable cost; no worker should be fired in a bad situation, even if some money could be saved for a short time.

- Thereby the unit variable cost (operation cost) =1,757.64 RM/ ton.
- Fixed costs are: 1,424,052 RM/ton.

As a result, the break-even quantity of the biodiesel production:

- When sale price1 = RM2.30

**BEP1**=1,424,052 RM / (2,300 - 1,757.64) RM/ton = 2,625.7 ton.

- When sale price1 = RM2.60

**BEP2**=1,424,052 RM / (2,600 - 1,757.64) RM/ton = 1690.6 ton.

The main advantage of break-even analysis is that it points out the relationship between cost, production volume and returns. It can be extended to show how changes in fixed cost-variable cost relationships, in commodity prices, or in revenues, will affect profit levels and break-even points. Break-even analysis is most useful when used with partial budgeting or capital budgeting techniques. The major benefit to using break-even analysis is that it indicates the lowest amount of business activity necessary to prevent losses.

**Table 4.13:** Income statement

| | 20013 | 20014 | 20015 |
|---|---|---|---|
| ***Sales*** | 448,000 | 6,464,000 | 6,624,000 |
| Direct Cost of Sales RM | 681,347.2 | 1,145,600 | 1,161,600 |
| Total Cost of Sales RM | 681,344 | 1,145,600 | 1,161,600 |
| Gross Margin RM | 233,344 | 5,318,400 | 5,462,400 |
| Gross Margin % | -52,09% | 82,28% | 82,46% |
| Operating expenses: | | | |
| Advertising/Promotion RM | 7,680 | 6,400 | 6,400 |
| Travel RM | 27,200 | 19,200 | 19,200 |
| Miscellaneous RM | 38,400 | 38,400 | 38,400 |
| Payroll Expense RM | 167,040 | 167,040 | 167,040 |
| Payroll Burden RM | 83,520 | 83,520 | 83,520 |
| Depreciation RM | 140,800 | 384,000 | 384,000 |
| Leased Equipment RM | 288,000 | 288,000 | 288,000 |
| Utilities RM | 35,200 | 76,800 | 76,800 |
| Insurance RM | 48,000 | 76,800 | 76,800 |
| Transportation RM | 160,960 | 160,960 | 160,960 |
| Rent RM | 192,000 | 192,000 | 192,000 |
| Contract/Consultants RM | 19,200 | 19,200 | 19,200 |
| Total Operating Expenses RM | 1,209,280 | 1,512,320 | 1,512,320 |
| Profit Before Interest and Taxes RM | 1,442,624 | 3,806,080 | 3,950,080 |
| Taxes Incurred RM | 7,21,312 | 1,903,040 | 1,975,040 |
| Extraordinary Items RM | 3,840 | 6,400 | 6,400 |
| Net Profit RM | 717,472 | 1,909,440 | 1,981,440 |
| Net Profit/Sales | -160,15% | 29,54% | 29,91% |

## 4.10 PROFIT AND LOSS ANALYSIS

Direct costs were calculated in accordance to market prices of chemicals, all other expenses were also properly allocated in the income statement as shown in Table 4.13. The cash flow depends on assumptions for accounts receivable management. The project "consumes" much cash at the first year, during installation, and generates positive flow afterwards as shown in Table 4.14 and balance sheet is shown in Table 4.15.

Capacity of plant –5000 Ton/Yr

**Table 4.14:** Cash flow statement.

| | **20013** | **20014** | **20015** |
|---|---|---|---|
| *Net Profit RM* | 717,472 | 1,909,440 | 1,981,440 |
| Plus: | | | |
| Depreciation RM | 140,800 | 384,000 | 384,000 |
| Change in Accounts Payable RM | 31,049.6 | 22,748.8 | 892.8 |
| Subtotal RM | 545,622.4 | 2,316,189 | 2,366,333 |
| Less: | 20013 | 20014 | 20015 |
| Change in Accounts Receivable RM | 57,600 | 773,484.8 | 20,572.8 |
| Change in Other Short-term Assets RM | | | |
| Capital Expenditure RM | 4,480,000 | 32,000 | 32,000 |
| Dividends | | | |
| Subtotal RM | 4,537,600 | 805,484.8 | 52,572.8 |
| Net Cash Flow RM | 5,083,222 | 1,510,704 | 2,313,763 |
| Cash Balance RM | 356,777.6 | 1,867,482 | 4,181,245 |

