Production of biodiesel
from vegetable oils

MSc. thesis

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ABSTRACT

The production of biodiesel using vegetable oils is studied. Palm oil and its use for production of biodiesel have been focused. Palm tree is very productive and one of the most profitable for biodiesel production. The oil palm tree produces more oil per hectare than any other oil oilseed crop. The production of palm oil at the industrial plantation level has caused environmental damage. The Roundtable on Sustainable Palm Oil has established principles and criteria in order to certify a sustainable cultivation of the palm oil.

The experimental work involves the production of biodiesel using corn oil. Ethanol and methanol are used as alcohols. Sodium and potassium hydroxides are selected as catalyst.

The ratio alcohol to oil is the most important parameter in the production of biodiesel. An excess of alcohol is required to drive the reaction to the right. In the experiments with ethanol the yield of biodiesel increased with the ratio ethanol/oil achieving the highest yield at a molar ratio ethanol/oil: 7.78. In the experiments with methanol, using 0.9 g NaOH and 1 hour reaction time the highest yield was obtained with a molar ratio methanol:oil = 9. Using KOH as catalyst and 2 hour reaction time a very good yield is already obtained with a molar ratio methanol:oil = 4.5.

The amount of catalyst is another studied parameter. In the experiments with ethanol, the amount of 0.8 mg NaOH and 1.2 mg KOH for 200 ml corn oil (0.22 mol) is enough in order to obtain a good yield. An increase of the amount of catalyst does not produce an increase of the yield of biodiesel. In experiments with methanol, using the lowest tested amount catalyst (0.85 g KOH and 0.23 g NaOH) a good yield of biodiesel is obtained.

The effects of the reaction time, rate of mixing and the reaction temperature were studied in the experiments with methanol. The yield of biodiesel increased when the reaction time is increased from 1 to 2 hours. The yield of produced biodiesel increased from 90% to 94% when the rate of mixing was increased from 500 to 1500 rpm. Often the transesterification is carried out at a temperature near the boiling point of alcohol. The highest yield was obtained at 60 °C with KOH and at 55 °C using NaOH but already at 40 °C a good yield was obtained (89%).
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1 Introduction

Currently one of the environmental challenges facing humanity is global warming. This factor is due, among others, the growing use of fossil fuels and cars in cities.

The production of biodiesel stimulates agricultural markets and reduces poverty in rural areas providing employment for people with low incomes. Countries can use their own natural resources for the production of biodiesel. Biodiesel can use the existing distribution infrastructure of the fossil diesel. Biodiesel causes less damage to the environment than fossil diesel and is an alternative fuel in order to reduce CO2 emissions.

Due to the great need to reduce consumption of non-renewable fossil fuels, the possibility of other sources of alternative fuels like biodiesel is studied.

Biodiesel is a liquid biofuel derived from lipids such as vegetable oils or animal fats reacting with alcohol through industrial processes of esterification and transesterification.

This thesis includes a study regarding production of biodiesel from vegetable oils. Palm oil and its use for production of biodiesel are focused. The work concludes with a series of experiments for obtention of biodiesel from corn oil. Ethanol and methanol are used as alcohols. Sodium and potassium hydroxides are selected as catalyst.

2 Vegetable oils

2.1 Vegetable oil production

There are two types of processes for the production of vegetable oils. One is mechanical while the other is chemical. The method is chosen depending on the used crop. In the mechanical method the oil is extracted by pressing of oil seeds and oleaginous fruit. In the chemical method, solvents are used for extract the oil.
2.1.1 Mechanical method

In the mechanical method is used a press. A press is a screw extruder capable of generating high pressure and extracting the oil from the fruit or seed. When the material moves within the screw, its mass is compressed against the cylinder walls. The oil is squeezed from the seeds. The oil is obtained and the residue, the cake, (compressed material and oiling) is discharged. (Machuca, 2007).

The extracted oil contains small solid particles. The particles are separated by means of any of three methods: filtering, decanting or centrifugation (Machuca, 2007).

2.1.2 Chemical method

The chemical method is also called solvent extraction method. The oily material is immersed in a solvent, which dissolves the oil contained in cake or oil seeds. The oil is collected by vaporizing solvent out. The mixture oil-solvent is heated to 150 ° C in order to remove the solvent. The solvent is later recycled (Machuca, 2007).

2.2 Types of vegetable oils.

There different types of vegetable oils:

- Oilseed oils: sunflower, rapeseed, soybeans.
- Alternative vegetable oils such as sativa, Pogianus.
- Oils from genetically modified oilseed with high content of oil.
- Recycled oils

2.2.1 Edible vegetable oils.

Edible vegetable oils have a vital role in our body. Edible vegetable oils are one of the most important sources of energy. They are essential to maintain the balance of lipids, cholesterol and lipoproteins that circulate in the blood. They provide vitamins A, D, E and K. They highlight some characteristics of foods, such as taste, aroma and texture.
2.2.2 Cottonseed oil

This oil is obtained from the seeds of cotton (Gossypium spp) by mechanical and solvent extraction. Crude oil looks dark and requires a chemical treatment in order to purify reducing the content of gossypol founded in untreated cottonseed oil. Cotton seed contains 70% unsaturated fatty acids including 18% monounsaturated (oleic), 52% polyunsaturated (linoleic) and 26% saturated (primarily palmitic and stearic). Cottonseed oil does not contain linolenic acid. Cottonseed oil is used as salad or cooking oil.

2.2.3 Sunflower oil

It is obtained both by mechanical and solvent extraction from sunflower seed (Helianthus annus). By biotechnological methods different varieties of sunflower has been developed. The original oil contains high levels of linoleic acid. The crude oil contains a high percentage of waxes. The waxes have to be removed from the oil. The refined oil has a crystalline appearance and yellow colour.

2.2.4 Corn oil

The crude oil from the germ of corn (Zea mays) is obtained by mechanical and / or solvents. The oil is refined, bleached and deodorized. The refining includes also winterization (the removal of waxes). The finished oil looks clear and reddish yellow with a flavour very well accepted by consumers.

2.2.5 Soybean oil

Soybean oil is obtained from soy bean (Glycine max). The production of soy bean in the world is very high. Soybean oil is obtained both by solvent extraction and by mechanical methods. The crude oil contains between 2.5 to 3.0% of phospholipids. The phospholipids have to be removed from the oil by refining process and chemical degumming. The oil contains unsaturated fatty acids especially linoleic and linolenic acid. The crude oil is refined, bleached and deodorizes ready for bottling.
2.2.6 Palm oil

2.2.6.1 Background

Palm oil has been consumed for more than 5,000 years and is obtained from the fruit of the palm tree, Elaeis guineensis. This tree is native to western Guinea. From the fifteenth century was introduced to other parts of Africa, Southeast Asia and Latin America along the equator.

Oil palm was introduced in Malaysia in 1870 as an ornamental plant. The palm was cultivated on an industrial scale after the First World War, drawing on experiences from the plantations of Sumatra (Killmann, 2001). Currently Indonesia, Malaysia, Thailand, Nigeria and Colombia are the world's largest producers of palm oil (USDA, 2009).

In the Central and South America the first plantations were established in the forties. In Colombia, in 1957 began the cultivation of palm for ornamental purposes. Then the palm cultivation takes place on an industrial scale. In 2008 there were 350,000 hectares of planted area, with a tendency to increase over the next decade. In November 2009, Colombia is the fifth largest producer of palm oil with a production of 800,000 tons (FEDEPALMA, 2009).

Palm tree takes from 2 to 3 years to start producing fruit. Palm tree can produce fruit during 25 years. Among the oilseed crops palm tree produce more oil per hectare. The fruit contains 50% oil. The palm tree can yield 3,000 to 5,000 kg of pulp oil per hectare and 600 to 1,000 kg of kernel oil per hectare from the kernel (Murillo, 2003).

2.2.6.2 Classification of the oil palm

The palm is a perennial plant. There are several genera and species in the Arecaceae family, the family of the Palms (Rich, 2008).

