TECHNICAL UNIVERSITY OF CRETE

DEPARTMENT OF ENVIRONMENTAL ENGINEERING

PSP: ENVIRONMENTAL AND SANITARY HEALTH

Master's thesis

«BIODIESEL PRODUCTION IN GREECE»

Technical and Experimental Evaluation

Che Franklin N.

Advisory Committee:

Asst. Prof. THEOCHARIS TSOUTSOS (*Supervisor*)

Prof. VASSILIS GEKAS

Prof. NIKOLAS KALOGERAKIS

August 2008, Chania

Acknowledgement

I wish to express my appreciation to my supervisor Asst. Prof. Theocharis Tsoutsos whose guidance throughout my graduate program contributed immensely to the success of this work. I thank members of my advisory committee, Prof. Vassilis Gekas and Prof. Nikolas Kalogerakis for their helpful discussions and suggestions. I am particularly indebted to Prof. Vassilis Gekas who generously allowed me the use of his laboratory.

I express my sincere appreciation to my partners of the Greek-Cameroonian Mondialogo Biodiesel group, and especially to Ioannis Sarantopoulos for all the discussions and suggestions. I thank all my friends for supporting me to complete this work successfully.

I thank the **Hellenic Association of Petroleum Products Marketing Companies (ΣΕΕΠΕ)** for providing me with a scholarship for my research project. The financial support from the **Managing Authority of Operational Programme Education and Initial Vocational Training (ΕΠΑΕΚ)** Department of Environmental Engineering, TUC during my graduate tenure is gratefully acknowledged.

My warmest thanks are reserved to my family (both close and extended) for their enthusiastic support which encouraged me throughout my academic pursuits.

Foreword

In late 2005, the Greek government in an effort to enforce the EU Directive 2003/30 passed the national law 3423/2005 which outlined the National Strategy for the Promotion of Biofuels in Greece. According to this law, biodiesel was to be the main biofuel for the Greek transport with bio-ethanol playing a secondary role till 2008. The promotion of biofuel in Europe is an ongoing effort which is being motivated by the EU's desire to: (1) Strengthen its energy security by lessening its dependency on imported oil; (2) fight climate change by reducing the emission of GHG; (3)promote its agricultural economies or policies by ensuring that it is sustainable and efficiently funded. Following this context, member states are required to ensure by setting and meeting national indicative targets that a minimum share of biofuels or other renewable fuels is placed on their market (HL, 2006).

According to the estimated consumption of diesel in the period from 2005-2010, to satisfy the EU directive indicative targets for Greece, 47,000 t of biodiesel was required to meet the target of 2% for 2005 and 148,000 t will be required for the indicative target of 5.75% for 2010 (YPAN, 2006). To satisfy these needs, Greece has to either import or produce more resources for biodiesel production as the currently available resources are not sufficient.

One way to boost the production of biodiesel locally and to make it more competitive economically with respect to diesel fuel is to use less expensive feedstocks. Examples of this type of feedstocks includes most non edible oils, animal fats and oils, recycled or waste oil and by-products of the refining vegetable oil like Crude Olive Kernel Oil. Also, they usually contain high fatty acids.

Crude olive kernel oil is extracted by means of a solvent from the press pulp of the olive fruit derived during virgin olive oil processing. It is very acidic, colored and oxidized. Due its high free fatty acid (22%) it is difficult to process to biodiesel. Other interesting resource for biodiesel production which could be exploited in Greece is imported crude palm oil (CPO). CPO which is produced in high quantities in tropical regions of Africa and South Eastern Asia at remarkable yields also has a high FFA content. To effectively process these feedstocks to biodiesel, a pretreatment stage to reduce the FFA content must precede the main reaction step.

Biodiesel is defined as the mono alkyl esters of long fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats, for use in compression ignition (diesel) engines.

The main goal of this project is to discuss the experimental procedures carried out to optimize the pretreatment process as well as to produce biodiesel from feedstocks containing high FFA values. The aim of the pretreatment step was to reduce the FFA content (8.28%, 19.80% and 22.11% resp.) of Crude palm oil (CPO), Crude Palm kernel oil (CPKO) and Crude olive kernel oil (COKO) to levels below 1%. Another goal of this paper is to evaluate biodiesel production as well as its options in Greece. According to the experimental results, reducing the FFA content of the feedstocks greatly improves their biodiesel production yield. Also biodiesel production in Greece is feasible and beneficial.

These goals are presented in seven thematic units thus: Chapter 1 gives a general overview of biofuels in current European and global energy mix. In chapter 2 the benefits of biodiesel as well as the Greek National Strategy for its promotion is discussed. Chapter 3 addresses the factors (e.g. feedstock availability) affecting biodiesel production potential in Greece, while Chapter 4 presents the biodiesel production processes and technologies. Chapter 5 describes the experimental setup and procedure which was used to optimize as well as produce biodiesel from high FFA feedstocks. Chapter 6 presents and discusses the results of these experiments while Chapter 7 is the conclusion and recommendations made based on the study.

All the data presented in this study were obtained directly from articles or from other official sources. The sources used represent the latest available data.

Table of Contents

Chapter 1: GENERAL OVERVIEW: BIOFUEL IN CURRENT ENERGY MIX

1.1 Energy World

At present, the consumption of primary energy in developed and developing world is highly dependent on fossil fuels. The Fig 1.1 shows the current energy situation in the world.

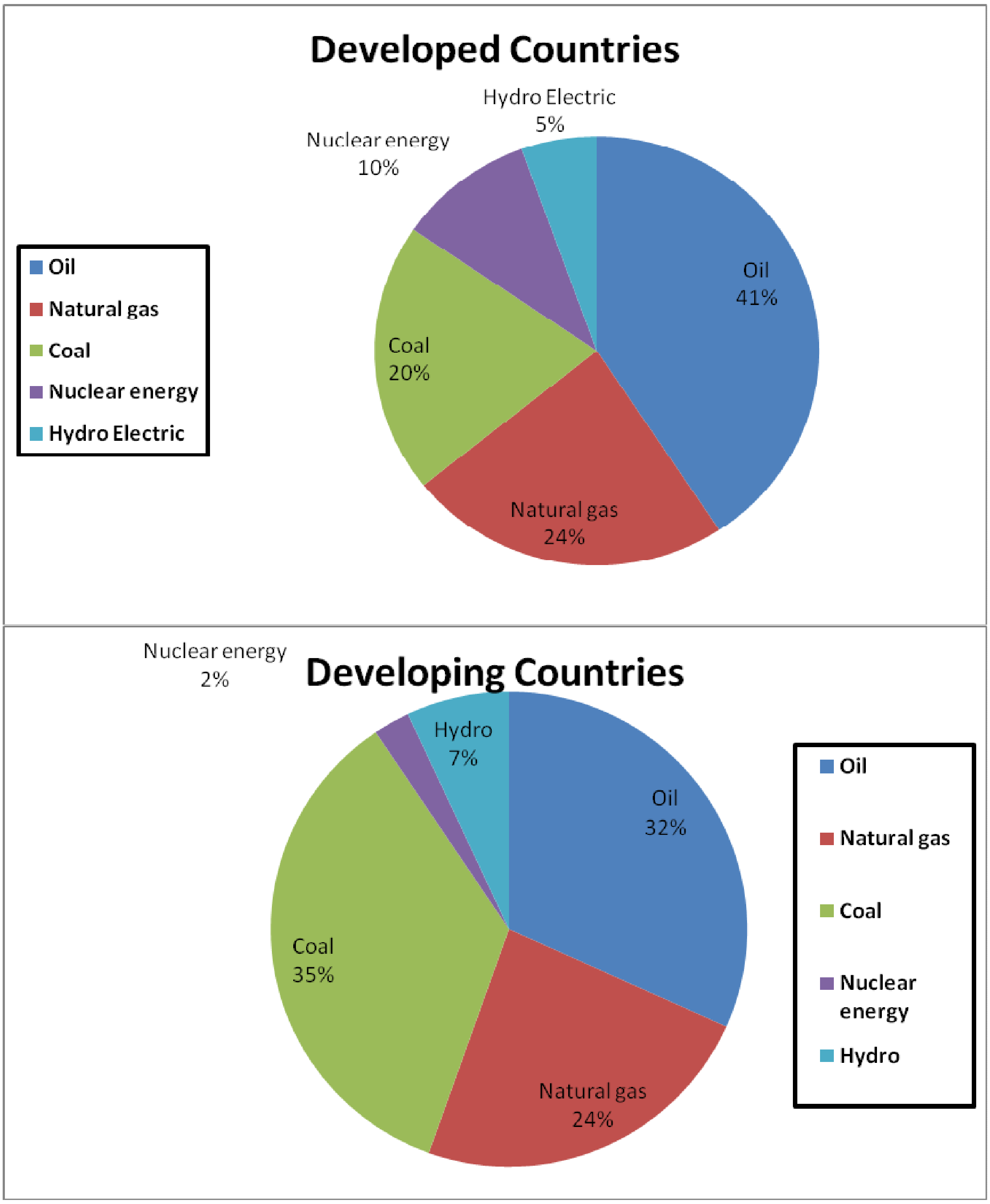


Fig 1.1 - Primary energy consumption in developed and developing countries (BP, 2007),

Fuels from crude oil supply about 96% of the worldwide energy demand for transportation. Other forms of energy (coal, natural gas, alcohols, electric energy) only have a significant role at a local level or for specific transport applications (IEA, 2004).

The nearly total dependence on fuels from crude oil is clearly not ideal. Crude oil reserves are limited and unevenly distributed in the world, with the most important reserves in politically unstable regions. Real or anticipated distortions of crude oil supply have led to sharp increases in crude oil prices and to economic uncertainty.

The situation of worldwide supplying countries is shown in Fig 1.2.

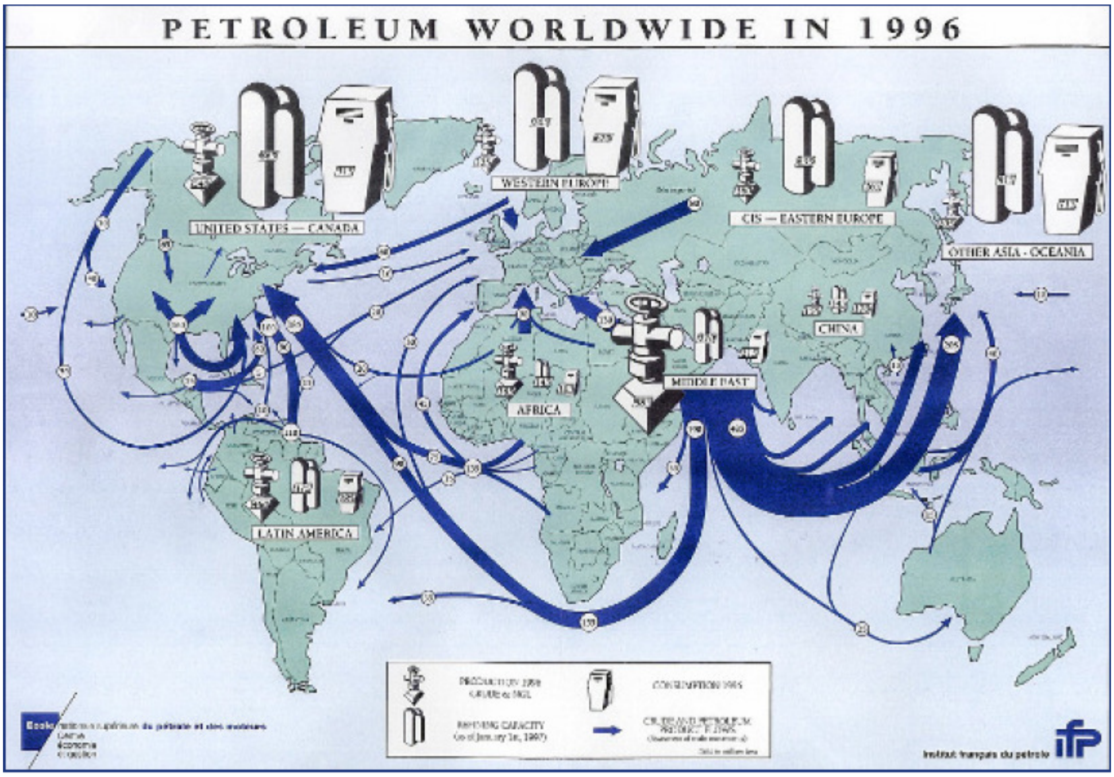


Fig 1.2 - Petroleum Worldwide in 1996 (www.ifp.fr)

Therefore, a diversification of primary energies for fuel production will be necessary, especially to energy forms, which are either locally available or at least more evenly distributed than crude oil. All kinds of primary energy are being discussed for fuel generation but, for environmental reasons, renewable forms of energy are of particular interest.

1.2 Biomass Overview

Biomass is material that comes from plants. Plants use the light energy from the sun to convert water and carbon dioxide to sugars that can be stored, through a process called photosynthesis. Some plants, like sugar cane and sugar beets, store the energy as simple sugars. These are mostly used for food. Other plants store the energy as more complex sugars, called starches. These plants include grains like corn and are also used for food.

Another type of plant matter, called cellulosic biomass, is made up of very complex sugar polymers (complex polysaccharides), and is not generally used as a food source. This type of biomass will be the future feedstock for bioethanol production. Specific feedstocks being tested include agricultural and forestry residues, organic urban wastes, food processing and other industrial wastes, and energy crops.

There are many types of biomass resources currently used and potentially available. This includes everything from primary sources of crops and residues harvested/collected directly from the land; to secondary sources such as sawmill residuals, to tertiary sources of post-consumer residuals that often end up in landfills. Biomass resources also include the gases that result from anaerobic digestion of animal manures or organic materials in landfills (DOE, 2006).

1.3 Brief Overview of Biofuels

A variety of fuels can be produced from biomass resources including liquid fuels, such as ethanol, methanol, biodiesel, Fischer-Tropsch diesel, and gaseous fuels, such as hydrogen and methane. Biofuels are primarily used to fuel vehicles, but can also fuel engines or fuel cells for electricity generation.

1.3.1 Types of biofuels

Ethanol

Ethanol is made by converting the carbohydrate from biomass into sugar, which is then converted into ethanol in a fermentation process similar to brewing beer. Ethanol is the most widely used biofuel today with current capacity of 4.3 billion gallons per year based on starch crops, such as corn. Ethanol produced from cellulosic biomass is currently the subject of extensive research, development and demonstration efforts. It is used as biofuel to replace or blend for gasoline: E5 contains 5% ethanol and 95% petrol; E85 contains 85% ethanol and 15% petrol.

Biodiesel

Biodiesel is produced through a process in which organically derived oils are combined with alcohol (ethanol or methanol) in the presence of a catalyst to form ethyl or methyl ester. The biomass-derived ethyl or methyl esters can be blended with conventional diesel fuel or used as a neat fuel (100% biodiesel). B30 is a blend of petroleum-based diesel (70%) and biodiesel (30%). Biodiesel can be made from any vegetable oil, animal fats, waste vegetable oils, or microalgae oils. Soybeans and Canola (rapeseed) oils are the most common vegetable oils used today. It has a similar density and cetane number to diesel fuel and its flash point is higher than that of diesel which means more security in use.

BioOil

A totally different process than that used for biodiesel production can be used to convert biomass into a type of fuel similar to diesel which is known as BioOil. The process, called fast or flash pyrolysis, occurs when heating compact solid fuels at temperatures between 350 and 500^{o}C for a very short period of time (less than 2 secs). While there are several fast pyrolysis technologies under development, there are only two commercial fast pyrolysis technologies as of 2006. The BioOils currently produced are suitable for use in boilers for electricity generation. Additional research and development is needed to produce BioOil of sufficient quality for transportation applications.

Biofuels from Synthesis Gas

Biomass can be gasified to produce a synthesis gas composed primarily of hydrogen and carbon monoxide, also called syngas or biosyngas. Syngas produced today is used directly to generate heat and power but several types of biofuels may be derived from syngas. Hydrogen can be recovered from this syngas, or it can be catalytically converted to methanol. The gas can also be run through a biological reactor to produce ethanol or can also be converted using Fischer-Tropsch catalyst into a liquid stream with properties similar to diesel fuel, called Fischer-Tropsch diesel. However, all of these fuels can also be produced from natural gas using a similar process.