**Table 4.15:** Balance sheet

| ***Assets*** | **20013** | **20014** | **20015** |
|---|---|---|---|
| Short-term Assets RM | | | |
| Cash RM | 356,777.6 | 1,867,482 | 418,044.8 |
| Accounts Receivable RM | 57,600 | 831,084.8 | 851,657.6 |
| Other Short-term Assets RM | 0 | 0 | 0 |
| Total Short-term Assets RM | 414,377.6 | 2,698,566 | 5,032,902 |
| Long-term Assets RM | 0 | 0 | 0 |
| Capital Assets RM | 4,480,000 | 4,512,000 | 4,544,000 |
| Accumulated Depreciation RM | 140,800 | 524,800 | 908,800 |
| Total Long-term Assets RM | 4,339,200 | 3,987,200 | 3,635,200 |
| Total Assets RM | 4,7535,78 | 6,685,766 | 8,668,102 |
| | | | |
| Liabilities and Capital | | | |
| Accounts Payable RM | 31,049.6 | 53,798.4 | 54,694.4 |
| Subtotal Short-term Liabilities RM | 31,049.6 | 53,798.4 | 54,694.4 |
| Total Liabilities RM | 31,049.6 | 53,798.4 | 54,694.4 |
| | | | |
| Paid in Capital RM | 5,449,600 | 5,449,600 | 5,449,600 |
| Retained Earnings RM | 9,600 | 727,072 | 1,182,368 |
| Earnings RM | 717,472 | 1,909,440 | 1,981,440 |
| Total Capital RM | 4,722,528 | 6,631,968 | 8,613,408 |
| Total Liabilities and Capital RM | 4,753,578 | 6,685,766 | 8,668,102 |
| Net Worth RM | 4,722,528 | 6,631,968 | 8,613,408 |

# CHAPTER 5

## CONCLUSIONS AND RECOMMENDATIONS

As it has been presented on this thesis, there is an urgent need to reduce petroleum dependency. Countries all over the world are developing strategies to enhance the biodiesel market to grow. In this study, it has been shown that Castor oil is a suitable raw material for the production of biodiesel. In the optimum conditions of reaction, esters content was 94.66%, close to 96.5% required by European Standard EN 14214.The most suitable catalyst for this process proved to be potassium methoxide. The other basic catalyst, potassium hydroxide, achieved similar results but its methyl esters contents were slightly lower. The optimum concentration of potassium methoxide catalyst was 1 wt%. The best molar ratio of methanol was 9:1, for both acid and basic catalysis. This variable exerted a positive influence in obtaining methyl esters until this value. Above 9:1, the conversion of methyl esters begins to decrease slightly.

"The cost associated to oils and fats is relatively high constituting about 80% of the total cost of the biodiesel production" Vieira et al., (2006). In Malaysia, the price of biodiesel being higher at RM 2.70 per liter compared to diesel extracted from fossil-based oil at RM 1.70 per liter. Even though it is more expensive than diesel, saving the environment is the main reason (Daily Express, 2012). However, growing concerns over first generation biodiesel in terms of their impact on food prices and the environment have led to an increasingly bad press in the last year. As the replacement of fossil fuels takes place irrespective of these concerns, the way to avoid the negative effects of producing biodiesel from food supplies is to make lignocellulosic-derived fuels available within the shortest possible time (i.e. second generation biodiesel). This commitment to biodiesel in the present will make the transition to the second generation biodiesel more economically convenient. But at present the technology to produce these replacement fuels is still being developed.

Biodiesel from castor oil which is second generation is a clean burning fuel that is renewable and biodegradable. Castor oil methyl ester showed performance characteristics close to diesel, therefore can be used in compression ignition engines (CI engines) in rural area for meeting energy requirement in various agricultural operations .With this use engine develops better power when compared with power output with diesel which a high power output is reported in many other studies it may be due to better lubricity which reduces friction loss and better combustion of blends.

A profitability analysis was performed by examining the ROI and PP by modeling MATLAB program, using two different sell prices (RM 2.30 and RM 2.60). The ROI is (about 14.48% and 42.05%) and PP is (o.64 and 0.36) respectively, this model is meant as a research and planning tool. It is flexible in those elements of the scale, process or physical plant can be modified by the user to estimate the effects of changes in these parameters on capital and production costs. Also, it serves as the basis for future work, presently underway here, to estimate the cost of production of biodiesel from other feedstock.

The following research topics are proposed for future work:

- Exploration of new reaction pathways and processing schemes (This entails a combination of experimental and theoretical work).
- Although, it has been discussed early in this study, it is obvious that due to the high importance that feedstock has on the production of biodiesel; there is an important need to do much more research in this area. In particular, it is important to determine the potential land required the distribution around the world, the competition with food crops, and eventually the different prices and market balance for a truly global analysis.

- Searching start from castor agricultural and opportunities for farmers and agricultural technology could make land more efficient and thus its impact of biodiesel production so get costs down.

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