The classification of the oil palm in varieties is mainly done by the form, colour, composition of fruit and leaf shape. The mesocarp and endocarp vary in thickness. This characteristic is directly related to oil production. The shell and mesocarp contain palm oil. The crude palm oil (CPO) is produced from the mesocarp of the fruit. It is one of the
few oils produced from the mesocarp of the fruit. The other is olive oil. The crude palm kernel oil (CPKO) is produced from the inner nut or kernel (figure 1). There are three varieties of the oil palm fruit: dura, tenera, and pisifera. The tenera produces fruit with higher oil content.

Figure 1. Oil palm tree

- **Dura (Deli dura).**
  Dura was grown commercially in the world until the late sixties. Its main feature is the presence of a large kernel 2 to 8 mm and a thin mesocarp. This decreases the percentage of pulp in the fruit and therefore its oil content is low. There are still some small plantations

- **Pisifera.**
  The pisifera palm produces a fruit that has no endocarp or shell. This variety produces smaller fruit than the Dura. Because of the size of the fruit and the lack of shell, this variety produces little oil. So it is used only to improve the variety by crossing.
• **Tenera (Django Tenera).**

The kernel of the fruit is thin. The proportion of pulp is considerably higher, so the oil content is significantly abundant. Tenera differs from the Dura variety because their fibers are darker. Tenera variety is the most widely used commercially in the world. However, the Dura variety is also cultivated (Deli dura) (Rica, 2008).

### 2.2.6.3 Morphology

The oil palm is a monocot plant. The primary roots develop from a bulb located below the stem. The horizontal roots predominate in the first 50 cm of the soil. Other roots descend into the soil. Secondary roots develop on the primary roots. The trunk grows 35 to 75 cm in height each year (in Malaysia the growth is about of 45 cm every year). With this growth in height of the palm fruit harvest becomes very difficult after 15 years of age of the plants. The leaves are green, have a length of 6 to 8 m and are arranged in spirals on the trunk.

Under normal conditions, the trunk holds between forty and fifty-six leaves. These should be pruned or cut during harvesting and maintenance activities, otherwise the leaves accumulate on the trunk (20 or 30 leaves per year). The oil palm reaches maturity at 10 to 12 years (CORPODIB, 2005).

### 2.2.6.4 Agronomics requirements

The oil palm prefers warm-temperate to tropical climates with regular water in hot weather. Optimally the oil palm requires at least 1 600 to 2 000 mm of annual rainfall and also sunlight (approximately 5 hours per day on average during the year). The relative humidity should be above 75%. The soil water loss by direct evaporation and transpiration through the leaves affects the development of palm oil. The relative humidity is influenced by the insolation from the sun, the vapour pressure of the atmosphere, temperature, wind and soil moisture.
It is needed an average maximum temperature of around 29 °C and a mean minimum temperature of about 22 °C to 24 °C. Lower temperatures stop the growth and reduce the yield of adult palms (FEDEPALMA, 2009).

It takes approximately 4 to 5 years to begin to bear fruit, and reaches its highest productivity just before 20 years. However, it is a crop that can withstand periods of drought and floods, extreme weather conditions prevalent in countries where it is cultivated (Castro, 2007).

2.2.6.5 Composition of the seed.

The palm oil is a natural food that is extracted from the seeds and fruit without chemical solvents, so reducing the risk of contamination.

The palm oil contains equal proportions of saturated fatty acids and unsaturated fatty acids. It contains 40% oleic acid (monounsaturated), 10% linoleic acid (polyunsaturated), 44% palmitic acid (saturated) and 5% stearic acid (saturated). The unrefined palm oil is an important source of vitamin A. This oil is also a natural source of vitamin E, tocopherols and tocotrienols.

Palm oil has high solid glycerides content, which make it semi-solid. It is normally used in its natural state without hydrogenation. (Gibon, 2007).

2.2.6.6 Products and byproducts of the palm

Oil palm is a stable source of the world supply of vegetable oil. It is considered to reach highest oil yield per hectare. The variation in the reached oil yield is related to the type of tree, the different fertilizers and rate of maturation of the plant.

The palm fruit produces two different types of oils: palm acid oil from the mesocarp and lauric palm kernel oil from its kernel.

The fresh fruit bunches are crushed in a pressing machine to obtain crude palm oil and palm kernel. The palm kernel is further crushed to produce palm kernel oil and protein flour (palm kernel cake) (FEDEPALMA, 2009). Ideally, the crops can produce up to 20
tons of fruits per hectare and per year. It is possible to extract up to 25% palm oil (five tons) and 5% of palm kernel oil (one ton). This amount is greater than the amount produced by any other source of vegetable oil (CORPODIB, 2005).

Only 10% of the palm yields oil (palm oil and palm kernel oil). The remaining 90% of biomass includes empty fruit bunches (EFB), fibers, kernels, fonds and trunks. If this rest of biomass is burn open or left to settle in waste ponds, it will emit carbon dioxide and methane contributing to global warming. By using the oil palm in the mills of the oil palm industry, as fuel for production of heat and power, the emission of greenhouse gas is reduced. The use of the biomass from palm oil for production of heat, electricity and biofuels should continue developing.

- **Palm kernel cake.**

  The palm kernel cake is used almost exclusively for animal feed. According to several studies, the use of palm kernel cake in animal feed favours the healthy development of the animals. Additionally, it is estimated that the integration of palm kernel cake with palm oil in animal feed increases the animal's weight gain, ensuring higher returns for farmers (CORPODIB, 2005).

- **By-products from palm oil extraction.**

  Ash from kernel wood is used as fertilizer because of its potassium, phosphorus, and calcium content. Fibers and shell materials can be as solid fuel in furnaces. The stone can be used as supplement in construction materials (eg for access roads to the plantations) and for activated carbon (Rica, 2008).

- **Crude palm oil and palm kernel.**

  Once extracted, the crude oil is processed into two products: the olein (liquid) that is used almost exclusively as food and stearin (solid) whose main use is in cosmetics, soaps and detergents.
2.2.6.7 Quality of palm oil biodiesel

The high cetane number of biodiesel from crude palm oil (CPO) is a characteristic of the ignition quality, widely reported, for this type of biofuel. (Benjumea, 2008).

In literature it is reported cetane numbers for palm biodiesel with values between 42 and 62 (Mittelbach, 2004; Leevijit, 2008), even exceeding values of pure diesel. ASTM D613 and EN ISO 5165 limit the cetane number of biodiesel to a minimum of 51.

Current regulations for diesel and biodiesel do not specify values for the calorific value. The calorific value of the crude palm oil is close to 39.5 MJ/kg similar to other biodiesel. The calorific value of the fossil diesel is about 43-45 MJ/kg.

Some of the disadvantages of and problems with biodiesel are the high values of all the cold flow properties of fuel, such as cloud point, pour point (PP) and cold filter plugging point (CFPP) in comparison to those for petroleum diesel. For example the cloud point of biodiesel is around 18 °C. The cloud point is the temperature at which crystals begin to form in the fuel. This value is directly associated with the chemical nature of the esterified fatty acids, which in the case of palm oil methyl esters are in great proportion saturated. The poor cold flow properties of biodiesel from CPO limit their use as pure fuel in places subject to low temperatures (Benjumea, 2004). For use in cold climate regions, a solution to these problems is to use mixed with conventional diesel in suitable proportions. Another possibility is to use additives in order to decrease the pour point. A more radical option would be to try to split the biodiesel using a process similar to the winterisation of crude oils. In tropical regions with temperatures not lower than 25 °C the palm biodiesel can be used in a greater proportion (Benjumea, 2004).

2.2.6.8 Uses of palm oil.

Palm oil is used as cooking oil and the production of margarines containing a low percentage of trans fatty acids (considered harmful to health). It is also used in bakery, confectionery and ice cream industries (Castro, 2007).
Palm kernel oil (PKO) is not used in large extent as food. It is mainly used in the oleochemical industry for production of detergents, cleaners and cosmetics.