Other less popular types of biofuels includes:

- Biomethanol: Methanol produced from biomass. It is considered an interesting prospect for fuel cell propelled cars due to its high hydrogen content.
- Bio-ETBE: Ethyl-Tertio-Butyl-Ether is produced from a blend of bioethanol (45% volume) and isobutylene. ETBE is used as a fuel additive to increase the octane rating and reduce knocking down. It can be use on gasoline engines without any modification on them.

- Bio-MTBE: Methyl-Tertio-Butyl-Ether is produced from biomethanol (36% volume) and isobutanol. It is similar to Bio-ETBE.
- Bio-DME: Dimethylener produced from biomass. It is similar to LPG (liquid petrol gas) in terms of physical characteristics, therefore can be used as a replacement for LPG and as an addictive of gasoline blends.
- Biogas: It is mainly produced by anaerobic fermentation of wet biomass. It can be purified to natural gas quality for use as biofuel.
- Biohydrogen: Hydrogen produced from biomass and/or the biodegradable fraction of waste for use as biofuel.
- Pure vegetable oil: Oil produced from oil plants through pressing, extraction or comparable procedures, crude or refined but chemically unmodified, which can be used as biofuel when compatible with the type of engine involved and the corresponding emission requirements.

1.3.2 Biofuel Conversion Technologies

Various biofuels conversions paths from lignocellulosic biomass, sugar/starch crops, oil plants and recover vegetable oil (RVO) can be observed in Fig 1.3.

The conversions processes are represented by white rectangles and the biofuels obtained are shown on the right part of the graph with shaded rectangles.

Thermo-chemical conversion of wood, straw and refuse includes both indirect liquefaction through gasification, and direct liquefaction through pyrolysis and liquefaction in pressurized solvents. Biochemical conversion is based on a different set of feedstock's that includes wood as well as wheat and sugar beet. Both acid and enzyme hydrolysis are included as options, followed by fermentation. The liquid products produced include gasoline and diesel which in some cases require minor refining to convert them into marketable products, and conventional alcohol fuels of methanol and ethanol which established opportunities for utilization. In terms of absolute fuel costs, thermo-chemical conversion offered the lowest cost products, with the least complex processes generally having an advantage. Biochemical routes were the least attractive. The most attractive processes from comparing production costs to product values are generally the alcohol fuels which enjoy a higher market value (Agarwal, 2007).

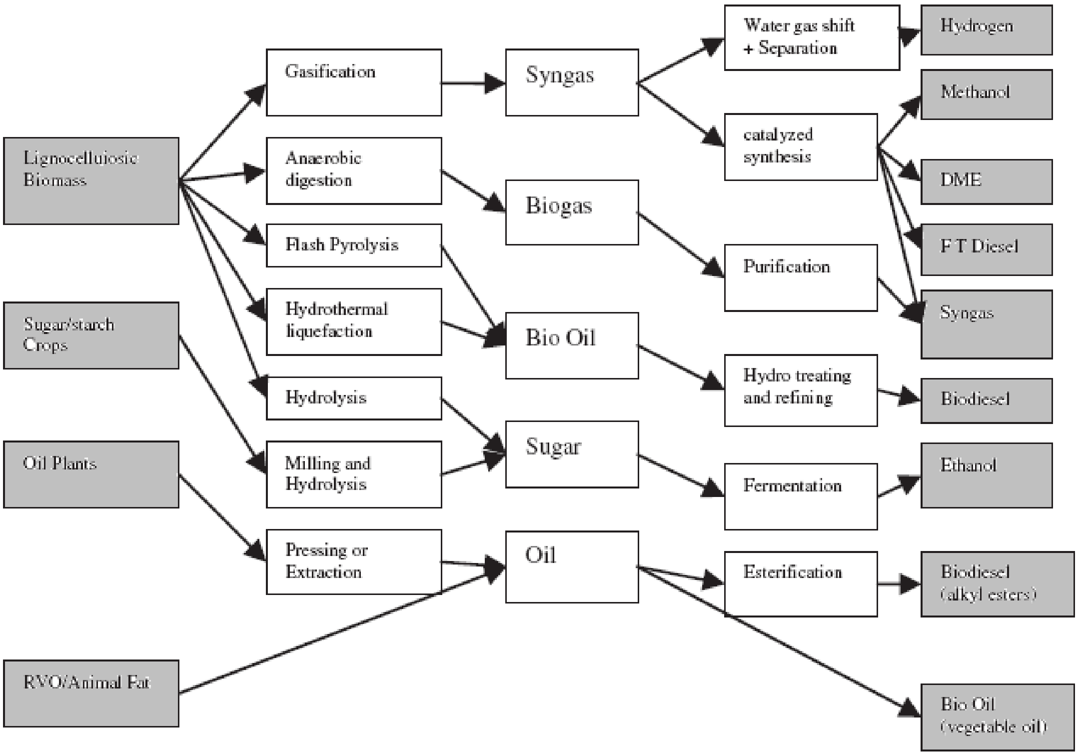


Fig 1.3-Overview of conversion routes to biofuels (Agarwal, 2007)

1.1.4 POTENTIAL BENEFITS AND DRAWBACKS OF BIOFUELS

Biofuels have several potential benefits relative to petroleum-based fuels.

- The use of biofuels can reduce emissions of some pollutants relative to gasoline or diesel fuel.
- Most biofuels lead to lower emissions of greenhouse gases than petroleum fuels — some can lead to substantial greenhouse gas reductions.
- Biofuels can be produced domestically to displace some petroleum that would otherwise be imported.
- Some biofuels can reduce overall fossil energy consumption, given that much of the energy needed to grow the feedstock plant material is supplied by the sun.

There are also many potential drawbacks to biofuels.

- In nearly all cases, biofuels are more expensive to produce than petroleum fuels.
- Infrastructure limitations can lead to even higher costs for biofuels than for conventional fuels.

- Biofuels have their own potential environmental drawbacks, including increased emissions of some pollutants and the potential for increased greenhouse gas emissions (in some cases, depending on the particular biofuel) when the entire production process is taken into account.

1.2 Promotion of Biofuels in Europe

Biofuels are transport fuels produced from renewable organic materials. The most common biofuels today are biodiesel (made from vegetable oils), bioethanol (made from sugar and starch crops) and biogas (obtained from the fermentation of wet biomass).

The production and use of biofuel in the European Union is motivated by the following three main reasons:

1. 2.1 strengthening of energy security

As far as security of supply is concerned, Biofuel help to strengthen energy security by changing the fuel mix in transport. In Europe, the road transport sector which accounts for 30% percent of energy consumed is almost entirely dependent on oil (98%). This represents a severe security of supply challenge in Europe as most of this oil is imported from politically unstable parts of the world. In 2005 oil imports amounted to over 560 million t. It is clear that using more ‘home grown’ biofuels as transport fuel would strengthen energy security by decreasing the volume of oil EU needs to import. The desire to reduce oil imports goes hand to hand with the motivation to reduce carbon emissions from transport fuels (HL, 2006).

1.2.2 Reduction of carbon emission

Concerning climate change, Fig 1.4 shows that, there is a particular need for greenhouse gas savings in transport as its annual emissions are expected to grow by 77 million t between 2005 and 2020 – three times as much as any other sector (COM, 2007). According to the Sustainable Development Commission,

“*biofuels can lead to a substantial reduction in emissions of greenhouse gases. But these reductions are not automatic and must be won through carefully designed measures to minimise the greenhouse gas emissions in crop management, subsequent processing and transport to the point of use*” (HL, 2006).

Biofuels presents a great advantage because their production and use leads to greenhouse gas saving.

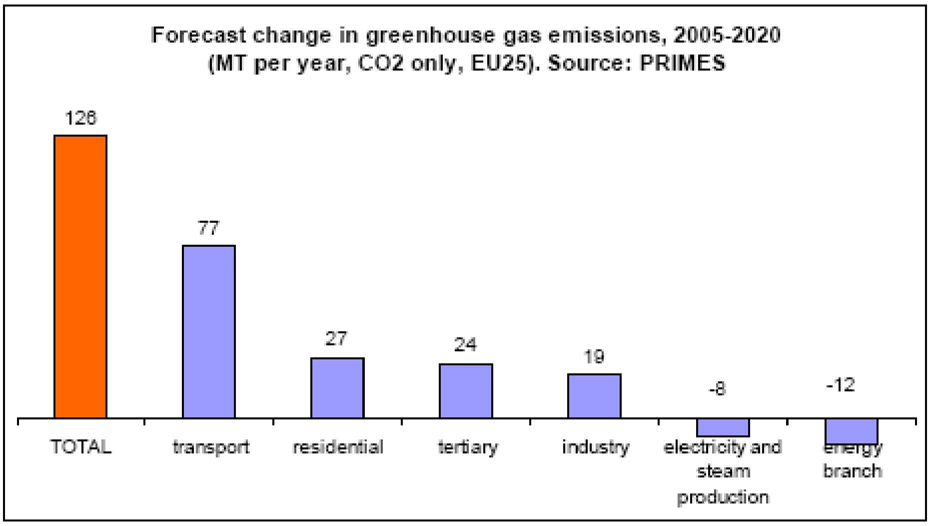


Fig 1.4 - Forecast change in greenhouse gas emissions, 2005-2020 (COM, 2007).

1.2.3 Development of agricultural economies

Finally, the promotion of biofuel would help develop the EU agricultural economies. This is supported by measures under the Common Agricultural Policy, especially following its reform in 2003. By breaking the link between payments made to farmers and the particular crops they produce, the reform allowed them to take advantage of new market opportunities such as those offered by biofuels. In addition, while farmers cannot cultivate food crops on set-aside land, they can use this land for non-food crops including biofuels. The "cross-compliance" system makes payments to farmers conditional on respect for Community environmental legislation and on keeping agricultural land in good environmental condition. It ensures that crops used for biofuels as well as for food meet standards of environmental sustainability (COM, 2007).

1.3 EU Biofuel Policy

In 2003 the European Commission adopted a Directive aimed at promoting the use of biofuels and other renewable fuels in the transport sector.3 The ‘Biofuels Directive’ is designed to promote “*the use of biofuels or other renewable fuels to replace diesel or petrol for transport purposes in each Member State, with a view to contributing to objectives such as meeting climate change commitments, environmentally friendly security of supply and promoting renewable energy sources*”. Under Article 3 of the

Biofuels Directive, Member States must ensure that a minimum proportion of biofuels and other renewable fuels are placed on effect. The EU therefore recommends a "reference value" for these targets calculated on the basis of energy content, for all petrol and diesel used in the transport sector. These reference values are set at 2% by 31 December 2005 and 5.75% by 31 December 2010 (HL, 2006).

1.4 Global biofuel production and consumption

Biofuels production of 33 billion L in 2004 is small compared to 1,200 billion L of gasoline produced annually worldwide. Brazil has been the world's leader (and primary user) of fuel ethanol for more than 25 years, producing slightly less than half the world's total in 2004. All fuelling stations in Brazil sell pure (95%) ethanol (E95) and gasohol, a 25% ethanol/75% gasoline blend (E25). The US is the world's second-largest consumer and producer of fuel ethanol. The growth of the US market is a relatively recent trend; ethanol production capacity increased from 4 billion L in 1996 to 14 billion L in 2004. Other countries producing and using fuel ethanol include Australia, Canada, China, Columbia, Dominican Republic, France, Germany, India, Jamaica, Malawi, Poland, South Africa, Spain, Sweden, Thailand, and Zambia (BRAC, 2006).

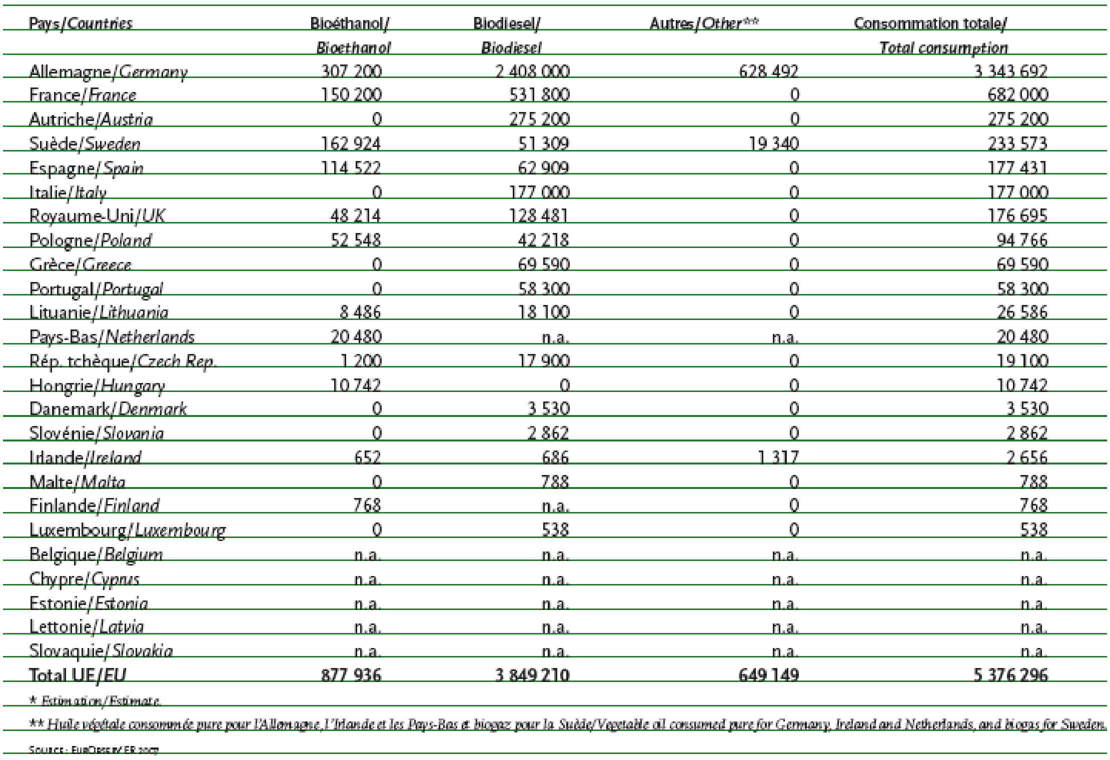
Total world production of biodiesel in 2004 was more than 2 billion L, of which more than 90% was produced in the EU25. Growth has been most marked in Germany where pure biodiesel (B100) in Germany enjoys a 100% fuel-tax exemption, and the country now has over 1,500 fuelling stations selling B100. Other biodiesel producers and users are France and Italy, with lesser amounts produced and used in Austria, Belgium, Czech Republic, Denmark, Indonesia, Malaysia, and the United States (BRAC, 2006).

1.5 EU25 biofuel production and consumption

Biofuel production in the EU is dominated by biodiesel, which accounted for 81.5% of total biofuel production in the region in 2005 (GPBE, 2006). The bio-ethanol sector is growing strongly though, with production observing a growth rate over 70% in the period 2004-2005 and 2005-2006. Biodiesel is predominantly produced from rapeseed while bio-ethanol is from wheat and to a lesser extend sugar beet (BRAC, 2006).

Germany is the by far the largest producer of biodiesel in the EU (2.66 million t in 2007), France produces less than one third of this volume, followed by Italy, the UK, Austria, Poland, the Czech Republic and Spain (EBB, 2008). The spectacular growth in Germany's market is explained by a total tax exemption for biofuels, whether pure or in blended form. The greatest production of bio-ethanol for 2007 was achieved in France (578 million L) where the production almost doubled. Germany (394 million L) and Spain (348 million L) were the next largest producers (ebio, 2008).

Table 1.1 - Biofuel Consumption in European Union for 2006 (in TOE) (BB, 2007)



Pays/*Countries*	Bioéthanol/ *Bioethanol*	Biodiesel/ *Biodiesel*	Autres/*Other***	Consommation totale/ *Total consumption*
Allemagne/*Germany*	307 200	2 408 000	628 492	3 343 692
France/*France*	150 200	531 800	0	682 000
Autriche/*Austria*	0	275 200	0	275 200
Suède/*Sweden*	162 924	51 309	19 340	233 573
Espagne/*Spain*	114 522	62 909	0	177 431
Italie/*Italy*	0	177 000	0	177 000
Royaume-Uni/*UK*	48 214	128 481	0	176 695
Pologne/*Poland*	52 548	42 218	0	94 766
Grèce/*Greece*	0	69 590	0	69 590
Portugal/*Portugal*	0	58 300	0	58 300
Lituanie/*Lithuania*	8 486	18 100	0	26 586
Pays-Bas/*Netherlands*	20 480	n.a.	n.a.	20 480
Rép. tchèque/*Czech Rep.*	1 200	17 900	0	19 100
Hongrie/*Hungary*	10 742	0	0	10 742
Danemark/*Denmark*	0	3 530	0	3 530
Slovénie/*Slovania*	0	2 862	0	2 862
Irlande/*Ireland*	652	686	1 317	2 656
Malte/*Malta*	0	788	0	788
Finlande/*Finland*	768	n.a.	0	768
Luxembourg/*Luxembourg*	0	538	0	538
Belgique/*Belgium*	n.a.	n.a.	n.a.	n.a.
Chypre/*Cyprus*	n.a.	n.a.	n.a.	n.a.
Estonie/*Estonia*	n.a.	n.a.	n.a.	n.a.
Lettonie/*Latvia*	n.a.	n.a.	n.a.	n.a.
Slovaquie/*Slovakia*	n.a.	n.a.	n.a.	n.a.
Total UE/*EU*	**877 936**	**3 849 210**	**649 149**	**5 376 296**

* *Estimation/Estimate.*

** *Huile végétale consommée pure pour l'Allemagne, l'Irlande et les Pays-Bas et biogaz pour la Suède/Vegetable oil consumed pure for Germany, Ireland and Netherlands, and biogas for Sweden.*

Source : EurObserv'ER 2007

Biodiesel and ethanol are mainly used blended with diesel or gasoline, respectively, in low proportions, but high proportion blends, e.g. ethanol used for adapted vehicles (Flexifuel), and pure forms are also available in some countries. Most ethanol is processed into ethyl tertiary butyl ether (ETBE) as an additive to gasoline (BRAC, 2006).

High cereal prices have impacted the European market. Due to this the share of raw materials in bio-ethanol production costs went up to a level that made production no longer profitable. EU consumption of bio-ethanol fuel in 2007 is estimated at close to 2.7 billion L. Fuel ethanol imports have seen a record high in 2007 with an estimated volume of almost 1.0 billion L. This equals nearly 37% of total EU consumption (ebio, 2008).

1.6 APPLICATIONS

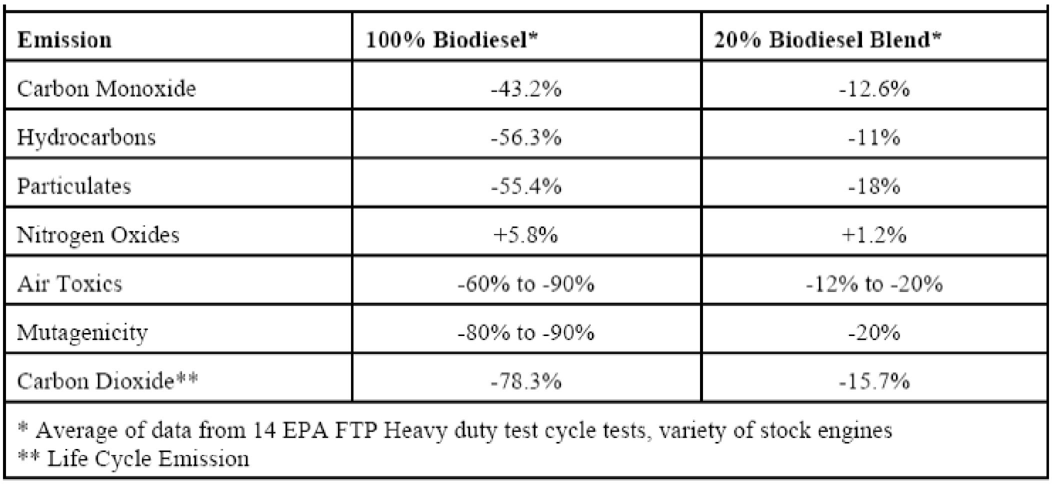
Technically, biofuels constitutes an attractive prospect because they are today the only direct substitute of oil in transport that is available on a significant scale. They are used blended or pure. Unlike other technologies with enormous potential like hydrogen, biofuels can be used in ordinary vehicle engines with little or no modifications (COM, 2007).

Chapter 2: BIODIESEL BENEFITS AND GREEK NATIONAL STRATEGY

2.1 Benefits of biodiesel

General speaking, basic emissions from biodiesel and its various blends ratios reports decrease in emissions of total hydrocarbon, carbon monoxide and dioxide, particulates, sulphur and an increase in nitrogen oxide emission when compared to fossil diesel emissions.

Table 2.1 -Biodiesel emissions compared to conventional diesel (Shumaker et al, 2003)



Emission	100% Biodiesel*	20% Biodiesel Blend*
Carbon Monoxide	-43.2%	-12.6%
Hydrocarbons	-56.3%	-11%
Particulates	-55.4%	-18%
Nitrogen Oxides	+5.8%	+1.2%
Air Toxics	-60% to -90%	-12% to -20%
Mutagenicity	-80% to -90%	-20%
Carbon Dioxide**	-78.3%	-15.7%

* Average of data from 14 EPA FTP Heavy duty test cycle tests, variety of stock engines
** Life Cycle Emission

The benefits of biodiesel can be divided in four main and usually interrelated categories namely: Health, Environmental, Employment (social) and other Benefits.

2.1.1 Health Benefits

The use of recycled edible oil or waste grease for the production addresses the problem of sewage or other inappropriate disposal of used or waste edible oil. Normally, these oils are thrown in the drains/sewers where they serve as food for many rodents. As experienced in many cities, this enhances their uncontrollable multiplication which presents undeniable health risk.

As depicted in Table 2.2, biodiesel represents less health hazard for all parties involved in its handling and distribution. Biodiesel is essentially a non toxic fuel with higher flash point than mineral diesel which makes it non-flammable and non explosive.

Table 2.2 - Biodiesel/Diesel Hazard Comparison

Property	Biodiesel	Petroleum Diesel (CARB low-sulfur)
Biodegradability[1]	Readily biodegrades 3+ times faster than diesel	Poor biodegradability
Flashpoint	150° C	51.7° C
Toxicity[2]	Essentially non-toxic	Highly toxic
Spill Hazard	Benign. Biodiesel is safe to handle with no dangerous fumes. No training required for handling.	Dangerous and toxic. Hazmat training required.

Biodiesel and its blends produce much fewer emissions than mineral diesel for many air pollutant precursors. Moreover, it has a lower toxicity particulate matter (PM) emission. As a result of this reduced emissions, the health benefits for the overall population especially those related to asthma and other respiratory diseases caused from air pollution is increased.

Decrease in particulate matter, aromatic hydrocarbons, alkenes, aldehides, and ketones in biodiesel and biodiesel diesel blends exhaust emissions benefits with less mutagenic effects on mammals than mineral diesel exhaust emissions itself. Biodiesel has a straight chain molecule which has no aromatics. This gives great advantage to biodiesel and its blends over mineral diesel regarding toxic and cancer type of illness.

The consumption of biodiesel in transport brings numerous benefits regarding the population health. The health benefits increase together with the population density of an area. Therefore biodiesel is strongly recommended for application in public transport in urban areas.

Specifically, the substitution of mineral diesel with biodiesel in city transport would result in increased air quality in densely populated urban areas, which would in turn insure a lower health risk associated with air pollution. The emission reduction of particulates, carbon monoxides and sulphur oxides is especially important because of the prominent role they play in public health risks; especially in urban areas where the acute effects of these pollutants may be greater. It is important to note that most of these reductions occur because of lower emissions at the tailpipe and for busses and vehicles operated in urban areas this translates to an even greater potential benefit (Sekliziotis, 2007).

Since biodiesel has low emissions, it is ideal for use in places like marine areas, national parks and forests, and heavily polluted cities. Smoke (particulate material) and soot (unburned fuel and carbon residues) are of increasing concern to urban air quality problems that are causing a wide range of adverse health effects for their citizens, especially in terms of respiratory impairment and related illnesses. As an oxygenated vegetable hydrocarbon, biodiesel itself burns cleanly, but it also improves the efficiency of combustion in blends with petroleum fuel. As a result of cleaner emissions, there will be reduced air and water pollution from vehicles operated on biodiesel blends (Scotland, 2006).

Biodiesel is the only alternative fuel in the U.S. to complete the EPA Tier 1 Health Effect Testing under Section 211(b) of the Clean Air Act, which provide the most thorough inventory of environmental and human effects attributes that current technology will allow. Health effects in Tier 1 testing were defined to include both animal and human toxicity studies of any duration, via any exposure route, as well as in vitro, metabolic and structure-activity analyses. Several aspects were used to test for health evaluations. Conclusions of the tests recorded that the only biologically significant biodiesel exhaust exposure effect was a small effect in lungs at the high exposure level. Thus, no observable adverse effect level was the medium level.

2.1.2 Environmental Benefits

One of the major driving forces for the introduction and utilization of biodiesel is its environmental benefits. Biodiesel and its blends have reduced greenhouse gasses (GHG) emissions compared to those of fossil diesel. Specifically, using biodiesel instead of fossil fuels reduces net emissions of carbon dioxide, which are associated with global climate change. To elaborate, although emissions of carbon dioxide are present in biodiesel combustion process, the level of total carbon is not increased since the carbon was not below but above the earth’s surface. Made entirely from vegetable oils, biodiesel does not contain any sulphur, aromatic hydrocarbons, metals or crude oil residues and thus has many advantages over mineral diesel in the environmental aspects such as air, water and soil pollution.

All health benefits described in the previous part can be applied on all mammals which make biodiesel little, if any, threat to the habitat. Furthermore, biodiesel is totally biologically degradable thus making spills and leaks both in water and soil less of a concern.

The absence of sulphur in neat biodiesel leads to a reduction in the formation of acid rain by sulphate emissions which generate sulphuric acid in the atmosphere. The reduced sulphur in the blend will also decrease the levels of corrosive sulphuric acid accumulating in the engine crankcase oil over time.

Only in the emissions of NOx, biodiesel showed either the same or higher level of emissions than the mineral diesel. Still, those emissions could be lowered down to 25% by adjusting fuel injection timing in vehicles running on biodiesel for which catalytic converters and biodiesel sensor software has been already developed.

The overall results of life cycle paths for biodiesel and mineral diesel production give the same positive impression of the biodiesel’s environmentally friendly superiority where “each litre of biodiesel saves the equivalent of 2.2 kg greenhouse gases” (IFEU, 2003). EU studies and data published by the Commission estimate the CO_2 emissions from traditional fuels used in transport (i.e. diesel) at 3.2t/1,000 L including the whole cycle of fuel production and use. The replacement of traditional fuels by biofuels is calculated to produce CO_2 saving in the order of 2-2.5 t/1,000 L.

There are some other impacts on the environment provoked by traditional means of acquiring petroleum, including exploring, drilling and transporting crude oil. More importantly, the use of mineral diesel significantly contributes for many of the environmental problems – greenhouse gases, air pollution, groundwater and soil contamination, and others. Utilization of biodiesel can play an important role in reducing emissions from transport for many air pollutants, and unlike other 'clean fuels' such as compressed natural gas, biodiesel and other biofuels are produced from renewable materials, like agricultural crops, that assimilate carbon dioxide from the atmosphere to become plants and vegetable oil. Biodiesel has a higher cetane rating than mineral diesel, which means more efficient biodiesel combustion.

The lack of heavy petroleum oil residues in the vegetable oil esters that are normally found in diesel fuel means that engines operating with biodiesel will have less smoke, and less soot produced from unburned fuel. In other word, biodiesel utilization could reduce city smog and improve air quality. Further, since the biodiesel contains oxygen, there is an increased efficiency of combustion even for the petroleum fraction of the blend. The improved combustion efficiency lowers particulate material and unburned fuel emissions especially in older engines with direct fuel injection systems.

The lack of toxic and carcinogenic aromatics (benzene, toluene and xylene) in biodiesel results in the fuel mixture combustion gases having a reduced impact the environment.

Introduction of rapeseed as a third crop culture would improve yield and soil recuperation of all cultures (such as maize and wheat) involved via crop rotation. In other words, reduced input of agrochemicals in the sense of pest protection agents and fertilizers would decrease impact of agriculture towards soil pollution and degradation.

2.1.3 Social Benefits and Employment

The introduction of biodiesel production in Greece is playing a significant role not only from energy point of view, but will also help in regulating the unemployment rate, especially regional unemployment deriving from the structural changes in agriculture which are taking place. Production of biodiesel from feedstocks like recycled edible Oil, sunflower oil, cottonseed oil and rapeseed oil methyl ester, is expected to create several new job opportunities in the feedstock supply chain, both in the urban areas due to the required labour for waste oil collection and cleaning, and more importantly in rural areas due to the required labour for oilseed agricultural production, which will also lessen the urge to abandon land and reduce the ongoing migration into cities.

Studies at EU level have demonstrated that the production of biodiesel requires directly or indirectly 50 times more work-effort than the refining of the same amount of diesel. This implies that, increase production of raw materials for biofuels will contribute to the multi functionality of agriculture and provide a stimulus to the rural economy through the creation of new sources of income and employment, since biofuels are relatively labour-intensive, especially in rural areas during the exploitation phase. Furthermore, in many cases in the agro-food and forestry industry, biofuels could turn problematical waste production into a sustainable product.

Biodiesel production could contribute to agricultural diversification and form part of the job creation policy, which will contribute to putting in place a consistent and lasting framework for guaranteeing the future of the rural community. From the farmer’s point of view, oilseed growing for production of biodiesel could provide better income stability.

By developing plants at the community level, using local, recycled materials, and by distributing the biodiesel back into the same community should result in a more sustainable and price stable fuel. This community enabling focus will help build knowledge about, and participation in, renewable energies.

2.1.4 Other Benefits

The promotion of biodiesel in Greece would decrease its dependence on imported fossil fuels consumption through the utilization of national energy sources. This will result in diversification concerning energy types and consequently it will lead to increase of the security of energy supply in the country.

The development of production and use of biodiesel in Greece could create a mushrooming effect of new innovative technologies and facilitate technology transfer from the EU to the whole Balkan region. Moreover, it offers an opportunity for trade to promote sustainable development, since the need for biodiesel in the EU, and subsequently in other countries, could open a new market for innovative agriculture products which could particularly benefit countries dependent on agriculture.

Assuming that biodiesel will not be affected by the possible rise in crude oil prices, its introduction on the market can be expected to have a modest effect in dampening the effect of changes in crude oil prices on prices paid by consumers.

2.2 Biodiesel in Greece

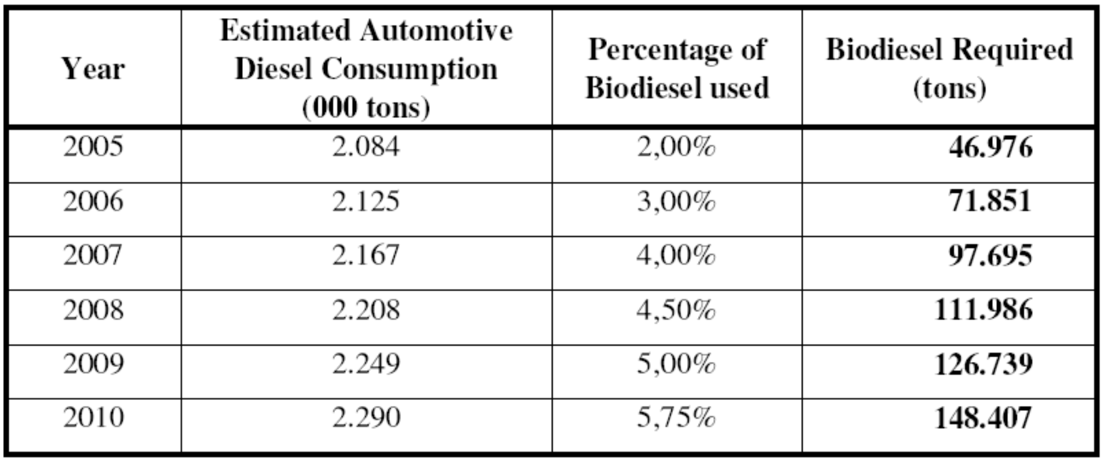
2.2.1 Greek National Strategy and Objectives

Directive 2003/30/EC of the European Parliament and the Council of 8 May 2003 aims at promoting the use of biofuels or other renewable fuel to replace diesel or gasoline for transport in each Member State, with a view to contributing to objectives such as meeting climate change commitments, as well as promoting environmental-friendly security of supply and renewable energy sources. In this context, Member States should ensure that a minimum share of biofuels or other renewable fuels is placed on their markets and, to that effect, they shall set national indicative targets.