Biodiesel can be produced both from palm oil and from palm kernel oil.

2.2.6.9 Sustainable cultivation of palm oil

The production of palm oil at industrial plantation level has caused environmental damage such as destruction of forest, lost biodiversity, release of greenhouse gases and soil impoverishment.

In 2004 the Roundtable on Sustainable Palm Oil (RSPO) was created in Zurich aiming the protection of the rainforest by a sustainable cultivation of the oil palm. In order to certify the palm oil as sustainable 8 principles and 32 criteria were selected. Around 10 % of the world palm oil production are today filling the selected principles and criteria.

2.2.6.10 World production and prices.

World production of palm oil was 45 million tonnes (USDA, 2009). In March 2012 the price of palm oil was 1100 USD per metric ton (FOB Brazil) (IndexMundi, 2009). Table 1 shows the production of palm oil in the world.

<table>
<thead>
<tr>
<th>Country</th>
<th>amount ( million tonnes )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indonesia</td>
<td>20.75</td>
</tr>
<tr>
<td>Malaysia</td>
<td>18.50</td>
</tr>
<tr>
<td>Thailand</td>
<td>1.30</td>
</tr>
<tr>
<td>Nigeria</td>
<td>0.82</td>
</tr>
<tr>
<td>Colombia</td>
<td>0.80</td>
</tr>
<tr>
<td>Others</td>
<td>2.85</td>
</tr>
</tbody>
</table>

Table 1 Palm oil producers (USDA, 2009)

Figure 2 shows the main producers of palm oil in 2001 (FAO). Figure 3 shows the price of the Malaysian palm oil between April 2011 and April 2012.
Figure 2. Main producers of palm oil in 2001.

Figure 3. Malaysian palm oil price between April 2011 and April 2012 (IndexMundi)
3 Biodiesel

Biofuels are alcohols, esters and other organic compounds produced from biomass such as herbaceous and woody plants, residues from agriculture and forestry, and some agroindustrial waste such as waste from the food industry.

The term biomass refers to any substance which can be obtained by photosynthesis. Most plants utilize solar energy to create sugars, starting from simple substances such as water and carbon dioxide. This energy is stored in molecules of glucose, starch, oil, etc. Biofuels could include ethanol, biodiesel, and biomethanol among others. Most developed and used are bioethanol and biodiesel (Stratta, 2003).

3.1 Historical development of biodiesel

The idea of using vegetable oils as fuel for internal combustion engines is from 1895, when Rudolf Diesel developed his engine. In presenting the diesel engine at the World Exhibition in Paris in 1900, Mr. Diesel used peanut oil as fuel (Knothe, 2005).

The high viscosity of the oils (about 10 times more than diesel) limited their use, because this implies a poor fuel atomization and an incomplete combustion. The high flash point of vegetable oils and their tendency to oxidize thermally hindered also the use of the oil, due to the formation of deposits in the injector nozzles and a decrease in lubricity. However it was attempted to modify the properties of the oils to approximate those properties to those of diesel, through other methods such as dilution or microemulsion, pyrolysis or transesterification (Agarwal, 2007). But due to low oil prices, the fossil diesel took an important place and the use of vegetable oil was not developed as an alternative (Mittelbach, 2004).

The idea of using vegetable oil diesel in their engines, reborn in the late twentieth century, this time in the form of biodiesel (which is only modified vegetable oil) mainly driven by environmental concerns related to climate change. Other motivations, in addition to the ecological, to encourage the use of biodiesel were the surplus soybean production in the United States, or the surplus of agricultural production in Europe.
However it was required significant subsidies or tax cuts to ensure its viability, as prices of vegetable oils were substantially higher than those of diesel (Girard, 2006).

It was with the great rise in oil prices since 2004, and July 2008 ($ 133.90 a barrel of Brent (IndexMundi, 2009) that prices of vegetable oils and animal fats are beginning to equate with those of diesel.

Historically, the term biodiesel has been used to refer to all types of alternative fuels such as vegetable oils, vegetable oils mixed with diesel oil, vegetable oil microemulsions, pyrolysis products of vegetable oils, methyl and ethyl esters prepared from vegetable oils or animal fat. However, with increasing production and development of methyl and ethyl esters as diesel fuel, the term biodiesel increasingly refers to those esters (Crespo, 2001). ASTM (American Society for Testing and Materials) defines biodiesel as monoalkyl esters of long chain fatty acids derived from renewable lipids, such as vegetable oils or animal fats, used in compression ignition engines.

Biodiesel can be produced from agricultural raw materials such as vegetable oils and / or animal fats, as well as from waste cooking oils (Larosa, 2001). The use of biodiesel can be pure, designated B100, or blended with diesel fuel, designated BXX, where XX represents the percentage of biodiesel in the blend. The most common ratio is B20, which represents 20% biodiesel and 80% diesel.

From the point of view of flammability and toxicity, biodiesel is safer than petrodiesel (Aguilar, 2006). It is biodegradable. Biodiesel is formed by hydrocarbon chains which form esters with two oxygen atoms, which makes it biologically active. The conventional diesel is not biodegradable. The fossil diesel consists of a mixture of alkanes, branched alkanes, cycloalkanes, aromatic hydrocarbons, which are difficult to degrade. The biodiesel from rapeseed oil and soybeans is biodegradable in 88.49% after 28 days. The lubricating properties of the diesel are improved by adding biodiesel to petrodiesel (Larosa, 2005).

One of the major benefits of biodiesel is its low content of sulphur. Due to the presence of oxygen in their chemical composition, its combustion is more complete, reducing the particulate emissions, carbon monoxide and unburnt hydrocarbons, among other contaminants (Larosa, 2001, 2003, Ballesteros, 2003). During its production process is a
by-product, glycerine, is obtained. The glycerine after purification can be used in pharmaceutical and cosmetic industry (Castro, 2006).

### 3.2 Advantages and disadvantages in the use of biodiesel fuel

The use of biodiesel has energetic, environmental and economic advantages. Today's diesel engines require a clean fuel to be burned, as well as it remains stable under the different conditions.

Biodiesel can be used directly in any diesel engine without any necessary modifications in the engine. Their properties are similar to petroleum diesel fuel (equivalent density, viscosity only slightly higher). It can be mixed with fossil diesel in any proportion, without any problem (Hilbert, 2007). In comparison to fossil diesel, biodiesel has a lower calorific value (around 10%) and a worse performance at low temperatures with a tendency to solidify at extreme cold conditions, which requires the use of specific additives. Additional advantages include a high cetane number (Sebastian, 2006). A summary of these characteristics is shown in Table 2.

### Table 2. Characteristics of the biodiesel and fossil diesel.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Fossil diesel</th>
<th>Sunflower oil</th>
<th>Sunflower biodiesel</th>
<th>Rapeseed oil</th>
<th>Rapeseed Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific density (Kg/dm³)</td>
<td>0.835</td>
<td>0.924</td>
<td>0.88</td>
<td>0.0916</td>
<td>0.88</td>
</tr>
<tr>
<td>Viscosity (cSt) at:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 °C</td>
<td>5.1</td>
<td>65.8</td>
<td>---</td>
<td>77.8</td>
<td>7.5</td>
</tr>
<tr>
<td>50 °C</td>
<td>2.6</td>
<td>34.9</td>
<td>4.22</td>
<td>25.7</td>
<td>3.8</td>
</tr>
<tr>
<td>HHV (kcal/l)</td>
<td>9 216</td>
<td>8 760</td>
<td>8 472</td>
<td>8 928</td>
<td>---</td>
</tr>
<tr>
<td>LHV (kcal/l)</td>
<td>8 496</td>
<td>8 194</td>
<td>7 930</td>
<td>8 232</td>
<td>7 944</td>
</tr>
<tr>
<td>Cetane number</td>
<td>&gt;45</td>
<td>33</td>
<td>45-51</td>
<td>44-51</td>
<td>52-56</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>0.15</td>
<td>0.42</td>
<td>0.05</td>
<td>0.25</td>
<td>0.02</td>
</tr>
<tr>
<td>Sulphur (%)</td>
<td>0.005</td>
<td>0.01</td>
<td>0.001</td>
<td>0.002</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Table 3 shows the advantages and disadvantages of the use of biodiesel.