The Directive lays down a reference value for those targets of 2%, calculated on the basis of energy content, of all petrol and diesel for transport purposes placed on their markets by 31 December 2005. This should be increased to 5.75% by 31 December 2010.

Greece enforced the EU Directive 2003/30 by passing in 2005 a national **law 3423/2005**, which enables either the production or import and trading of biofuels. According to this, biodiesel will be the main biofuel for the Greek transport sector with bioethanol playing a lesser role till 2008. The amount of biodiesel required to satisfy the indicative target of 2% (on a lower calorific basis) for the year 2006 was estimated as to be approximately 80,000 t, while the amount to satisfy the 2010 indicative target of 5.75% has been estimated to be approximately 148,000 t as presented on Table 2.3.

Table 2.3 - Required biodiesel quantities for each year according to the EU Directive (2003/30/EC) (YPAN, 2004)



Year	Estimated Automotive Diesel Consumption (000 tons)	Percentage of Biodiesel used	Biodiesel Required (tons)
2005	2.084	2,00%	**46.976**
2006	2.125	3,00%	**71.851**
2007	2.167	4,00%	**97.695**
2008	2.208	4,50%	**111.986**
2009	2.249	5,00%	**126.739**
2010	2.290	5,75%	**148.407**

2.2.3 Current situation of biodiesel in Greece

Biodiesel is the first commercial biofuel in the Greek transport sector. The current law imposes the obligatory use of all detaxed biodiesel in the existing refineries (in an up to 5% blend). The detaxed quantities are determined on an annual basis under a quota scheme. In 2006, 14 investors applied for detaxed biodiesel production amounting to 91,000 m^3, which was the target for 2006. A higher number of investors have expressed interest in the coming years (YPAN, 2006).

Up to date, two biodiesel production plants have been constructed: (Boukis et al, 2008)

- One by the company **ELBY S.A.** in Kilkis which currently produces 40,000 t/a (with the capacity for doubling production), and with the possibility of using about $900{,}000*10^3$ m^2 of rape seed cultivations
- One by the company **ELINOIL S.A.** in Volos with a capacity of 40,000 t/a and a total investment cost of €11,000,000

Four more companies have announced plans for constructing biodiesel plants in Greece, namely:

- **Pettas S.A.** in Patra with a capacity of 50,000 t/a.
- **Greek biofuels S.A**. in Magnissia, with the aim to cultivate 1,500,000*10^3 m^2 of rape seed for supplying a biodiesel plant with a capacity of about 165,000 t/a.
- **AGROINVEST S.A.** (in Fthiotida), for a plant with a capacity of 240,000 t/a.
- **Biodiesel S.A.**, for a plant producing 100,000 t/a, in an area owned by the Sovel industry complex in Almyro Magnissia.

Chapter 3: KEY FACTORS AFFECTING BIODIESEL PRODUCTION POTENTIAL IN GREECE

3.1 Feedstock Supply Analysis

There are two steps that need to be taken to produce biodiesel on a large scale. They are: 1) growing the feedstocks, and 2) processing them into biodiesel. The main issue that is always debated is whether or not enough crops could be grown to provide the vegetable oil for producing the amount of biodiesel that would be required to completely replace petroleum as a transportation fuel or at least to meet the EU targets. So that is the main issue that will be addressed in this subsection. This subsection will examine the options for producing biodiesel in Greece, and see if it is capable of meeting the needs. The next chapter will examine the processes of biodiesel production.

3.1.1 Agriculture in Greece

Greece has a total land territory of 130,800 km^2 with the mainland accounting for 80% of the land area and the remaining 20% being divided among nearly 3000 islands. The Greek topography is one of the most mountainous in Europe, as almost 70% of its terrain consists of hills, steep slopes and many peaks reaching more than 2500 meters. As a result of this, 78% of the agricultural land and 70% of the total holdings are found in less- favored areas.

The area used for agricultural purposes is 3.8 million ha and represents only 30% of the country's total surface as compared with 40% in EU-15. Forest areas or woodlands accounts for 20%, 40% of land has permanent grassland and 4% is urbanized. In term of land use, 56% of total agricultural land is cultivated with arable crops, 26% with tree crops (including olive trees), 11% with cotton, 3% with vegetables, 3% with vines and 11% set aside (Panoutsou et al, 2007).

Greek agriculture employs 590,400 farmers, which is 12% of the total labour force and only produces 3.6% of the national GDP (about $11.33 billion annually) (CIA, 2008).

The Greek agriculture sector is heavily subsidised by the EU Common Agricultural Policy (CAP) schemes as well as from national funds. The national funds are earmarked for investment, including improvements of rural infrastructures and comparable grants for farm modernization programmes eligible for EU support. On the other hand, the CAP funds are used to protect the production of cotton, wheat, olive oil and tobacco (YPAN, 2004).

The Greek agricultural sector suffers from structural weaknesses which results to poor international competitiveness. Structural impediments to enhance productivity are mainly due to the large number of small inefficient farms. More precisely, 75% of the farms are less than 5ha in size, whereas the average size is 4.3ha, this being just 25% of the EU average holding (YPAN, 2004).

3.1.2 Potential Crops for Biodiesel Production

Several oleiferous crops are being cultivated in Greece for their seeds. The scale of these crops ranges from significant and important to field trial demonstrations. The cultivated oilseed crops include sunflower, soybean, cotton, tobacco, tomato, groundnut, sesame and rapeseed. The main cultivated oilseed crop is sunflower, accounting for some 4,750 ha in 2004. Groundnut and sesame are cultivated in relatively small area mainly for edible seed production and secondarily for oil extraction.

In the last few decades, the area cultivated with groundnut, sesame and soybean has significantly declined, while sunflower presented an upward trend since 1993. Soybean cultivation is negligible, while at the same moment considerable quantities of soy seeds and soy oil are imported. Rapeseed has been demonstrated in small trials. Other vegetable oils produced in Greece are corn oil, cotton oil and of course olive oil.

The area cultivated with the main oilseed crops, their production and oil production as well as their yields (years 1998-2003) are shown in Table 3.1. In the following paragraphs, more information on the oil-crops is provided.

Table 3.1 - Area, Production and Oil Production of Sunflower Seed, Cotton Seed and Soybeans in Greece (FAOSTAT, 2004)

Year	1998	1999	2000	2001	2002	2003
Sunflower Seed						
Acreage (ha)	31,336	34,600	24,780	17,457	17,076	17,000
Production (tons)	40,413	55,500	34,950	22,808	23,000	23,000
Oil production(tons)	37,188	31,892	37,882	31,479	24,483	17,483
yield (oilseed t/ha)	1.29	1.60	1.41	1.31	1.35	1.35

Cotton Seed						
Acreage (ha)	423,439	424,260	413,600	403,140	388,339	350,000
Production (tons)	1,186,628	1,367,000	1,259,628	1,326,458	1,282,000	1,300,000
Oil production(tons)	62,800	69,500	69,200	63,700	59,100	52,000
yield (oilseed t/ha)	2.80	3.22	3.05	3.29	3.30	3.71
Soya bean						
Acreage (ha)	2,000	2,000	2,000	2,000	2,000	2,000
Production (tons)	4,000	4,000	4,000	4,000	4,000	4,000
Oil production(tons)	53,576	51,348	44,152	68,064	60,258	60,258
yield (oilseed t/ha)	2.00	2.00	2.00	2.00	2.00	2.00

i. Sunflower

The **sunflower** (***Helianthus annuus***) is an annual plant native to the Americas in the family Asteraceae, with a large flowering head (inflorescence). It is a plant grown in spring and it presents great adaptability to the Greek soil and agricultural practices.

Fig 3. 1 - Sunflower (Leray, 2008)

In 2004, about 13% of the world total seed production was sunflower oil, with the EU being one of the leading producers. Its oil content ranges from 25 to 48% and crude protein from 15 to 20% (suitable for cattle feeding).

In Greece, the evolution of sunflower cultivation has been strongly influenced by the European common Agricultural policy. Prior to joining the European Economic Community in 1981, the area cultivated with sunflower was limited to some 2900ha in northern Greece. During the 80s, the EEC, in an effort to limit its dependence on US soy oil, soybeans and soybean meal, provided substantial subsidies to oil crops cultivated in Europe. This resulted to a rapid expansion of the sunflower produced in Greece, reaching a maximum of 95,000ha in 1987. In 2004 the decreasing land area reached 4.700ha, due to declining subsidies. The oil content of the Greek cultivated varieties ranges from 40 to 45% and crude protein from 15 to 25%. The respective seed yield ranges from 1.3 to 3 t/ha dependent on soil fertility, irrigation application and prevailing climatic conditions. Sunflower is mainly grown in northern regions of Greece (Macedonia and Thrace) (Panoutsou et al, 2007).

ii. Groundnut

Groundnut (Arachis hypogea or peanut) is worldwide grown as an annual crop mainly for its seed. It is believed to have originated from Brazil. The world production of peanut kernel was 15 million t in 1999, while 4.5 million t of peanut oil was produced in 2004-2005. The main producers are China (37% of world crop and 32% of oil) and India (25%) (Leray, 2008).

Fig 3.2- Groundnut plant (Leray, 2008)

The oil content ranges from 40 to 50% and protein from 25 to 40%. Its unshelled seed yields range from 0.3 to 4.0 t/ha, depending upon variety, soil, climate and applied cultivation practices. The average seed yield for the Greece climate is 2.6 tons/ha (YPAN, 2004).

In Greece, groundnuts are exclusively grown in spring for its seeds, which are consumed mainly as dry nuts and seed. The cultivation is dominant in the southern part of the country (Peloponnisos) and to a minor extent to the north (Macedonia). However, the area cultivated and seed production has dramatically decreased over the last decade (YPAN, 2004).

iii. Sesame

Fig 3. 3 - Sesame plant (Leray, 2008)

Sesame (***Sesamum indicum, Pedaliaceae***) is mainly grown for its seed production, while its cake is used as a protein-rich animal feedstock. Sesame is believed to have its origin from the Indian sub-continent; the plant is cultivated in tropical and temperate zones, from 40^{o}N to 40^{o}S latitude. India is the highest producer (25% of world production) followed by

China (21%). The world production of sesame seeds was in 1999 about 2.4 million t while 0.8 million t sesame oil was produced worldwide in 2004-2005 (Leray, 2008).

The sesame seed contain oil in the range 44 to 63% and protein from 19 to 26%. Average seed yields range from 0.5 to 2.5 t/ha depending upon variety, climate and applied cultivation practices. For profitable commercial production 2 t/ha is required, this level being achieved in many countries (YPAN, 2004).

Sesame cultivation is spread all over Greece with focus on the Southern and Eastern Aegean islands. It should be noted that the area cultivated and seed production dropped dramatically over the last decade (YPAN, 2004).

iv. Soya bean

Soybean (Glycine soja) is a species of legume which originates from China. It is an annual plant that may vary in growth, habit and height. The world soybean production amounted to 156Mt in 1999-2000, with yields ranging from 2.3 to 4 t/ha. This production represents about 52% of total global oilseed production.

In 2004-2005, 32 million t of soya oil was produced worldwide and this accounted for 26% of world production. About 32% of soybean oil is produced in the United States while 11% is produced in EU-15. Other high producers are Brazil (17%), China (13.5%) and Argentina (12%) (Leray,2008). Soybean is mainly cultivated for its seeds that are utilized commercially for human consumption, animal feed and extraction of oil. Its seeds usually contain 15-22% oil, while the protein ranges from 40 - 50%. Average soybean seed yields range from 1.5 to 3.5 t/ha (YPAN, 2004).

Fig 3.4 - Soya bean plant (Leray, 2008)

Greece imports substantial quantities of soya seeds (345,000 t in 2004). Soybean is grown in western and southern regions (Ipiros and Peloponnisos, respectively). The cultivated area and the seed production were 30 ha and 13 t, respectively in 2004. The area cultivated and seed production of Soybean has dropped dramatically in the last decade, while a respective increase in imports has taken place. (Panoutsou et al, 2007)

v. Rapeseed:

Rapeseed (*Brassica napus, B. campestris*), also known as **rape**, **oilseed rape**, **rapa**, **rapaseed** and (in the case of one particular group of cultivars) **canola**, is a bright yellow flowering member of the family *Brassicaceae* (mustard or cabbage family). Its origin are not clear but is believed to be from India.

Fig 3. 5 - Rapeseed (Leray, 2008)

In 2001, about 12% (13.5 Mt) of the world oil production was rapeseed oil**,** of which 26% was produced in EU. The world production of rapeseed was 38.5 Mt in 2001-2002, with France and Germany being the leading producers, accounting for 11% and 9% of the world production, respectively (YPAN, 2004). According to the United States Department of Agriculture, rapeseed was the third leading source of vegetable oil in the world in 2000, after soybean and oil palm, and also the world's second leading source of protein meal, although only one-fifth of the production of the leading soybean meal (Leray, 2008). World production is growing rapidly, with FAO reporting that 36 million t of rapeseed was produced in the 2003-4 season, and 46 million t in 2004-5. Rapeseeds usually contain 30-50% oil (up to 60% has been observed), while the rape cake contains a considerable amount of crude protein (10-45%), (YPAN, 2004).

In Greece, rapeseed can be cultivated as a winter or spring annual crop. At the moment, no statistical data are available, since its cultivation has been conducted on experimental and demonstration scale only. The ability to grow at low temperatures is the most important feature of rapeseed compared to the other oleiferous crops grown in Greece (YPAN, 2004).

Results from an experiment conducted by CRES and lasting four years (1997- 2000) have shown high average yields up to 17t dry biomass/ha and 0.7-3 t.seed/ha, depending on the prevailing soil/climate conditions. (Panoutsou et al, 2007)

vi. Cotton:

Cotton is a soft, staple fiber that grows around the seeds of the cotton plant (*Gossypium* sp.), a shrub native to tropical and subtropical regions around the world, including the Americas, India and Africa (Leray, 2008). The plant is cultivated mainly for its fibres. It is used in the textile, plastic materials, oil production and soap industries, as well as animal feed and fertilizer. However, cottonseed oil is considered a potential feedstock for biodiesel production in Greece (YPAN, 2004).

Fig 3.6 Cotton seed (Leray, 2008)

The world production of cottonseed amounted to 36 million t in 1999, of which China was the main producer (26% seed, 33% for oil). The kernel comprises about 50% of the seed and contains about 30% of oil. About 5 million t of cottonseed was produced in 2003 (Leray, 2008).

Cotton constitutes one of the most dynamic crops in Greece. Cotton seed oil is a by-product of the cotton crop and it has an average yield of 260kg/ha. It has been identified as a potential source for biodiesel that may produce over 100,000 t of oil based on 2000 production figures. (Panoutsou et al, 2007)

Cotton is a very important crop in Greek agriculture. The production area increased almost three fold from 126,000ha to 37,000ha 2004, with corresponding cottonseed production of 35,900 t and 1.2Mt. Average cotton yields in Greece are 3.2t/ha. Cotton in Greece is cultivated in central Greece (55%) and northern Greece (40%). (Panoutsou et al, 2007)

vii. Tobacco and Tomato seed

According to recent preliminary studies carried out by CRES and NTUA, tobacco seed oil and tomato seed oil have given very promising results as alternative feedstock for biodiesel production in Greece. It should be noted that both seeds are produced in sufficient quantities every year as by-products of tobacco cultivation and tomato juice industry respectively.