**Table 3. Advantages and disadvantages of the use of biodiesel**

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Biodiesel is a renewable resource, biodegradable and nontoxic.</td>
<td>- Increased emissions of NOx and aldehydes.</td>
</tr>
<tr>
<td>- Lower emissions of carbon monoxide, unburnt hydrocarbons and carbon</td>
<td>- Because it is a good solvent, it can dissolve sediments in the engine fuel</td>
</tr>
<tr>
<td>particles, contributing to the reduction of greenhouse gases.</td>
<td>system and cause filter plugging during its first use in engines usually</td>
</tr>
<tr>
<td></td>
<td>working with fossil diesel. So it is recommended to clean the fuel system</td>
</tr>
<tr>
<td></td>
<td>when switching from diesel to biodiesel.</td>
</tr>
<tr>
<td>It can be used directly in direct injection engines without special</td>
<td>Below 0 °C, the biodiesel tends to freeze causing engine deposits.</td>
</tr>
<tr>
<td>adaptations.</td>
<td></td>
</tr>
<tr>
<td>- The engine performance improves when using biodiesel instead of fossil</td>
<td>- Biodiesel has about 8% less energy per liter than diesel. The power and</td>
</tr>
<tr>
<td>diesel, due to its high lubricity.</td>
<td>fuel consumption of the engine is decreased.</td>
</tr>
<tr>
<td>It is safer, because it has a high flash point.</td>
<td>- The feedstocks for biodiesel require vast areas for cultivation and could</td>
</tr>
<tr>
<td>- The gases from combustion of biodiesel do not contain sulphur dioxide,</td>
<td>affect the food prices.</td>
</tr>
<tr>
<td>main cause of acid rain.</td>
<td>Biodiesel tends to oxidize more rapidly than diesel.</td>
</tr>
<tr>
<td>- Promotion of local and regional development.</td>
<td>- High costs of production.</td>
</tr>
</tbody>
</table>

### 3.3 Overview of biodiesel in the world

The global production of biodiesel has increased exponentially (Figure 4 and Table 4).
Table 4. World production of biodiesel.

<table>
<thead>
<tr>
<th>Region</th>
<th>Million litres</th>
<th>Feedstocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>EU</td>
<td>9 906</td>
<td>Rapeseed (50%), Soy (40%), Palm (5%), Tallow (5%)</td>
</tr>
<tr>
<td>USA</td>
<td>1 682</td>
<td>Soy (40%), Tallow (20%), Canola (20%), Palm (20%)</td>
</tr>
<tr>
<td>Brazil</td>
<td>1 386</td>
<td>Soy (80%), Tallow (10%), Other vegetable oils (10%)</td>
</tr>
<tr>
<td>Argentina</td>
<td>1 250</td>
<td>Soy</td>
</tr>
<tr>
<td>Thailand</td>
<td>614</td>
<td>Palm</td>
</tr>
<tr>
<td>Malaysia</td>
<td>284</td>
<td>Palm</td>
</tr>
<tr>
<td>Colombia</td>
<td>205</td>
<td>Palm</td>
</tr>
<tr>
<td>China</td>
<td>182</td>
<td>Waste vegetable oils</td>
</tr>
<tr>
<td>South Korea</td>
<td></td>
<td>Palm (33%), Soy (33%), Waste vegetable oils (33%)</td>
</tr>
<tr>
<td>Indonesia</td>
<td>170</td>
<td>Palm</td>
</tr>
<tr>
<td>Singapore</td>
<td>124</td>
<td>Palm</td>
</tr>
<tr>
<td>Philippines</td>
<td>108</td>
<td>Coconut</td>
</tr>
<tr>
<td>Canada</td>
<td>102</td>
<td>Tallow</td>
</tr>
<tr>
<td>Other South America</td>
<td>63</td>
<td>Palm</td>
</tr>
<tr>
<td>Australia</td>
<td>57</td>
<td>Tallow</td>
</tr>
<tr>
<td>Taiwan</td>
<td>43</td>
<td>Palm (33%), Soy (33%), Waste vegetable oils (33%)</td>
</tr>
<tr>
<td>Central America</td>
<td>38</td>
<td>Palm</td>
</tr>
<tr>
<td>India</td>
<td>23</td>
<td>Waste vegetable oils</td>
</tr>
<tr>
<td>Other, Oceania</td>
<td>6</td>
<td>Waste vegetable oils</td>
</tr>
<tr>
<td>Other, Asia</td>
<td>5</td>
<td>Waste vegetable oils</td>
</tr>
<tr>
<td>TOTAL WORLD</td>
<td>16 436</td>
<td></td>
</tr>
</tbody>
</table>
Biodiesel is usually obtained by transesterification of oils or fats by reacting a short-chain alcohol, like methanol, in the presence of a homogeneous base-catalyst (typically NaOH). The most common raw materials for production of biodiesel are vegetable oils from sunflower, soybean, oil palm and other (Knothe, 2005; Dias, 2008).

The transesterification reaction mainly depends on the nature of the feedstock, catalyst concentration, the molar ratio alcohol-oil, temperature, agitation rate, pressure and reaction time as well as moisture content and amount of free fatty acids (Mittelbach, 2004; Canakci, 2001; Dorado, 2002; Ma, 1999).

In the transesterification reaction, one mole of triglyceride is reacted with three moles of alcohol to form one mole of glycerol and three moles of the respective fatty acid alkyl ester in a sequence of three reversible reactions where the triglycerides are converted to diglycerides and then to monoglycerides (figures 5 and 6). Glycerol is produced as byproduct. After the reaction the mixture forms two phases: the glycerin-rich-phase and ethyl esters-rich-phase. The two phases can be separated by decantation or centrifuging.

There are several types of catalysts for transesterification. The most commonly used catalyst for production of biodiesel is the homogeneous catalysis. The homogeneous catalysis used for biodiesel production can be divided mainly in alkaline and acidic
catalysts. Heterogeneous catalysts (solid phase) is also used. Another interesting alternative may be to use lipases as enzymatic catalysts (Haas, 2005).

\[
\begin{align*}
    H_2C - OCOR' & \xrightarrow{k_1} H_2C - OH \\
    HC - OCOR'' + CH_3OH & \xrightarrow{k_2} \rightleftharpoons H_2C - OCOR' + HC - OCOR'' \quad H_2C - OCOR''
\end{align*}
\]

Triglicérido \hspace{1cm} Metanol \hspace{1cm} Metiléster \hspace{1cm} Diglicérido

\[
\begin{align*}
    H_2C - OH & \xrightarrow{k_3} H_2C - OH \\
    HC - OCOR'' + CH_3OH & \xrightarrow{k_4} \rightleftharpoons H_2C - OCOR'' + HC - OH \quad H_2C - OCOR''
\end{align*}
\]

Diglicérido \hspace{1cm} Metanol \hspace{1cm} Metiléster \hspace{1cm} Monoglicérido

\[
\begin{align*}
    H_2C - OH & \xrightarrow{k_5} H_2C - OH \\
    HC - OH + CH_3OH & \xrightarrow{k_6} \rightleftharpoons H_3C - OCOR'' + HC - OH \quad H_2C - OH
\end{align*}
\]

Monoglicérido \hspace{1cm} Metanol \hspace{1cm} Metiléster \hspace{1cm} Glicerol

Figure 5. Stages in the transesterification reaction
4.1 Homogeneous Catalysis

4.1.1 Base catalysis

The homogeneous alkaline transesterification is the preferred process by the industry in order to produce biodiesel. Usually the homogenous alkaline catalyst is faster and less expensive compared with homogenous acid catalyst or other catalysts. Strong bases such as NaOH and KOH are the most used catalysts.