Tobacco cultivation has been relatively stable in the last decade. Tobacco seed is a by-product of tobacco leaves production. The seed has high oil content that range from 36-41% on a dry weight basis. The oil extracted from tobacco seed is non edible with physical, chemical and thermal fuel properties that compare favorable with those of other oils. Potential quantity produced in Greece has been estimated to 15,000 t/yr assuming oil content of 38% (Panoutsou et al, 2007).

Tomato seed is the major by-product of the tomato paste-manufacturing industry. Oil content is in the range of 32-37% on a dry weight basis. In 2004, the area cultivated with tomato was 39,510 ha, with corresponding production of more than 1 million t. Both the cultivated and production have been stable in the last decade (Panoutsou et al, 2007).

viii. Olive kernel (Pomace)

Olive fruit is obtained from Olive trees (*Olea europaea*; family Oleaceae), a traditional tree crop of the Mediterranean Basin. It originated from Asia Minor. The world production of the fruit amounted to 14 million t in 1999. About 14% of olive fruit is produced in Greece. Spain (32%) and Italy (19%) are the highest producers.

The amount of olive oil available varies from year to year. However, 2.7 million t were produced worldwide in 2005. Greece devotes 60% of its cultivated land to olive growing. Greece holds third place in world olive production with more than 132 million trees, which produce approximately 350,000 t of olive oil annually of which 82% is extra-virgin. About half of the annual Greek olive oil production is exported. Greek exports primarily target European Union (EU) countries, the main recipient being Italy, which receives about three-quarters of total exports. Olives are grown for oil in mainland Greece, with Peloponnese being the source of 65% of Greek production, as well as in Crete, the Aegean Islands and Ionian Islands.


Fig 3.7 Olive fruit (Leray, 2008)

The olive fruit consists of a pulp which is rich in oil (75% on dry weight basis) and the kernel containing only 12-28% oil. Olive oil is the juice obtained when olives are pressed. It represents the liquid phase of the fruit and accounts for 15-25% of the olive. The pressed pulp (olive pomace) containing the fruit's kernel represents the solid phase.

Olive-pomace is the by-product derived from virgin olive oil processing. Olive pomace contains about 8% oil that can be extracted by means of a solvent from the pressed pulp. Its main use is for soap making and industrial processes. Crude olive-pomace oil is often very acidic, colored and oxidized. Intensive refining is thus required to make it suitable for human consumption. However, its high free fatty acid content (15–45%) makes it very difficult to process by neutralization. The yield of product is also very low and it increases the cost per unit of product produced (Fadiloglu et al, 2003). Crude Olive-pomace is however an exciting complimentary feedstock that could be used for biodiesel production.

ix. *Palm and Palm Kernel*

Fig 3 8 African Palm oil (Leray, 2008)

The oil palm or Elaeis guineensis is a plant belonging to the Aracaceae family along with coconuts and dates. It originated from the rainforests of western Africa and now thrives abundantly in other regions of the world; mainly in a belt of ±10^{o} latitude around the equator. The African oil palm is outstanding in yield, one tree can produce up to 20 t of fruit bunches per year (Shay, 1993). Its average yield worldwide is approximately 4 t/ha per year, and this value far exceeds the yield of other vegetable oils. Moreover, the production cost of palm oil is relatively cheaper compared to other vegetable oils (Tan et al, 2007). The world oil palm production amounted to 95 million t in 1999 leading to 17 million t of oil. In 2004-2005, 32.5 million t of palm oil was produced worldwide. This production represents 18% of total global oil production. The highest production occurs in South East Asia (45% in Malaysia, 28% in Indonesia) and Africa (8% in Nigeria) (Leray, 2008).

The palm fruit consist of a hard kernel (seed) inside a shell (endocarp), which is surrounded by a fleshy mesocarp. The mesocarp contains about 49% of oil and the kernel about 50% palm kernel oil. In 2004-2005, global palm kernel oil production amounted to 3.8 million t. The greatest producers are Malaysia (52%) and Indonesia

(28%). Crude palm oil contains high quantities of beta-carotene which attributes to it, its reddish color. On the other hand, Crude palm kernel oil is golden yellowish in color and has a fatty acid composition different from that of palm oil.

Palm oil and palm kernel oil are used for manufacturing of soaps, vegetable oil and margarine. Beside their industrial applications, the use of palm oil in biodiesel production is increasing, mainly in Europe (about 500,000 t in 2005).

3.1.3 Imports and exports of vegetable seeds and oils

Although, Greece has negligible production for some of the previously mentioned vegetable oil crops, (e.g. soybean and rapeseed), it has significant imports and exports of various seeds and oils suitable for biodiesel production. Table 3.2 presents data for imports and exports of important seeds and oils during the period 2001-2004.

Table 3.2 - Greek imports and exports of oleiferous seeds and oils for the period 2001 to 2004 (Panoutsou et al, 2007)

	Imports				Exports			
Seeds	**2001**	**2002**	**2003**	**2004**	**2001**	**2002**	**2003**	**2004**
Soya	375,635	334,912	391,337	344,634	1,630	1,148	19	1,529
Rape	21	24	91	42	-	-	-	-
Sunflower	58,407	28,250	42,890	47,639	774	788	2274	7
Cotton	8,896	12,263	7,869	42	191,394	193,273	164,468	173,887
Oil								
Soya	1,048	1,262	2,252	505	17,266	21,659	22,875	5,494
Palm	44,496	41,186	50,330	47,281	746	1,695	1347	2,192
Sunflower	27,532	36,066	56,778	59,817	2,951	3,396	7077	5,156
Cottonseed	454	5,985	487	-	8,651	9,086	7749	4,660
Rapeseed	99	48	82	-	1,391	559	-	-
Seed oils total	**73,629**	**84,547**	**109,929**	**107,603**	**31,005**	**36,396**	**39,048**	**17,502**

As far as seed imports are concerned, soy seeds and sunflower seeds represents the most important quantities. In 2004, their import quantities amounted to 345,000 t and 48,000 t respectively. Among seed exports, cotton seeds represent highest quantities for the above 4-year period, although on a declining trend. In 2004, around 174,000t of cottonseeds were exported.

Palm oil and sunflower present the greatest among oil imports, about 47,000t and 6,000 t in 2004. Concerning vegetable oil exports, soy oil exports were the highest among all others during the period and this can be explained by the increased import of soy seeds. (Panoutsou et al, 2007)

3.1.4 Prices of seeds and vegetable oils

Table 3.3 shows average prices of imports and exports for the main seeds and seed-oil types. With the exception of only cotton seeds (1.71 and 1.85€/kg in 2002 and 2003, respectively), seeds prices for the period 2002-2005 varied at levels below 0.78€/kg. The exports average prices of cotton seeds (0.16-0.27 €/kg for the same period) is much lower than their respective imports. Concerning oil, prices range from 0.40 to 0.81€/kg for imports and from 0.43 to 0.70€/kg for exports.

Table 3.3 - Average prices (€/kg) of imports and exports of seeds and oils of vegetable oil crops during 2002–2005 (Panoutsou et al, 2007)

	Imports				Exports			
	2002	2003	2004	2005	2002	2003	2004	2005
Seeds								
Soya seeds	0.23	0.24	0.27	0.23	0.28	0.78	0.24	0.25
Rapeseed	0.54	0.39	0.33	0.33	–	–	–	–
Sunflower seeds	0.30	0.25	0.26	0.26	0.65	0.37	–	0.46
Cotton seeds	1.71	1.85	0.45	0.21	0.27	0.20	0.19	0.16
Oils								
Soya oil	0.95	0.61	0.56	0.55	0.47	0.50	0.43	0.55
Palm oil	0.40	0.43	0.43	0.39	0.55	0.57	0.56	0.48
Sunflower oil	0.68	1.61	0.60	0.87	0.70	0.62	0.58	0.62
Cottonseed oil	0.60	0.88	0.74	0.64	0.52	0.60	0.62	0.56
Rapeseed oil	1.25	0.81	0.76	0.61	0.57	–	–	–

Considering that the average price of exported oil (especially sunflower) is much lower than the corresponding price of the imported one, while, as indicated before, Greece has sufficient sunflower seeds production and imports. This market characteristic makes sunflower a good candidate for biodiesel production in Greece. Furthermore, soybean and palm oil, although they have important alternative uses, may also be considered as feedstock for biodiesel production (YPAN, 2004).

3.1.5 Fuel properties of vegetable oils

A summary of the physical and chemical properties of various seed oils produced in Greece are presented in Table 3.4. It is notable that the heating values are in the range of 30 MJ/kg to 40 MJ/kg which are low compared to diesel fuels (about 45MJ/kg). Kinematic viscosity varies in the range of 30-40 mm^2/s at 38^{o}C and the flash points are above 200^{o}C. The cetane numbers are in the range 32-40 and iodine values range from 80 to 136. In addition, all vegetable oils exhibit poor cold point properties (Panoutsou et al, 2007).

Table 3.4 - Properties of vegetable oils produced in Greece (YPAN, 2004)

Properties	Sunflower oil	Corn oil	Soya bean oil	Sesame oil	Cotton oil	Rapeseed oil	Peanut oil
Density at (kg/l)	0.916	0.909	0.914	0.913	0.916	0.915	0.903
Heating value (MJ/kg)	39.6	39.5	39. 6	39. 3	39. 5	39. 7	39. 8
Kin. viscosity at 38 °C (mm^2/s)	33.9	34.9	32.6	35.5	33.5	37	39.6
Iodine number	125.5	122.6	112.5	106.6	105.7	130	80–106
Cetane number	37.1	37.6	37.9	40.2	41.8	37.6	41.8
Flash point (°C)	274	277	254	260	234	246	271
Pour point (°C)	−15	−40	−12.2	−9.4	−15	−31.7	−6.7
Cloud point (°C)	7.2	−1.1	−3.9	−3.9	1.7	−3.9	12.8
Ash (% wt)	<0.01	0.01	<0.01	<0.01	0.01	0.054	0.005
Sulphur (% wt)	0.01	0.01	0.01	0.01	0.01	0.01	0.01

The chemical and physical properties of crude seed oils can be improved through transesterification. Transesterification leads to a lowering of viscosity and a small increase in cetane number and heating value to levels similar to those of diesel fuel. Table 3.5 gives additional chemical qualities produced from different seed oils available in Greece, as compared to the EN 14214 Standard values.

Table 3.5 - Properties of biodiesel from different vegetable oils produced in Greece (Panoutsou et al, 2007)

Properties	Sunflower oil	Corn oil	Soya bean oil	Cotton oil	Rapeseed oil	PrEN standards
Density at (kg/l)	0.860	0.886	0.885	–	0.882	0.860–0.900
Viscosity at 38 °C (mm^2/s)	4.6	4.5	4.80	–	4.58	3.5–5
Iodine number	125.5	115	133.2	105.7	97.4	120 max
Cetane number	49	65	45	51.2	52.9	51
Flash point (°C)	183	111	178	110	170	120 min

3.2 Possible Complimentary Source

3.2.1 Waste Vegetable Oil (WVO) as Complimentary Source

Considering the present situation in Greece, the quantities of vegetable oil produced annually are at the moment are insufficient to meet the indicative targets set for biofuels under the EC directive. According to (Panoutsou et al, 2007), an increase in cultivated area as well as the exploitation of other feedstock options such as tomato seed oil is required if targets are to be met from indigenous sources. However, tomato seed oil is not yet commercially available in Greece. Also, production from marginal lands is not competitive as the economic and sustainable criteria have not yet been met. Waste vegetable oil can therefore serve as an important additional resource for biodiesel production.

The production of biodiesel from waste vegetable oil can thus be expected to benefit from a raw material advantage (security) and eventually from improved technology. If significant development of recycled oil to biodiesel production occurs, it will help reduce the overall biodiesel cost.

The utilisation of recycled oil for biodiesel production can also help in eliminating the currently poor practices of wasteful and environmentally harmful, as well as economically disadvantageous, disposal through the sewage system. Experience from several large cities has shown that sewage disposal of waste edible oil can also cause problems with uncontrollable multiplication of rodents living in the sewers as the waste oil serves as food, which also presents an undeniable health risk. Moreover as in the case of Greece, waste treatment at the treatment plants is made difficult by the grease.

Disadvantages of using waste vegetable oil as a source for biodiesel production include the difficulties in setting up a collection system large enough to provide substantial quantities of the used oil and the need for filtration and cleaning of the oil, both of which considerably raise the investment costs. Data related to prices and supply and demand of WVO in Greece are not available, thus making a thorough analysis is difficult.

Biodiesel production from recycled edible oil is especially interesting from this aspect: several studies show that the net CO2 emissions looking at the whole production-consumption cycle are negative. The main reason for this reduction are the avoided emissions that would normally be generated within the oilseed production cycle, but also due to the utilisation of resources that would otherwise be dumped in the environment.

3.2.3 Algae

Photosynthesis is the key to organisms making use of direct solar energy. The organisms including plants, algae (microalgae and seaweed), and some photosynthetic bacteria, use energy from the sun to combine water with carbon dioxide to create biomass. While the mechanism of photosynthesis in microalgae is similar to that of higher plants, they are generally more efficient converters of solar energy because of their simple cellular structure. In addition, because the cells grow in aqueous suspension, they have efficient access to water, CO2 and other nutrients. For these reasons, microalgae are capable of producing 30 times the amount of oil per unit area of land, compared to terrestrial oilseed crops (DOE, 1998).

Answers to questions concerning the algae technology can be found from the following reports: "**A Look Back at the U.S. Department of Energy's Aquatic Species Program – biodiesel from algae**" (DOE, 1998) and "**Algae as a Biodiesel Feedstock: A Feasibility Assessment –DRAFT"** (Putt, 2007)**.**

3.3 Energy Supply, Consumption and Climate Change in Greece

3.3.1 Total Primary Energy Supply (TPES) and Total Final Consumption (TFC)

Although Greece is a country rich in renewable energy sources (RES) like solar energy and wind energy, it lacks basic fossil energy resources.

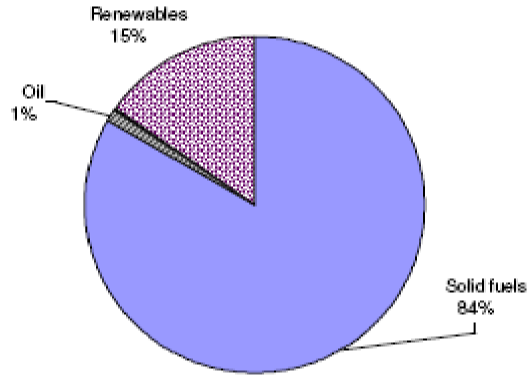


Fig 3. 9- 2004 Domestic Energy Production

The only available energy resource is lignite, which is poor in thermal value. Solid fuels (lignite) dominate Greece's domestic production with an 84% share in 2004. Renewable sources account for about 15% of domestic production (above EU-27 average of 12%). Table 3.6 shows total primary energy supply by sector over the period 1973-2010. According to the table, Greece has a high dependency on imported energy (IEA, 2006).

Table 3.6 - Total energy supply (Mtoe) during 1973-2010 in Greece (IEA, 2006)

		1973	1990	2000	2004	2010

	Total Production(MTOE)	**2.33**	**9.2**	**9.99**	**10.35**	**11,88**
1	Coal	1.69	7.12	8.22	8.61	9.85
2	Oil	-	0.84	0.26	0.12	-
3	Gas	-	0.14	0.04	0.03	0.05
4	Comb. Renewables and waste	0.45	0.89	1.04	1	0.93
5	Hydro	0.19	0.15	0.32	0.39	0.55
6	Solar/Wind/Other	-	0.06	0.14	0.2	0.45
	Total Net Import	**11.12**	**12.74**	**18.13**	**21.21**	**23.75**
1	Coal	0.45	0.73	0.77	0.49	0.79
2	Oil	10.67	11.76	15.67	18.3	18.5
3	Gas	-	-	1.69	2.17	4.11
4	Electricity	0	0	0	0.24	0.35
	Total Supply	**12.36**	**22.18**	**27.82**	**32.74**	**35.63**

Gross inland consumption has been steadily increasing in Greece, showing a total increase of 34% over the period 1990-2004. The share of oil and solid fuels in primary energy supply is significant. Total primary energy supplied (TPES) was 32.74 Mtoe and total final consumption (TFC) 23.49 Mtoe in 2004. These values are projected to 32.63Mtoe and 24.27Mtoe respectively, for 2010. The difference in energy supply and consumption figures is due to losses in conversion processes and energy transfer. (IEA, 2006)

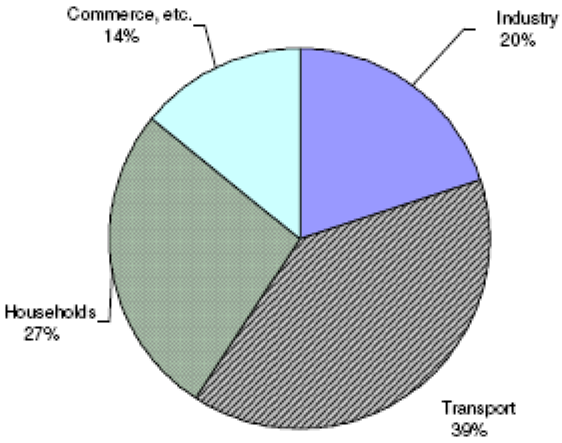
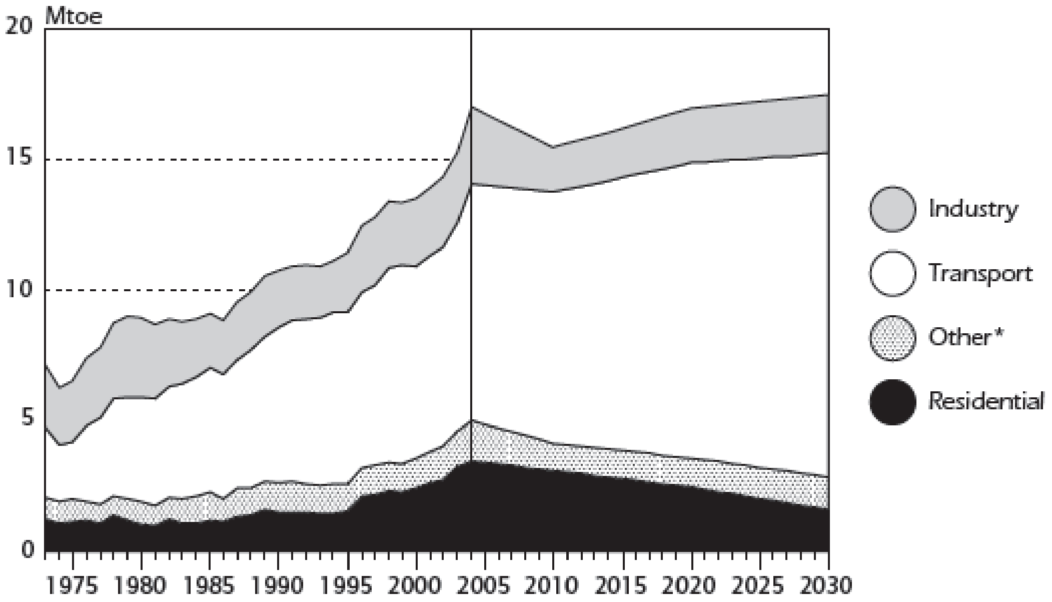


Fig 3.10- 2004 Final Energy consumption by sector

The transport sector is the main consumer of energy, with 9.1 Mtoe in 2004, a rise of 3 Mtoe or 58% compared to 6 Mtoe in 1990. In 2004, the transport sector consumed 39% of energy in Greece, largely unchanged from the 38% in 1990 (IEA, 2006).

3.3.2 Oil Supply and Consumption

In 2004, oil accounted for 19.5 Mtoe, or 59.5% of Greek TPES, almost all of which is imported. This represents a slight increase in the share of TPES, compared to the 57.8% it accounted for in 1990. This share of oil in TPES is very high compared to other IEA member countries, such as Italy (48.3%) or Spain (50.7%). Saudi Arabia, Iran and Russian Federation are the main suppliers of oil to Greece (IEA, 2006).



* includes commercial, public service and agricultural sectors.

Sources: *Energy Balances of OECD Countries*, IEA/OECD Paris, 2005 and country submission.

Fig 3.11 Final consumption of oil by sector, 1975-2030 (IEA, 2006)

In 2004 oil accounted for 17 Mtoe of Greek Total Fuel Consumption. Its share stood at 72.4%, a slight increase compared to 69.5% in 1990. A significant amount of oil (15.1% in 2003) in Greece is used for power generation, primarily on the non-interconnected islands which depend mostly on diesel generators for their electricity supply. However, transport is also the largest oil consuming sector. In 2004, it accounted for 53% of oil consumption in Greece. The other sectors consume 5 Mtoe, 29.5% of the total, while industry consumes 2.9 Mtoe, 17% of total consumption. Road transport is almost completely dependent on oil, and oil will be increasingly used in transportation (IEA, 2006).

3.3.3 Climate Change and Transport

Climate change refers to changes in the weather and environment caused by increasing levels of carbon dioxide and other greenhouse gases-GHG (methane, nitrous acid, HFC) that are released into the atmosphere (www.foei.org).

In 2003, Greek GHG emissions stood at 138 Mt of CO_2 equivalents. This was an increase of 23% above base-year levels. The main share of GHG emissions in Greece is from energy use, which contributed 80% of all Greek GHG emissions in 2002. In 2002, 92% of all CO_2 emissions originated from the production, transport and use of energy. Within energy-related CO_2 emissions, recent steep increases of oil combustion have led to oil becoming the main source of emissions. In 2003, oil contributed 55% of all energy-related CO_2 emissions, while lignite contributed 40%. With future plans for efficiency improvements and the closure of some old lignite power stations, the share of lignite is likely to decline further (IEA, 2006).

It follows therefore that the transport sector is the single largest source of greenhouse gas emissions in urban centres producing a number of emissions with varying degrees of environmental impact. These include global pollutants (such as carbon-dioxide which increase global warming), national or regional pollutants (sulphur and nitrogen oxides which produce acidification or acid rain) and local pollutants (such as particulate matter which contributes to respiratory health problems).

The environmental and economical cost of climate change in Greece is very high. According to a report made by the University of Athens in an attempt to evaluate the cost of climatic changes in Greece in the case of carbon dioxide doubling, the following interesting preliminary estimates where obtained:

- A 36 % decrease of agricultural output. This could cost Greek agriculture $2.35-3.93 billion per year (base year: 1990).
- The cost for ameliorating the impacts of a sea-level rise of 1m for the next 50-100 years of some $3.56 billion, or an equivalent of $35.6-71.2 million per year.
- An expected death poll of almost 400 per year. Assigning a price to human life, the economic cost could be viewed as some $238-1,936 million per year.
- A minimum cost for the preservation of biodiversity at risk from climatic change of some $8.4 million per year (although the authors mention that the real cost is much higher).

Adding the above, including placing a value on human life, the total economic cost for Greece is estimated to be $2.64 - 5.95 billion per year (Dalianis and Petassis, 1993).

Chapter 4: Biodiesel Production

4.1 Vegetable oils as Fuel – General Overview

4.1.1 Introduction

Vegetable oils were transesterified as early as 1853 by the scientists E. Duffy and J. Patrick. The diesel engine was first mentioned in 1893 when the famous German inventor Rudolph Diesel published a paper entitled 'The theory and construction of a rational heat engine'. This paper described a revolutionary engine in which a high temperature was caused by air compressing a piston at very high pressures. Rudolph Diesel designed the original diesel engine to run on vegetable oil. In 1898, Dr Rudolph Diesel's compression ignition engine was demonstrated using virgin peanut oil as fuel at the World's Exhibition in Paris. Because of the high temperatures created, the engine was able to run a variety of vegetable oils including hemp and peanut oil. At the 1911 World's Fair in Paris, Dr R. Diesel ran his engine on peanut oil and declared 'the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it.' One of the first uses of transesterified vegetable oil was powering heavy-duty vehicles in South Africa before World War II. The name 'biodiesel' has been given to transesterified vegetable oil to describe its use as a diesel fuel (Demirbas, 2005).

4.1.2 Chemical Compositions

Vegetable oils are the mixture of organic compounds ranging from simple straight chain compound to complex structure of proteins and fat-soluble vitamins. Fats and oils are water-insoluble, hydrophobic substances in the plant and animal kingdom composed primarily of one mole of glycerol and three moles of fatty acids commonly referred to as triacylglycerides (triglycerides). A glycerol is an alcohol with a hydroxyl group on each of its carbon atoms.

Vegetable oils are usually triglycerides generally with a number of branched chains of different lengths, and have structure notation as shown in Fig 4.1. Fig 4.1 shows the structural reaction for the formation of triglycerides.

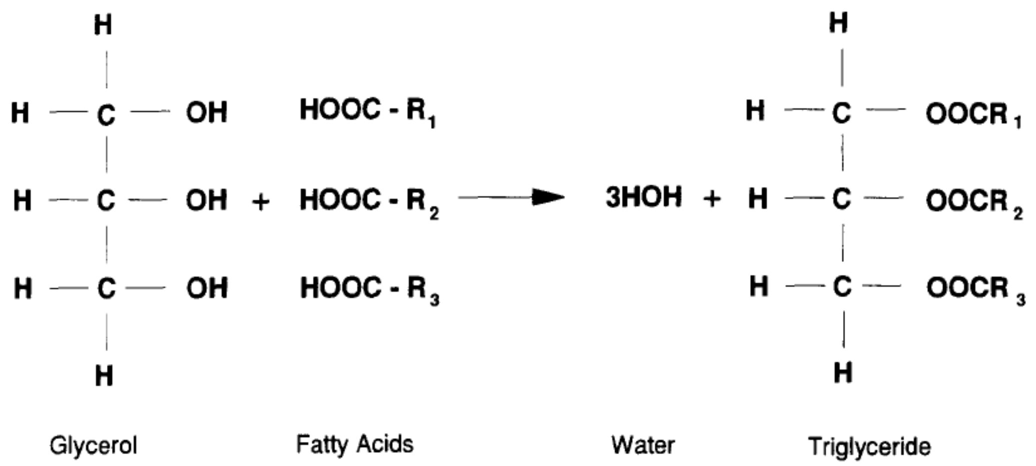


Fig 4.1 - Chemical structure of vegetable oils (Ali and Hanna, 1994)

R1, R2, R3 represent hydrocarbon chain of fatty acids.

The five types fatty acids commonly encountered in vegetable oils and animal fats are: Palmitic acid; Stearic acid; Oleic acid; Linoleic acid; and Linolenic acid. The others are present in smaller quantities. The fatty acids vary in their carbon chain length and in the number of unsaturated bonds (double bonds) they contain. When the three fatty acids are identical, the product is a simple triglyceride; when they are dissimilar, the product is a mixed triglyceride.

The structures of common fatty acids are given in Table 4.1, and fatty acid compositions of some vegetable oils are given in Table 4.2.

Table 4.1- Chemical structure of common fatty acids found in vegetable oils (Srivastava and Prasad, 2000)

Fatty acid	Systematic name	Structure[a]	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	cis-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	cis-9,cis-12, cis-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucic	cis-13-Docosenoic	22:1	$C_{22}H_{42}O_2$

[a] *xx*:*y* indicates *xx* carbons in the fatty acid chain with *y* double bonds.

Table 4.2 - Chemical composition of vegetable oils (Srivastava and Prasad, 2000)

Vegetable oil	Fatty acid composition (wt%)									
	14.0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr	0	0	25	0	6	Tr
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
H.O. Safflower	Tr	5	2	Tr	0	0	79	0	13	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0
Rice-bran	0.4–0.6	11.7–16.5	1.7–2.5	0.4–0.6	—	0.4–0.9	39.2–43.7	—	26.4–35.1	—
Sal	—	4.5–8.6	34.2–44.8	6.3–12.2	—	—	34.2–44.8	—	2.7	
Mahua	—	16.0–28.2	20.0–25.1	0.0–3.3	—	—	41.0–51.0	—	8.9–13.7	—
Neem	0.2–0.26	13.6–16.2	14.4–24.1	0.8–3.4	—	—	49.1–61.9	—	2.3–15.8	—
Karanja	—	3.7–7.9	2.4–8.9	—		1.1–3.5	44.5–71.3	—	10.8–18.3	—

Tr: Traces.

4.1.3 Properties of vegetable oils as fuel

Vegetable oils have about 10% less heating value than diesel due to the oxygen content in the molecule. The viscosity of vegetable oil is several times higher than that of mineral diesel due to large molecular weight and complex chemical structure. The fuel related properties (Physical and Thermal) of some of the vegetable oils are listed in Table 4.3.

Table 4.3 - Physical and thermal properties of vegetable oils (Srivastava and Prasad, 2000)

Vegetable oil	Kinematic viscosity[a]	Cetane no.	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (Kg/l)	Carbon residue (wt%)	Ash (wt%)	Sulfur (wt%)
Corn	34.9	37.60	39.50	−1.1	−40.0	277	0.9095	0.24	0.010	0.01
Cotton-seed	33.5	41.8	39.5	1.7	−15.0	234	0.9148	0.24	0.010	0.01
Cramble	53.6	44.6	40.5	10.0	−12.2	274	0.9044	0.23	0.050	0.01
Linseed	22.2	34.6	39.3	1.7	−15.0	241	0.9236	0.22	<0.01	0.01
Peanut	39.6	41.8	49.8	12.8	−6.7	271	0.9026	0.24	0.005	0.01
Rapeseed	37.0	37.6	39.7	−3.9	−31.7	246	0.9115	0.30	0.054	0.01
Safflower	31.3	41.3	39.5	18.3	−6.7	260	0.9144	0.25	0.006	0.01
H.O. safflower	41.2	49.1	39.5	−12.2	−20.6	293	0.9021	0.24	<0.001	0.02
Sesame	35.5	40.2	39.3	−3.9	−9.4	260	0.9133	0.25	<0.01	0.01
Soyabean	32.6	37.9	39.6	−3.9	−12.2	254	0.9138	0.27	<0.01	0.01
Sunflower	33.9	37.1	39.6	7.2	−15.0	274	0.9161	0.23	<0.01	0.01
Palm	39.6	42.0	—	31.0	—	267	0.9180	—	—	—
Babassu	30.3	38.0	—	20.0	—	150	0.9460	—	—	—
Tallow	—	—	40.0	—	—	201	—	6.21	—	—

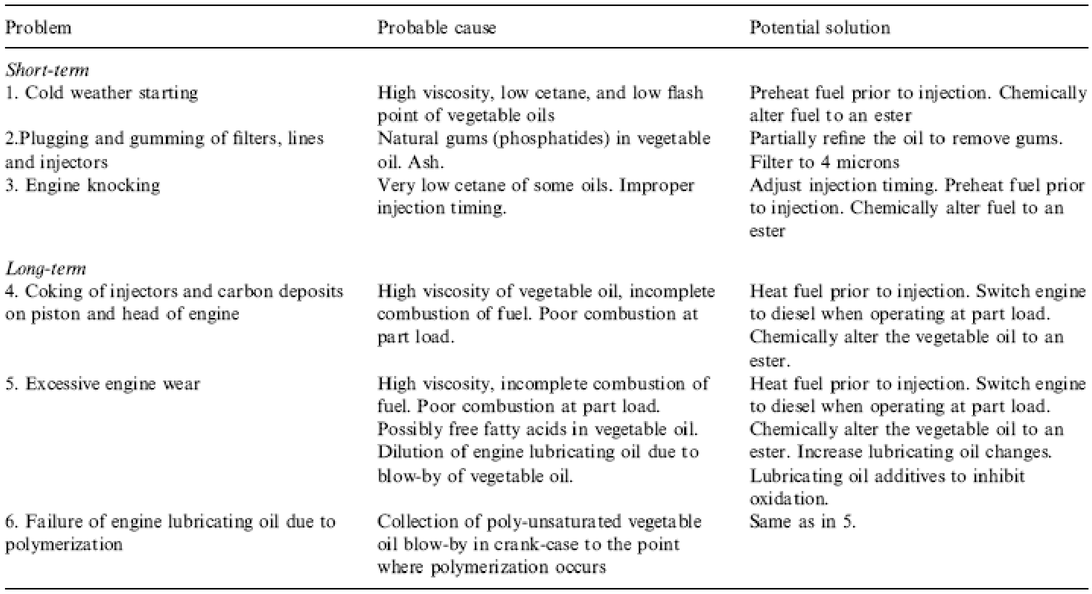
[a] At 40 °C.