These hydroxides have high conversions under mild conditions and short reaction times. They are less corrosive. Small amounts of alcohol are required, which represents smaller and cheaper reactors (Agarwal, 2007; Mittelbach, 2004; Moser, 2009). However, it is required oils with a low concentration of free fatty acids, without gums and impurities. It is also essential that the moisture content is low, otherwise side reactions will be presented saponification or neutralization (Figure 7) (Knothe, 2005, Rashid, 2008; Canakci, 2001).
In the case of alkaline catalysis, it is important that the catalysts are maintained in an anhydrous state. Prolonged contact with the air should be avoided, as their effectiveness should be reduced due to interaction with moisture and carbon dioxide (Agarwal, 2007; Meher, 2006). Usually a solution of sodium or potassium methoxide is created by dissolving sodium hydroxide or potassium hydroxide in methanol (Dias, 2008; Zhou, 2006). Other alkoxides, such as calcium ethoxide were used for the production of biodiesel, although with increased demands of alcohol and catalyst (Liu, 2008). Furthermore, NaOH, KOH, NaOCH₃ and KOCH₃ have been used for transesterification of waste oils (Dias, 2008, Encinar, 2002, Phan, 2008; Tomasevic, 2003, Golden, 2002; Felizardo, 2006). The needed amount catalyst depends of the treated oil. Usually from 0.4 to 1.5 wt% catalyst is necessary.

4.1.2 Acid catalysis

Acid catalysts include sulphuric, phosphoric and hydrochloric acid (Helwani, 2009). The acid catalysts are recommended for oils with a high content of free fatty acids such as palm oil or waste oil (May 2004). The acid catalysis is also used to pre-treat some oils as a step prior to the basic transesterification. In this case the free fatty acids are esterified until the amount of FFA is lower than 0.5 % (Pinzi, 2009). Then, additional methanol and
base catalyst are added to finish the reaction. However, the reaction is slow and requires higher temperatures and pressures, and likewise demands higher amounts of alcohol

4.2 Heterogeneous catalysis

Heterogeneous catalysts act in a different phase than the reactants. They do not dissolve in alcohol, oil or biodiesel. They are in solid state and are easily recoverable by decantation or filtration at the end of the reaction (Helwani, 2009). Transesterification with homogeneous catalysis has presents problems such as formation of soaps and need for purification and disposal of byproducts of the reaction, the treatment of waste effluents and in the case of acid catalysts problems related to corrosion (Meng, 2008).

Examples of Heterogeneous catalysts are hydrotalcites (Trakarnpruk, 2008), calcium carbonate and tin, magnesium and zinc oxides, among others. Using heterogeneous catalysis only the evaporation of methanol is required and no waste effluents are produced, in addition it is also obtained pure glycerol (Melero, 2009). However their high cost due to the necessity of elevated temperature and pressure conditions as well as large volumes of alcohol, is not still allowing a commercial production of biodiesel using heterogeneous catalysts (Mittelbach, 2004).

4.3 Enzymatic Catalysis

Enzymatic catalysts such as lipases are able to catalyze the transesterification of triglycerides (Helwani, 2009). Enzymatic catalysts have the advantage of being reusable. The glycerol is easily removed. The free fatty acids are converted into esters. Enzymatic catalysts are not inhibited by the presence of water. However, enzyme inactivation due to the excess of methanol and glycerol accumulation on the immobilized enzyme can take place. The major drawback is the cost of production of lipases. Lipases are more expensive than alkaline and acid catalysts (Mittelbach, 2003; Haas, 2005; Meher, 2006; Fukuda, 2001).
4.4 Presence of free fatty acids (FFA)

A fatty acid is an organic molecule consisting of a long aliphatic chain of an even number of carbon atoms. At the end of the chain there is a carboxyl group. A fatty acid is a carboxylic acid of high molecular weight.

The content of free fatty acids and moisture are key parameters that determine the feasibility of the process of transesterification. The content of free fatty acids determines the catalytic route to be utilized for the transesterification. For a basic catalyst the amount of FFA in the oil should be less than 3% because the high acidity of the oil causes a low biodiesel yield (Gold, 2002). When oil has more than 5% FFA, it can not be transesterified by alkaline catalysis, due to the formation of soaps which inhibit the separation of glycerol and biodiesel. Also formation of emulsions during washing takes place (Van Gerpen, 2005). The presence of FFA causes formation of soap and hampers the separation of the biodiesel and glycerol. Besides, a high amount of catalyst is consumed and the catalytic efficiency is considerably reduced.

One difficulty of this process is the presence of water. The accumulation of water produced during the esterification can stop the reaction before it is complete.

Using the acid catalysis biodiesel from soybean oil containing 1-2% FFA has been obtained with an efficient conversion of 99% after 26 hours (Goff, 2004). For the transesterification reaction at 100 °C of dewaxed/degummed rice bran oil containing 24.5% and 49.5% FFA with methanol the reached conversion was 62% and 73% respectively (Zullaiker et al., 2005). An increase in the amount of methanol or catalyst has a negligible effect on conversion. The water generated during the process forms another phase which absorbs methanol and sulphuric acid. This water phase probably prevents the transesterification of triglycerides and further esterification of residual FFA (Goff, 2004).

The reaction of transesterification of beef fat catalyzed by sodium hydroxide in the presence of FFA and water (Ma, 1999). Without the presence of FFA, high yields of methyl esters have been obtained. By adding 0.6% FFA the conversion decreases sharply to values lower than 5%. When adding 0.9% of water without adding FFA, the
conversion is about 17%. If the fat or oil contains a high percentage of FFA, these can be eliminated by saponification reaction with sodium hydroxide solution. However, for the transesterification of FFA, acid catalysis can be used. The transesterification process may be carried out in two stages (Zullaikah, 2005). In the first step FFA is converted to alkyl esters by acid catalysis and in the second step the transesterification process is completed by basic catalysis.

4.5 Alcohols

The alcohols which are traditionally used in the transesterification are of short-chain, mainly methanol (Rashid, 2008) and ethanol (Alamu, 2008). Other alcohols can be used such as propanol, isopropanol, butanol and pentanol (Encinar, 2002; Ma, 1999; Georgogianni, 2008), but these alcohols are much more sensitive to water contamination. They are also more expensive and larger molar ratios and higher temperatures are required. Methanol has a lower cost and presents some chemical and physical advantages over other alcohols, as the high rate of reaction with triglycerides. KOH and NaOH dissolve easily in methanol (Ma, 1999). It is important to mention the high toxicity of methanol, flammability, and the fact that methanol is mainly produced from non-renewable fossil fuels such as methane gas.

Ethanol, however, comes from renewable raw materials: sugar cane, sugar beet, vegetables and other cellulosic (Girard, 2006). So ethanol is of particular interest mainly because it is less expensive than methanol in some regions (Moser, 2009). It is also possible to obtain by dry distillation of wood, but this process is not applicable to large scale. However, the ethyl ester formation is comparatively more difficult than that of methyl ester. The formation of a stable emulsion during the ethanolysis is a problem (Zhou, 2006).

Ethanol and methanol do not dissolve with the triglycerides at room temperature and the mixture must be agitated mechanically to allow diffusion. During the reaction, generally an emulsion is formed. In the methanalysis this emulsion breaks down rapidly forming a lower glycerol-rich layer and an upper layer rich in methyl ester. However in ethanolysis this emulsion is more stable and complicates the separation and purification of the ethyl
esters. The emulsion is caused partly by the formation of monoglycerides and diglycerides intermediates containing both polar hydroxyl groups and non-polar hydrocarbon chains.