As shown from the above table, the flash point of vegetable oils are very high (above 200° C) reflecting their involatile nature. The volumetric heating values are of these oils are in the range 39 to 40 MJ/kg which are low compared to diesel fuels (about 45 MJ/kg). The cetane numbers or ignition qualities of the fuel are in the range of 32 to 40. The iodine value ranges from 0 to 200 depending upon un-saturation. The cloud and pour points of vegetable oils are higher than that of diesel oils. The remaining properties of vegetable oils are fairly close to the properties of diesel fuel (Srivastava and Prasad, 2000).

4.1.4 Vegetable oils as fuel

The high viscosity of vegetable oil, 35–60 cSt compared to 4 cSt for diesel at 40 °C, leads to problem in pumping and spray characteristics (atomization and penetration etc.). The inefficient mixing of oil with air contributes to incomplete combustion. High flash point attributes to its lower volatility characteristics. This results in high carbon deposit formation, injector coking, piston ring sticking and lubrication oil dilution and oil degradation. The combination of high viscosity and low volatility of vegetable oils results to poor cold engine starting, misfire and ignition delay. Some of the short- and long-term problems associated with utilization of vegetable oils in engine are shown in Table 4.4. This table also discusses probable reasons and potential solutions for these problems. Polyunsaturated nature of the vegetable oils causes long-term problems such as gum formation, ring sticking etc. Because of these problems, vegetable oils must be chemically modified to a more suitable and compatible fuel for existing engines (Srivastava and Prasad, 2000).

Table 4.4 Problems and possible solutions for using vegetable oils as engine fuels (Ma and Hanna, 1999)



Problem	Probable cause	Potential solution
Short-term		
1. Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
2.Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oil. Ash.	Partially refine the oil to remove gums. Filter to 4 microns
3. Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Preheat fuel prior to injection. Chemically alter fuel to an ester
Long-term		
4. Coking of injectors and carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load.	Heat fuel prior to injection. Switch engine to diesel when operating at part load. Chemically alter the vegetable oil to an ester.
5. Excessive engine wear	High viscosity, incomplete combustion of fuel. Poor combustion at part load. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil.	Heat fuel prior to injection. Switch engine to diesel when operating at part load. Chemically alter the vegetable oil to an ester. Increase lubricating oil changes. Lubricating oil additives to inhibit oxidation.
6. Failure of engine lubricating oil due to polymerization	Collection of poly-unsaturated vegetable oil blow-by in crank-case to the point where polymerization occurs	Same as in 5.

Petroleum-based diesel fuels have different chemical structures from vegetable oils. The former contain only carbon and hydrogen atoms which are arranged in normal (straight chain) or branched chain structures, as well as aromatic configurations. The normal structures offer a better ignition quality to this fuel. Diesel fuel can contain both saturated and unsaturated hydrocarbons, but the latter are not present in large enough amounts to make fuel oxidation a problem. The saturated non-branched molecules contain carbon atoms ranging between 12 and 18. The aromatics present are generally oxidation-resistant. On the other hand, in the case of vegetable oils, oxidation-resistance is markedly affected by the fatty acid composition. The large size of vegetable oil molecules (typically three or more times larger than hydrocarbon fuel molecules) and the presence of oxygen in the molecules suggest that some fuel properties of vegetable oils would differ markedly from those of hydrocarbon fuels (Ali and Hanna, 1994).

Finally, vegetable oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities which render them impossible to be used directly as fuel.

4.1.5 The use of vegetable oils and their derivatives as alternative diesel fuel.

Neat vegetable oils are not suitable as fuel for diesel engines; hence they have to be modified to bring their combustion-related properties closer to those of mineral diesel. This fuel modification is mainly aimed at reducing the viscosity to get rid of flow and combustion-related problems. Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of HC-based fuels. Vegetable oils can be used through at least four ways:

- Direct use and blending
- Micro-emulsion
- Pyrolysis (thermal cracking)
- Transesterification.

i. Direct use and blending

The direct usage of vegetable oils as biodiesel is possible by blending it with conventional diesel fuels in a suitable ratio and these ester blends are stable for short term usages. For short term use ratios of 1:10 to 2:10 oil to diesel have been found to be successful (Ma and Hanna, 1999). The blending process is simple which involves mixing alone and hence the equipment cost is low. But direct usage of these triglyceric esters (oils) is unsatisfactory and impractical for long term usages in the available diesel engines due to high viscosity, acid contamination, and free fatty acid formation resulting in gum formation by oxidation and polymerization and carbon deposition. The probable reasons for the problems and the potential solutions are shown in Table 4.4.

ii. Micro-emulsion

Microemulsification is another technique that has been reported to produce biodiesel and the components of a biodiesel microemulsion include diesel fuel, vegetable oil, alcohol, surfactant and cetane improver in suitable proportions (Ma and Hanna, 1999). A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1–150 nm range, formed spontaneously from two normally immiscible liquids. Alcohols such as methanol, ethanol and propanol are used as viscosity lowering additives, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers. Viscosity reduction, increase in cetane number and good spray characters encourage the usage of microemulsions but prolong usage causes problems like injector needle sticking, carbon deposit formation and incomplete combustion (Ma and Hanna, 1999). For example, short-term performance of micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of no. 2 diesel, in spite of the lower cetane number and energy content (Srivastava and Prasad, 2000).

iii. Pyrolysis

Pyrolysis refers to chemical change caused by application of heat to get simpler compounds from a complex compound. The process is also known as cracking. Vegetable oils can be cracked to reduce viscosity and improve cetane number. The products of cracking include alkanes, alkenes, and carboxylic acids. Soyabean oil, cottonseed oil, rapeseed oil and other oils are successfully cracked with appropriate catalysts to get biodiesel (Ma and Hanna, 1999). By using this technique good flow characteristics were achieved due to reduction in viscosity. Disadvantages of this process include high equipment cost and need for separate distillation equipment for separation of various fractions. Also the product obtained was similar to gasoline containing sulphur which makes it less eco-friendly (Ma and Hanna, 1999).

iv. Transesterification

The most popular method of producing biodiesel is the transesterification of vegetable oils. Biodiesel obtained by transesterification process is a mixture of mono-alkyl esters of higher fatty acids. The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. The high viscosity component, glycerol, is removed and hence the product has low viscosity like the fossil fuels. The mixture of these mono-alkyl esters can hence be used as a substitute for fossil fuels. The details of the process of transesterification and biodiesel production are given in the following paragraphs.

4.2 Process of Biodiesel Production

4.2.1 What is biodiesel?

According to the National Biodiesel Board, Biodiesel is “The mono alkyl esters of long fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats, for use in compression ignition (diesel) engines” (NBB, 1996). Biodiesel, which is considered as possible substitute of conventional diesel fuel is commonly composed of fatty acid methyl esters that are prepared from the triglycerides in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics. Biodiesel is compatible with conventional diesel and the two can be blended in any proportion.

4.2.2 Simple Transesterification Reaction

The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel (Strachan, 2003).

During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalyzed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production; either base can be used for the methyl ester. A common product of the transesterification process is Rape Methyl Ester (RME) produced from raw rapeseed oil reacted with methanol (Scotland, 2006).

4.2.3 Chemistry of transesterification reaction

Fig 4.2 presents the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

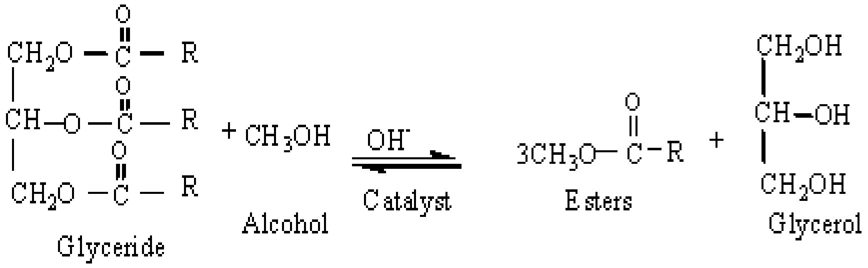


Fig 4.2 - Esterification process (Shay, 1993)

The overall transesterification reaction is given by three consecutive and reversible equations as depicted in Fig 4. 3 below:

$$\text{Triglyceride} + R^1OH \rightleftharpoons \text{Diglyceride} + RCOOR^1$$

$$\text{Diglyceride} + R^1OH \rightleftharpoons \text{Monoglyceride} + RCOOR^1$$

$$\text{Monoglyceride} + R^1OH \rightleftharpoons \text{Glycerol} + RCOOR^1$$

Fig 4. 3 - Transesterification of triglycerides

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order.

A successful transesterification reaction is signified by the separation of the ester and glycerol layers after the reaction time. The heavier, co-product, glycerol settles out and may be sold as it is or it may be purified for use in other industries, e.g. the pharmaceutical, cosmetics etc (Strachan, 2003).

4.2.4 Process Variables

The most important variables that influence the transesterification reaction are:

- Reaction temperature and time;
- Ratio of alcohol to oil;
- Catalyst type and concentration;
- Mixing intensity;
- Purity of reactants.

i. Reaction temperature and time

The transesterification can occur at any temperature depending on the oil used; when the oil is refined or contains low FFA levels, the reaction is conducted close to the boiling point of methanol (60^{o} - 70^{o} C) and at atmospheric pressure. However, for feedstocks with high FFA contents, pretreatment is not required if the reaction is carried under high pressure (9,000kPa) and high temperature (240^{o}C), where simultaneous esterification and transesterification take place (Ma and Hanna, 1999).

The maximum yield of esters occurs at temperature ranging from 60 to 80 ^{o} C at a molar ratio (alcohol to oil) of 6:1. Further increase in temperature might have a negative effect on the conversion (Barnwal and Sharma, 2005).

The conversion rate increases with reaction time. Generally, the reaction is very slow during the first minute due to the mixing and dispersion of the feedstock with methanol. From one to five minute, the reaction proceeds very fast. The maximum value for the production of methyl esters is achieved at about 15 minutes. For most oils (feedstocks) the conversion after 1 hr is almost the same (93-98%),(Ma and Hanna, 1999).

ii. *Ratio of vegetable to oil*

The stoichiometric ratio for the transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Transesterification is an equilibrium reaction in which to shift the reaction to the right, it is necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. The second option is preferred wherever feasible. However, when 100% excess methanol is used, the reaction is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl esters yields higher than 98% by weight (Srivastava and Prasad, 2000).

Generally, for molar ratios less than 6:1, the reaction is incomplete while for a molar ratio of 15:1 the separation of glycerin is difficult. Although higher molar ratios results in greater ester conversion in a shorter time (Fukuda et al, 2001), it interferes with the gravity separation of glycerin by increasing its solubility. Glycerin in solution not only increases the cost of the process but also lowers the yield of esters by driving the reaction to the left (Meher et al, 2006). The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters (Ma and Hanna, 1999).

iii. *Catalyst type and concentration*

Catalysts used for the transesterification reaction are classified as alkali, acid, enzyme or heterogeneous.

Alkali catalysts like sodium hydroxide (NaOH), sodium Methoxide, potassium hydroxide (KOH), potassium methoxide are more effective when compared to the other mineral catalysts. NaOH and KOH are widely used in industrial production because of their cheapness and because they are less corrosive to industrial equipments. A concentration in the range 0.5-1% (w/w) has been found to yield 94-99% conversion to vegetable oil esters. Further increase in concentration does not affect the conversion but adds to extra cost, as the catalyst needs to be removed from the reaction mixture after completion of reaction. (Meher et al, 2006; Barnwal and Sharma, 2005)

Acid catalysts: if the oil has high free fatty content and more water content, acid catalyzed transesterification is more suitable. The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Sulfuric acid has superior catalytic activity. (Ma and Hanna, 1999; Meher et al, 2006)

Alkaline earth metals: attempts have been made to use basic alkaline-earth metal compounds like magnesium oxide, calcium hydroxide, etc in transesterification for production of methyl esters. The reaction occurs only when methoxide ions are present in the reaction medium. Generally, the reaction catalyzed with alkaline-earth metal hydroxides, alkoxides and oxides proceeds slowly when compared to NaOH. This is because the reaction constitutes a three-phase system (oil-methanol-catalyst), which for diffusion reason inhibits the reaction. (Meher et al, 2006)

Enzymatic catalyst (lipases): Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water require treatment, and free fatty acid and water interfere the reaction.

Enzymatic catalysts like lipases (extracellular and intracellular) are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems, and can overcome the problems mentioned above. Specifically, the by-products; glycerol can be easily removed; while the free fatty acids contained in waste oils and fats are completely converted to alkyl esters. On the other hand, the production cost of a lipase catalyst is significantly greater than that of an alkaline one. (Fukuda et al, 2001)

Table 4. 5 -Comparison between alkali-catalysis and lipase-catalysis methods for biodiesel production (Fukuda et al, 2001)

	Alkali-catalysis process	Lipase-catalysis process
Reaction Temperature	60-70°C	30-40°C
Free fatty acids in raw materials	Saponified products	Methyl esters
Water in raw materials	Interference with the reaction	No influence
Yield of methyl esters	Normal	Higher
Recovery of glycerol	Difficult	Easy
Purification of methyl esters	Repeated washing	None
Production cost of catalyst	Cheap	Relatively expensive

iv. Mixing intensity

Mixing is very important in the transesterification reaction because oils or fats are immiscible with sodium hydroxide-methanol solution thus forming a two phase liquid system. The reaction is diffusion controlled and poor diffusion between the phases results in slow rate. However, once the two phases are mixed and the reaction is started, stirring is no longer needed. The mixing effect is most significant during the slow rate region of the reaction. Once the single phase is established mixing becomes insignificant. The effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design (Meher et al, 2006; Srivastava and Prasad, 2000).

v. Purity of reactants (effects of moisture and free fatty acid)

The starting materials used in alkali-catalyzed transesterification of triglycerides must meet certain specifications. The triglyceride should have an acid value less than 1 and all materials must be substantially anhydrous. If the acid value was greater than 1, more NaOH would be required to neutralize the free fatty acids. This addition compensates for higher acidity but results in the formation of soap. The presence of water also causes a partial reaction change to saponification, which produces soap. The soap consumes the catalyst and reduces the catalytic efficiency, as well as causes an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol. It is therefore important that the oils be dry and free from free fatty acids, as ester yields are significantly reduced when these conditions are not met (Ma and Hanna, 1999).

Since impurities in the oil affect the conversion level considerably. It has been suggested that the free fatty acid content of the refined oil should be as low as below 0.5%. Though free fatty acids in the crude oil interfere with the catalyst, this problem can be solved if the reaction is carried out under high temperature and pressure conditions. The hydroxide and methoxide of sodium and potassium should be maintained in anhydrous state. Prolonged contact with air will diminish their effectiveness through interaction with moisture and carbon dioxide (Fukuda et al, 2001; Barnwal and Sharma, 2005).

Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, there are large amounts of low cost oils and fats that could be converted to biodiesel. The problems with processing these low cost oils and fats are that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using alkaline catalyst. Therefore, two-step esterification process is required for these feed stocks. Initially the FFA of these can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction (Meher et al, 2006).

4.2.5 Biodiesel Production

The main focus of this study concentrates on crude vegetable feedstocks like crude palm oil, crude palm kernel oil and crude olive kernel oil which are characterized by their high free fatty acid contents. An example of a production flow chart for such feedstocks is presented in Fig 4.8. A brief explanation for each step is given below.

i. Oil feedstock pretreatment

The main aim of this step is the removal of the free fatty acids contained in the oil feedstock. The most popular methods of pretreatment are by caustic refining and acid esterification. To improve downstream processing, a growing number of companies are utilizing additional processes like degumming. Degumming is the process whereby gums and phophalitides are removed from crude vegetable oil. Most biodiesel producers are esterifying the fatty acids with a strong acid, neutralizing the acid with a strong base, and then feeding the mixture to the transesterification process. Using the acid esterification pre-treatment step requires more expensive processing equipment, but may be the best choice if oil feedstock includes waste oils and greases.

ii. Catalyst preparation

The catalyst is typically sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol (methanol) using a standard agitator or mixer.