The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to produce three moles of esters and one mole of glycerol. The transesterification is an equilibrium reaction requiring an excess of alcohol to drive the reaction to the right. The excess of methanol may be recovered after the reaction (Enweremadu, 2009). For maximum conversion it is recommended to use a molar ratio of 6:1. However this ratio will depend on the type of feedstock used. A high molar ratio alcohol/oil affects the separation of glycerol due to increased solubility. When the glycerol is maintained in the solution the reverse reaction moves to the left. The glycerol can react back into a monoglyceride and diglyceride. The product will contain monoglycerides and diglycerides, which crystallize very easily in the biodiesel and can cause clogging of filters and other engine problems (Agarwal, 2007; Knothe, 2005, Van Gerpen, 2005; Dorado, 2002).

4.6 Temperature and pressure

The transesterification can be performed at atmospheric pressure and at different temperatures depending on the used feedstock used. The temperature influences the yield of obtained biodiesel (Ma, 1999; Meher, 2006). Often the transesterification is carried out at a temperature near the boiling point of alcohol (at 60 °C when using methanol) (Fukuda, 2001).

Biodiesel can also be produced by methods at high pressures (eg 50-100 bar) and high temperatures (200-250 °C) using large amounts of methanol and without pretreatment of the raw material. Methods using methanol at supercritical conditions at 350 °C and 43 MPa have been also used. However, the costs of these processes are high (Pinzi, 2009, Mittelbach, 2004).
4.7 Reaction time

The transesterification increases with the reaction time. Using peanut, cottonseed, sunflower and soybean oils with methanol in a ratio methanol/oil of 6:1 at 60° C and NaOH as catalyst, and yield of 80% biodiesel was obtained after 1 min for soybean and sunflower oils. After 1 h the conversion was 93-98% for all four oils (Ma, 1999). In the transterification of palm oil with methanol at 50° C using 1% KOH as catalyst a conversion of 80% was observed after 8 min. and about 90% after 1 h. The formation of methyl esters is high in the first minutes. Then the rate diminished and finally reaches equilibrium after 1 h. (Darnoko, 2000).

4.8 Phase Separation

After the transesterification reaction, the reaction mixture is separated in two phases. The lower phase, the glycerol phase, can be separated by decantation or centrifugation. Emulsion can be formed due impurities in the feedstock. Emulsions use t cause difficulties in the phase separation. Saturated salt (sodium chloride) breaks the emulsion and speeds up the phase separation (Enweremadu, 2009).

Some ways to promote phase separation, mentioned by Mittelbach, are (Mittelbach, 2004):

• The addition of water, glycerol extra or hexane.
• Cool down the mixture.
• Application of high voltage to facilitate separation of the polar phase (glycerol and residues of alcohol and catalyst) from the nonpolar phase (esters and alcohol).

4.9 Purification of biodiesel.

After separation of phases, both the biodiesel and glycerol phase have to be washed and purified. In the industry the methanol is recovered by heating the ester phase. Glycerol and traces of catalyst can be removed from the biodiesel phase by washing with acidified water in order to neutralize the traces of catalyst. Free fatty acids can be recovered from
the ester phase by distillation, using the fact that FAME usually distilled at 30-50 °C lower than FFA. However this procedure increases considerably the costs (Mittelbach, 2004; Van Gerpen, 2005; Enweremadu, 2009).

Solid adsorbents have shown success in the removal of impurities from biodiesel. Some used adsorbents are magnesium silicate and silica gel (Predojevic, 2008). Ion exchange resins have been also tested for purification of biodiesel.

5 MATERIALS and METHODS

5.1 Experimental procedures

The experimental part of the work includes the production of biodiesel from corn oil. Ethanol and methanol has been used in the transesterification. Potassium hydroxide and sodium hydroxide have been selected as catalyst.

The reaction takes place in an Erlenmeyer flask as rector equipped by magnetic stirrer in a discontinuous process (figure 8). The Erlenmeyer flask is placed in a water bath maintained at a desired temperature by one electrical heater.

![Equipment for production of biodiesel](image)

Figure 8. Equipment for production of biodiesel

The alcohol (methanol or ethanol) and catalyst (NaOH or KOH) are mixed preferably at the temperature close to the main reaction temperature to avoid significant temperature
drop in reactor. Corn oil - which also is maintained at the constant temperature - is added to the mixture of alcohol-catalyst. After reaction finished the product is poured into a funnel to obtain a separated two phases. Upper phase is biodiesel and downer is glycerin.

Volume of oil is 200 ml (experiments with ethanol) or 250 ml (experiments with methanol) and reaction time alters between 1 and 2 hours for different conditions. The different conditions and the results of the experiments are in appendix 2, 3, 4 and 5.

The influence of ratio alcohol to oil, the amount of catalyst, the reaction time, the rate of mixing, the reaction temperature on the yield of produced biodiesel is studied.

The performance of the experiments includes the following steps:

- Measure quickly the catalysts (NaOH/KOH) on an electronic scale (Figure 9).

![Figure 9. An electronic scale.](image)

- Mix the alcohol and the catalysts (NaOH/KOH) in an Erlenmeyer flask under stirring to ensure complete solution (figure 10).

![Figure 10. Magnet and a digital magnetic stirrer.](image)
• Preheat the Erlenmeyer flask with alcohol and catalyst mixture in a water bath to a determined temperature. In this section, it is important to cover the flask with a lid due to vaporization during the reaction.

• The corn oil is preheated to the reaction temperature in a electric heater. Then the oil is added to the alcohol/catalyst solution in the Erlenmeyer flask placed in the water bath. The reaction is maintained for 1-2 hours under stirring at the set temperature to get complete conversion.

• The solution is poured into a separation funnel since the reaction is completed, i.e. two large phases are formed. The biodiesel product at the top and the by-product glycerol in the bottom of the funnel.

• Removal and measure of glycerol from biodiesel.

• The product after removal of glycerol is washed with 5wt% phosphoric acid to extract alkaline. A funnel is used in order to separate the washing water and the biodiesel (figure 11).

Figure 11. Separation of biodiesel and washing water.

5.2 Methods of analysis and calculations

5.2.1 Measuring density of biodiesel

Density of biodiesel is determined by gravimetric analysis measuring a volume of 25ml biodiesel with a glass cylinder and weighting the sample on the electronic scale. The density calculated by equation (1)
\[ \rho = \frac{m}{v} \]  

(1)

There, \( m [\text{g}] \) is weight of the sample and \( v [\text{cm}^3] \) volume of the sample.

5.2.2 Measuring Refractive index of biodiesel

The refractive index of a medium is a measure of how much the velocity of a wave is reduced inside that medium. In the experiments the Abbe refractometer is used (figure 12).

The light ray pitched on the interphase of phases then it was refracted. The impact angles, rebound and the refraction are measured between a ray running perpendicular to the phase interface. Ray break is a result of differences in the speed of light in both phases. Refractive index is the ratio of the speed of light in phases the light passes through. Its principle is the detection of limit angle fracture (\( \beta_{\text{max}} \)), which is the maximum possible angle fracture where the angle of impact is close to 90°.

![Figure 12: Abbe refractometer](image)

This is also used to identify the pure substances, purity, solution quantitative analysis, and to measure the dipole moment of substances and to know the optical properties of molecule by RI as function of wave length.

5.2.3 Measuring viscosity of biodiesel

The viscosity of biodiesel is measured by a falling-ball viscometer as in figure 13.
The falling-ball viscometer is used to measure the viscosity of liquid by measuring the time required for a ball to fall under gravity through a sample-filled tube that is inclined at an angle. The average time of ten testes is taken in this experiment.

![Figure 13. Falling-ball viscometer](image)

The viscosity can be determined by equation (2):

\[
\eta = k \times t \times (\rho_{\text{ball}} - \rho_{\text{medium}}) \tag{2}
\]

Where, \( \eta \) is the dynamic viscosity [g/cm, s], \( k \) is the geometrical constant of the ball [m\(^2\)], \( t \) is the fall time through the tube [s], \( \rho_{\text{ball}} \) is the density of the ball [g/cm\(^3\)] and \( \rho_{\text{medium}} \) is the density of the medium [g/cm\(^3\)].

The kinetic viscosity:

\[
\nu = \frac{\eta}{\rho} \tag{3}
\]

Where, \( \nu \) is the kinematic viscosity [g/cm, s].

The calculations of density, dynamic and kinematic viscosity are showed in Appendix 3.

5.2.4 Calculation of yield of biodiesel

The yield of produced biodiesel is calculated in appendix 1 according to:
The theoretical amount of produced biodiesel for a 100 % yield is calculated taking into account that 3 mol biodiesel are produced from 1 mol oil. The molar weight of Corn Oil is calculated and the volume and density of the corn oil are measured.

The real amount of produced biodiesel is calculated knowing the volume, density and molar weight of biodiesel.

6 RESULTS and DISCUSSION.

48 experiments for production of biodiesel from corn oil have been performed, 24 using ethanol and 24 using methanol as alcohol.

6.1 Influence of the ratio alcohol to oil

The molar ratio of alcohol to corn oil is investigated.

6.1.1 Using ethanol as alcohol

Figure 14 shows the yield of biodiesel as function of ratio ethanol/oil using NaOH (0.8 g and 1.8 g) and KOH (1.2 g and 2.6 g) as catalyst in a reaction time of 1h. The results for a reaction time of 2 h are shown in figure 15.

The yield of biodiesel is increased with the ratio ethanol/oil achieving the highest yield at a molar ratio ethanol/oil: 7.78.
Figure 14. Yield of biodiesel as function of ratio EtOH/Oil. Reaction time: 1 h

Figure 15. Yield of biodiesel as function of ratio EtOH/Oil. Reaction time: 2 h
6.1.2 Using methanol as alcohol

The influence of the molar ratio methanol: corn oil on the yield of produced biodiesel is shown in figures 16 and 17.

In the experiments shown in figure 16, the reaction time is 1 hour and the used catalyst is NaOH (0.9 g). The yield of produced biodiesel increases with the molar ratio methanol:oil obtaining the highest yield with a molar ratio methanol:oil = 9.

In the experiments shown in figure 17, the reaction time is 2 hours and KOH is used as catalyst (1.5 g). Already at a molar ratio methanol:oil = 4.5 a very good yield is obtained.

![Graph showing the yield of biodiesel as function of ratio MeOH/Oil. NaOH, 1 h](image)

Figure 16. Yield of biodiesel as function of ratio MeOH/Oil. NaOH, 1 h
6.2 Influence of the amount of catalyst

6.2.1 Using ethanol as alcohol

In figures 18 and 19 the influence of the amount of catalyst (NaOH and KOH) on the yield of produced biodiesel using ethanol is shown. The amount of 0.8 mg NaOH and 1.2 mg KOH for 200 ml corn oil (0.22 mol) is enough in order to obtain a good yield. An increase of the amount of catalyst does not produce an increase of the yield of biodiesel.
Figure 18. Yield of biodiesel as function of amount of NaOH. Ethanol

Figure 19. Yield of biodiesel as function of amount of KOH. Ethanol
6.2.2 Using methanol as alcohol

The yield of produced biodiesel at the studied condition (250 ml oil; ratio methanol/oil: 4.5; time: 2 h) increases from 96% to 99% when the amount of KOH catalyst was increased from 0.85 g to 1.44 g. (figure 20).

![Graph of KOH catalyst yield](image1)

Figure 20 Yield of biodiesel as function of amount of KOH. Methanol

![Graph of NaOH catalyst yield](image2)

Figure 21 Yield of biodiesel as function of amount of NaOH. Methanol
Using NaOH as catalyst, 1 h reaction time, the yield of produced biodiesel increased from 93% to 94% when the amount of catalyst increased from 0.23 g to 0.9 g. When 1.85 g NaOH was used, the yield of biodiesel decreased to 88% (figure 21).

Using the lowest amount catalyst (0.85 g KOH and 0.23 g NaOH) at the studied conditions a good yield of biodiesel has been obtained.

### 6.3 Effect of reaction time.

In figure 22 the influence of the reaction time on the yield of produced biodiesel is studied using both KOH (1.5 g) and NaOH (0.9 g) as catalyst and a ratio methanol:oil = 4.5. The yield of biodiesel increased when the reaction time is increased from 1 to 2 hours.

![Figure 22. Influence of reaction time. Methanol/oil ratio: 4.5](image)

### 6.4 Effect of rate of mixing

The effect of rate of mixing was studied conducting a few experiments numbered 42 and 49 (appendix 5) varying the rate of mixing between 500 and 1500 rpm. 0.9 g
NaOH catalyst was used and the reaction time was 1 hour. The yield of produced biodiesel increased from 90% to 94% when the rate of mixing was increased from 500 to 1500 rpm (figure 23).

![Figure 23. Influence of rate of mixing. Methanol. NaOH](image)

### 6.5 Effect of reaction temperature

In figures 24 and 25 the effect of the reaction temperature on the yield of produced biodiesel. The compared experiment using 1.5 g KOH were carried out with a ratio methanol to oil : 4.5 and 2 hours reaction time (figure 22). The experiments with 0.9 g NaOH were conducted during 1 hour with the same ratio methanol to oil (4.5). The highest yield was obtained at 60 °C with KOH. Using NaOH the highest obtained yield (90%) was at 55 °C but already at 40 °C a good yield was obtained (89%). A further increase of temperature is not recommended. High temperature also can lead to loss alcohol as vapour.
Figure 24. Influence of temperature. Methanol. KOH. 2 h.

Figure 25. Influence of temperature. Methanol. NaOH. 1 h.
7 Conclusions

The production of biodiesel using vegetable oils has been studied. Palm oil and its use for production of biodiesel have been focused. Malaysia and Indonesia are the two largest palm oil producers. Production of biodiesel from oil palm has been increasing in recent years, particularly in Africa and Latin America.

Palm tree is very productive and one of the most profitable for biodiesel production. It takes from 2 to 3 years to start producing fruit. Palm tree can produce fruit during 25 years. Among the oilseed crops, palm tree produces most oil per hectare. The palm tree can yield 3 000 to 5 000 kg of pulp oil per hectare and 600 to 1 000 kg of kernel oil per hectare from the kernel. Palm oil has a good availability and a competitive price.

The production of palm oil at the industrial plantation level has caused environmental damage. The Roundtable on Sustainable Palm Oil has established principles and criteria in order to certify a sustainable cultivation of the palm oil. 10 % of the produced palm oil is filling these principles and criteria.

The experimental work involves the production of biodiesel using corn oil. Both ethanol and methanol are used as alcohols. Sodium hydroxide and potassium hydroxide are selected as homogenous catalyst.

The ratio alcohol to oil is the most important parameter in the production of biodiesel. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to produce three moles of esters and one mole of glycerine. An excess of alcohol is required to drive the reaction to the right. In the experiments with ethanol the yield of biodiesel increased with the ratio ethanol/oil achieving the highest yield at a molar ratio ethanol/oil: 7.78. In the experiments with methanol, using 0.9 g NaOH and 1 hour reaction time the highest yield was obtained with a molar ratio methanol:oil = 9. Using KOH as catalyst and 2 hour reaction time a very good yield is already obtained with a molar ratio methanol:oil = 4.5.

The amount of catalyst is another studied parameter. In the experiments with ethanol, the amount of 0.8 mg NaOH and 1.2 mg KOH for 200 ml corn oil (0.22 mol) is enough in
order to obtain a good yield. An increase of the amount of catalyst does not produce an increase of the yield of biodiesel. In the experiments with methanol, using the lowest tested amount catalyst (0.85 g KOH and 0.23 g NaOH) at the studied conditions a good yield of biodiesel has been obtained.

The effects of the reaction time, rate of mixing and the reaction temperature were studied in the experiments with methanol. The yield of biodiesel increased when the reaction time is increased from 1 to 2 hours. The yield of produced biodiesel increased from 90% to 94% when the rate of mixing was increased from 500 to 1500 rpm.

Often the transesterification is carried out at a temperature near the boiling point of alcohol. The highest yield was obtained at 60 °C with KOH. Using NaOH the highest obtained yield (90%) was at 55 °C but already at 40 °C a good yield was obtained (89%). A further increase of temperature is not recommended. High temperature also can lead to loss alcohol as vapour.

8 References


9 Appendix

9.1 Appendix 1. Yield and viscosity of biodiesel

The molar weight of Corn Oil (Sunflower)

Table 5 The composition of corn oil (sunflower) \(^1\)

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Molar weight, g/mol</th>
<th>Content, w%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic (16:0)</td>
<td>256</td>
<td>11</td>
</tr>
<tr>
<td>Stearic (18:0)</td>
<td>284</td>
<td>2</td>
</tr>
<tr>
<td>Oleic (18:1)</td>
<td>282</td>
<td>28</td>
</tr>
<tr>
<td>Linoleic (18:2)</td>
<td>280</td>
<td>58</td>
</tr>
</tbody>
</table>

\[
M_{\text{corn oil}} = \frac{256 \times 11 + 284 \times 2 + 282 \times 28 + 280 \times 58}{3} \Rightarrow 833.90 \text{ g/mol} = 3 \times (R-COO)C_3H_7
\]

1 mol glyceride will form 3 mol esters.

The yield of produced biodiesel

The density of corn oil is calculated measuring the weigh and the volume:

\[
\rho_{\text{corn oil}} = \frac{m_{\text{corn oil}}}{V_{\text{corn oil}}} = \frac{22.890}{25} = 0.91560 \text{ g/cm}^3
\]

The molar amount of oil for a volume of 200 ml corn oil:

\[
n_{\text{corn oil}} = \frac{m}{M} = \frac{200 ml \times 0.9156 g/ml}{833.90 g/mole} = 0.2195 \text{ mol}
\]

Because 3 mol biodiesel are produced from one mol oil, for 100% yield the theoretical amount of biodiesel produced is:

\[0.2195 \text{ mol} \times 3 = 0.6587 \text{ mol}\]

The real amount produced of biodiesel (in mol) is calculated measuring the produced volume of oil \((V_{\text{biodiesel}})\) and the density of the biodiesel \((\rho_{\text{biodiesel}})\). The molar weight of the ethyl ester is 301 g/mol and the molar weight of the methyl ester is 287 g/mol

\[
\frac{\rho_{\text{biodiesel}} \cdot V_{\text{biodiesel}}}{M_{\text{biodiesel}}} = \text{real amount produced of biodiesel}
\]

The yield of biodiesel is:
\[
\eta = \frac{\text{real amount produced biodiesel}}{\text{theoretical amount biodiesel for 100\% yield}}
\]

**The viscosity of biodiesel**

\[
\eta = k \cdot t \cdot (\rho_{\text{ball}} - \rho_{\text{medium}})
\]  \hspace{1cm} (2)

For example, \( t = 2,458s \), \( m_{\text{ball}} = 1,305g \), \( v_{\text{ball}} = 1cm^3 \)

By equation (2):

\[
k = \frac{\eta_{\text{glycerol}}}{t \cdot (\rho_{\text{ball}} - \rho_{\text{glycerol}})}
\]

The density of ball:

\[
\rho_{\text{ball}} = \frac{m_{\text{ball}}}{v_{\text{ball}}} = \frac{1,305}{1} = 1,305 \text{ g / cm}^3
\]

The density of glycerol at 20\% with a temperature of 20°C: \(^2\)

\[
\rho_{\text{glycerol}} = 1,04690 \text{ g / cm}^3
\]

The viscosity of glycerol at 20\% with a temperature of 20°C: \(^3\)

\[
\eta_{\text{glycerol}} = 1,769 \text{ centipoises (cP)}
\]

The constant \( k \):

\[
k = \frac{1,769}{2,458 \cdot (1,305 - 1,04690)} = 2,7884 \text{ cP at 20°C}
\]

Thereby,

\[
\eta_{\text{biodiesel}} = 2,7884 \cdot t \cdot (1,305 - \rho_{\text{biodiesel}})
\]


9.2 Appendix 2. Experimental data. Ethanol. Sodium hydroxide/NaOH

There are 12 separated samples for the sodium hydroxide/NaOH in 1 hour and 2 hours in a temperature of 40°C with 200ml corn oil as shown in table 1 and 2.

“***” means the experiment was failed or no separation.

Table 6. Biodiesel from Ethanol. NaOH catalysed transesterification at 40°C.

<table>
<thead>
<tr>
<th>No.</th>
<th>EtOH (ml)</th>
<th>NaOH (g)</th>
<th>Oil (mol)</th>
<th>EtOH (mol)</th>
<th>Ratio (EtOH/Oil)</th>
<th>ρ (g/cm³)</th>
<th>t (h)</th>
<th>m (g)</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.8</td>
<td>0.220</td>
<td>1.02</td>
<td>4.67</td>
<td>***</td>
<td>1</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
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<td>4.67</td>
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<tr>
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<td>1.37</td>
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<td>0.783</td>
</tr>
<tr>
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<td>0.220</td>
<td>1.71</td>
<td>7.78</td>
<td>0.8648</td>
<td>1</td>
<td>217.1</td>
<td>0.876</td>
</tr>
<tr>
<td>6</td>
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<tr>
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<td>0.8719</td>
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<td>207.5</td>
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<tr>
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<td>1.8</td>
<td>0.220</td>
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Table 7. Falling time, volume, density and viscosity biodiesel. Ethanol. NaOH.

<table>
<thead>
<tr>
<th>No.</th>
<th>V [ml]</th>
<th>ρ [g/cm³]</th>
<th>t [s]</th>
<th>Dynamic η [cP]</th>
<th>Kinematic (η/ρ)[mm²/s]</th>
<th>Refractive index</th>
<th>pH</th>
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<tr>
<td>1</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>2</td>
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<td>1.801</td>
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</table>
9.3 Appendix 3. Experimental data. Ethanol. Potassium hydroxide/KOH

There are 12 separated samples for the potassium hydroxide/KOH in 1 hour and 2 hours in a temperature of 40°C with 200 ml corn oil as shown in table 3 and 4. “***” means the experiment was failed or no separation.

Table 8. Biodiesel from Ethanol. KOH catalysed transesterification at 40°C

<table>
<thead>
<tr>
<th>No.</th>
<th>EtOH (ml)</th>
<th>KOH (g)</th>
<th>Oil (mol)</th>
<th>EtOH (mol)</th>
<th>Ratio (EtOH/Oil)</th>
<th>ρ (g/cm³)</th>
<th>t (h)</th>
<th>m (g)</th>
<th>Yield</th>
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<td>4.67</td>
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<td>1</td>
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<tr>
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</table>

Table 9 Falling time, volume, density and viscosity of biodiesel. Ethanol. KOH

<table>
<thead>
<tr>
<th>No.</th>
<th>V [ml]</th>
<th>ρ [g/cm³]</th>
<th>t [s]</th>
<th>Dynamic η [cP]</th>
<th>Kinematic (η/ρ)[mm²/s]</th>
<th>Refractive index</th>
<th>pH</th>
</tr>
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<tr>
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<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
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9.4 Appendix 4. Experimental data. Methanol. Potassium hydroxide/KOH.

Table 10. Biodiesel from Methanol. KOH.

<table>
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<tr>
<th>No.</th>
<th>MeOH (ml)</th>
<th>KOH (g)</th>
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(1) Before washing; (2) After washing.
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### Table 13. pH, Viscosity, density of biodiesel. Methanol. NaOH.

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(1) Before washing; (2) After washing.
### Appendix 6. Viscosity determination. The time values of falling sphere

**Table 14 The time values of falling sphere**

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