Some care must be taken to ensure the potassium or sodium hydroxide does not absorb water in storage. This could cause the formation of large clumps which are hard to dissolve; additionally, the water has an adverse impact on the downstream processing.

iii. Reaction

The methanol catalyst mix is then charged into a reactor, either continuously or batch, and the oil is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept at approximately 65°C for one to eight hours. Excess methanol is normally added to ensure high levels of conversion of the fat to methyl esters. Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. This is because the catalyst will first react with any free fatty acids present in the oil making soaps, which can cause problems with emulsions and also hamper the separation of the glycerine by-product downstream (Van Gerpen, 2005).

iv. Product separation

Once the reaction is complete, two major products exist: glycerine and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The excess methanol tends to act as a solubilizer and can slow the separation. However, this excess methanol is usually not removed from the reaction stream until after the glycerol and methyl esters are separated due to concern about reversing the transesterification reaction. Water may be added to the reaction mixture after the transesterification is complete to improve the separation of glycerol. The reacted mixture is sometimes neutralized at this step if needed. The glycerine phase is much denser than biodiesel phase and the two can be gravity separated with glycerine simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster (Tyson and al, 2004).

v. Methanol recovery

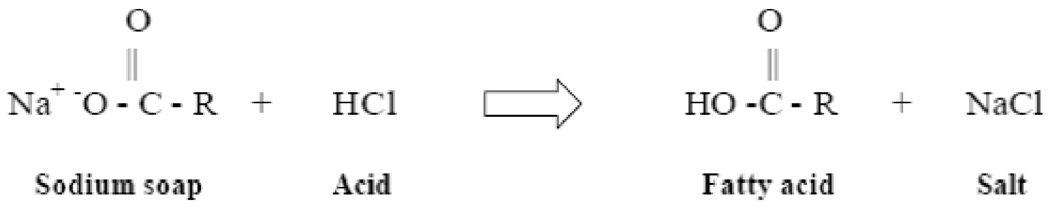
In some biodiesel processes, the excess methanol is removed after the reaction stage via a simple flash process or vacuum distillation. In other processes, the methanol is removed after the glycerine and esters have been separated. In either case, the excess methanol is recovered and distilled using a conventional distillation equipment to remove any water. Care must be taken to ensure no water accumulates in the recovered alcohol stream (Tyson and al, 2004).

vi. Glycerine recovery

The glycerine by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerine. In some cases the salt formed during this phase is recovered for use as fertilizer. In most cases the salt is left in the glycerine. Water and alcohol are removed to produce 80-88% pure glycerine that is ready to be sold as crude glycerine. In more sophisticated operations, the glycerine is distilled to 99% or higher purity and sold into the cosmetic and pharmaceutical markets (Van Gerpen, 2005), which can be useful for the local industry of Crete.

vii. Methyl Ester washing

After separation from the glycerol, the methyl esters enter a neutralization step and then pass through a methanol stripper, usually a vacuum flash process or a falling film evaporator, before water washing. Acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water soluble salts and free fatty acids, as shown in Fig 4.4.



$$\mathrm{Na^{+}\,{}^{-}O-\overset{\overset{O}{\|}}{C}-R} + \mathrm{HCl} \Longrightarrow \mathrm{HO-\overset{\overset{O}{\|}}{C}-R} + \mathrm{NaCl}$$

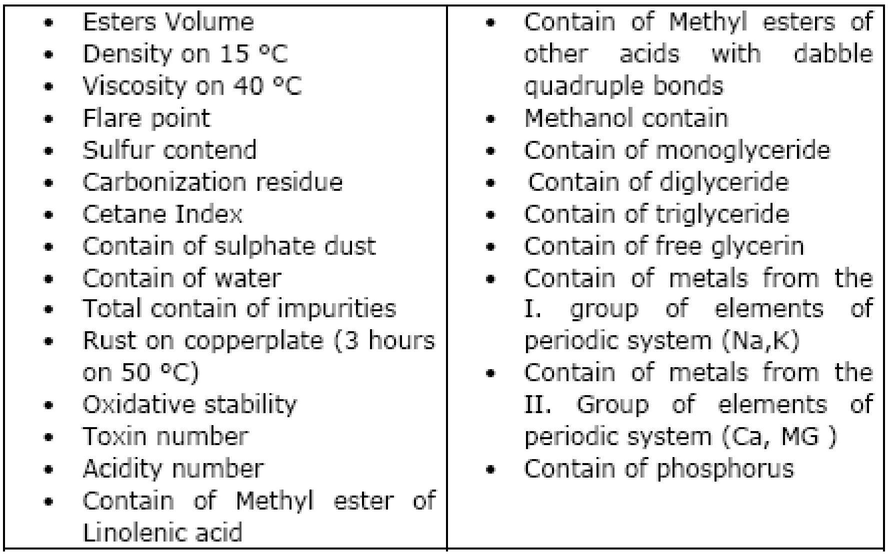
Fig 4.4- Reaction of soaps with the acid

The salts will be removed during the water washing step and the free fatty acids will stay in the biodiesel. The water washing step is intended to remove any remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel. The biodiesel 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 a viscosity similar to petro diesel. In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colorless biodiesel. Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel. Following the wash process, any remaining water is removed from the biodiesel by a vacuum flash process (Van Gerpen, 2005).

4.3 Biodiesel quality

In the early days of developing Biodiesel, it quickly became obvious that it would be of utmost importance to win the confidence of diesel engine producers, as stakeholders in this project. A working group was set up within the Austrian Standardisation Institute and the first Biodiesel fuel standard was issued already in 1991 as ON C 1190 (Friedrich, 2001). This was the basis for numerous diesel engine warranties issued by all key tractor companies in Europe. The most recent development is the completion of a standard for biodiesel with validity all over Europe, the EN 14214. Based on that, every delivered sample is tested for certain parameters. Those parameters show the quality of the sample and they are presented in Table 4.6

Table 4.6 - Types of required quality tests of biodiesel based on EN 14214 (Friedrich, 2001)



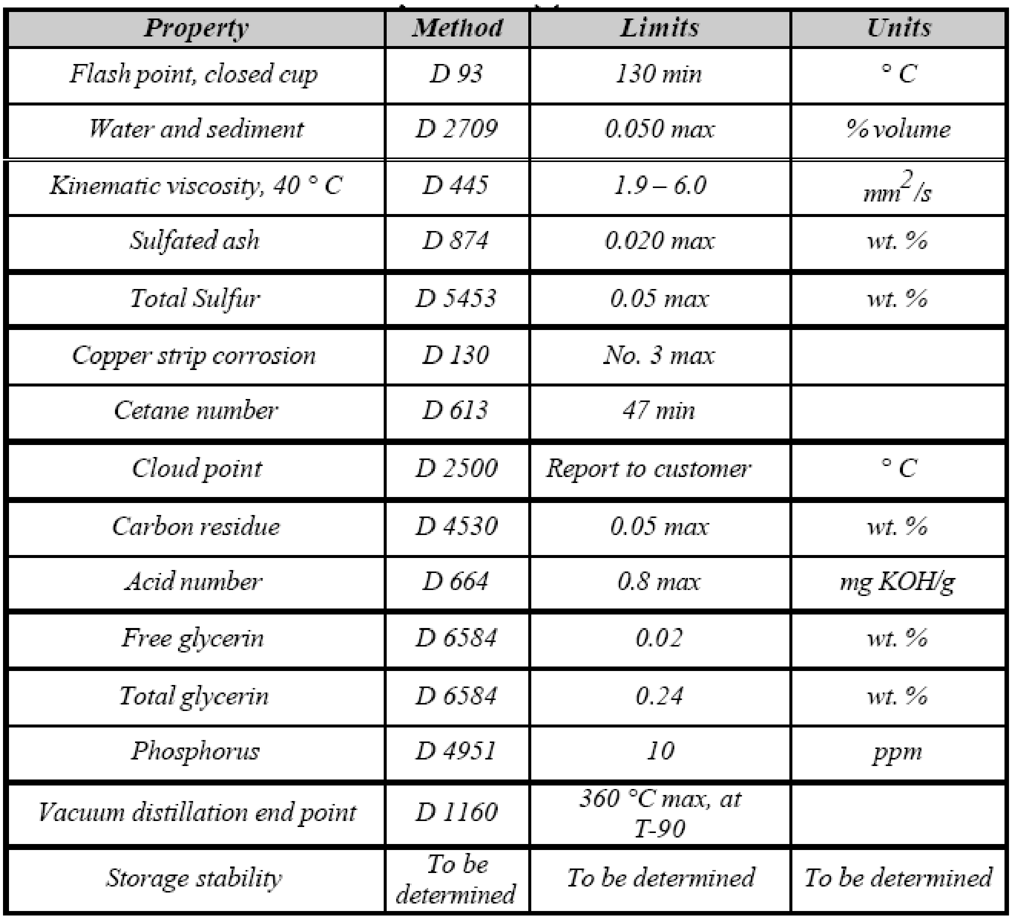
• Esters Volume • Density on 15 °C • Viscosity on 40 °C • Flare point • Sulfur contend • Carbonization residue • Cetane Index • Contain of sulphate dust • Contain of water • Total contain of impurities • Rust on copperplate (3 hours on 50 °C) • Oxidative stability • Toxin number • Acidity number • Contain of Methyl ester of Linolenic acid	• Contain of Methyl esters of other acids with dabble quadruple bonds • Methanol contain • Contain of monoglyceride • Contain of diglyceride • Contain of triglyceride • Contain of free glycerin • Contain of metals from the I. group of elements of periodic system (Na,K) • Contain of metals from the II. Group of elements of periodic system (Ca, MG) • Contain of phosphorus

In the United States, this standard is ASTM D 6751-02: “Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels”. Generally, the fuel quality of biodiesel can be influenced by several factors (Zanzi et al, 2006):

- The quality of the feedstock;
- The fatty acid composition of the parent vegetable oil or animal fat;
- The production process and the other materials used in this process;
- Post-production parameters.

Table 4.1 shows the property values required for a mixture of methyl esters to be considered biodiesel. When these limits are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine's durability and reliability. Even in low level blends with conventional diesel fuel, the biodiesel blending stock is expected to meet the standard before being blended. While some properties in the standard, such as cetane number and density, reflect the properties of the chemical compounds that make up biodiesel, other properties provide indications of the quality of the production process (Tyson *et al.*, 2004).

Table 4.7 - ASTM D 6751–02 Biodiesel Specifications [Tyson et al., 2004]



Property	*Method*	*Limits*	*Units*
Flash point, closed cup	*D 93*	*130 min*	*° C*
Water and sediment	*D 2709*	*0.050 max*	*% volume*
Kinematic viscosity, 40 ° C	*D 445*	*1.9 – 6.0*	mm^2/s
Sulfated ash	*D 874*	*0.020 max*	*wt. %*
Total Sulfur	*D 5453*	*0.05 max*	*wt. %*
Copper strip corrosion	*D 130*	*No. 3 max*	
Cetane number	*D 613*	*47 min*	
Cloud point	*D 2500*	*Report to customer*	*° C*
Carbon residue	*D 4530*	*0.05 max*	*wt. %*
Acid number	*D 664*	*0.8 max*	*mg KOH/g*
Free glycerin	*D 6584*	*0.02*	*wt. %*
Total glycerin	*D 6584*	*0.24*	*wt. %*
Phosphorus	*D 4951*	*10*	*ppm*
Vacuum distillation end point	*D 1160*	*360 °C max, at T-90*	
Storage stability	*To be determined*	*To be determined*	*To be determined*

Prior to use as a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets any required specifications. The most important aspects of biodiesel production to ensure trouble free operation in diesel engines are (Van Gerpen, 2005):

)

Complete Reaction: The most important issue during biodiesel production is the completeness of the transesterification reaction. The basic chemical process that occurs during the reaction is indicated by the sequence of events of Fig 4.5:

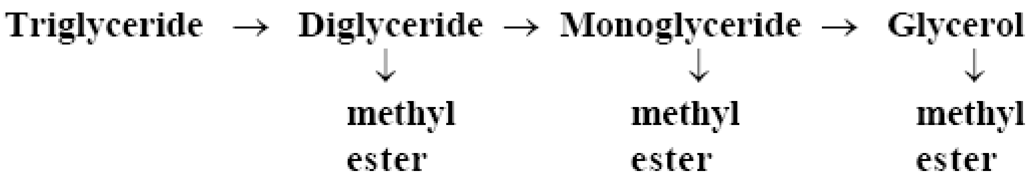


Fig 4.5 - Sequence of events of the transesterification reaction (Van Gerpen, 2005)

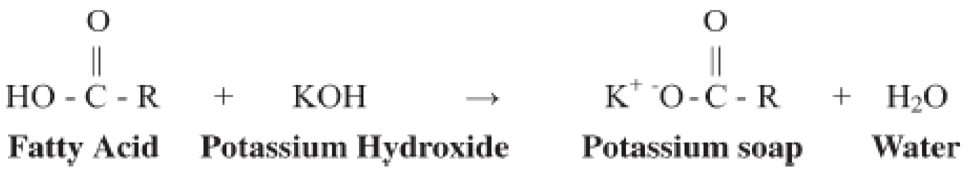
The triglycerides are converted to diglycerides, which in turn are converted to monoglycerides, and then to glycerol. Each step produces a molecule of a methyl ester of a fatty acid. If the reaction is incomplete, then there will be triglycerides, diglycerides, and monoglycerides left in the reaction mixture. Each of these compounds still contains a glycerol molecule that has not been released. The glycerol portion of these compounds is referred to as *bound glycerol*. When the bound glycerol is added to the free glycerol, the sum is known as the *total glycerol* (Tyson *et al.*, 2004).

Removal of Glycerin (glycerol): Free glycerol refers to the amount of glycerol that is left in the finished biodiesel. Glycerol is essentially insoluble in biodiesel so almost all of the glycerol is easily removed by settling or centrifugation. Free glycerol may remain either as suspended droplets or as the very small amount that is dissolved in the biodiesel. Alcohols can act as co-solvents to increase the solubility of glycerol in the biodiesel. Most of this glycerol should be removed during the water washing process. Water-washed fuel is generally very low in free glycerol, especially if hot water is used for washing. Distilled biodiesel tends to have a greater problem with free glycerol due to glycerol carry-over during distillation. Fuel with excessive free glycerol will usually have a problem with glycerol settling out in storage tanks, creating a very viscous mixture that can plug fuel filters and cause combustion problems in the engine (Tyson *et al.*, 2004).

Removal of Catalyst: Most of the residual catalyst is removed with the glycerol. Like the alcohol, remaining catalyst should be removed during the water washing (Van Gerpen, 2005).

Removal of Alcohol: Since methanol (and ethanol) and the alkaline catalysts are more soluble in the polar glycerol phase, most will be removed when the glycerol is separated from the biodiesel (Tyson *et al.*, 2004).

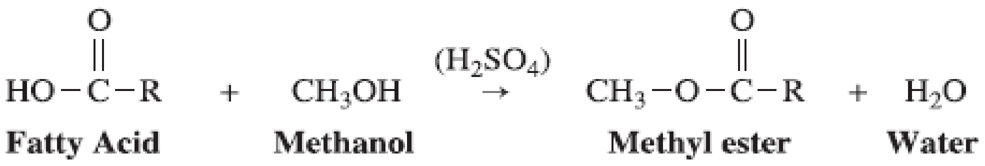
Absence of Free Fatty Acids (FFAs): Special processes are required if the oil or fat contains significant amounts of FFAs. Used cooking oils typically contain 2-7% FFAs and animal fats contain from 5-30% FFAs. Some very low quality feedstocks, such as trap grease, can approach 100% FFAs. When an alkali catalyst is added to these feedstocks, the free fatty acids react with the catalyst to form soap and water as shown in the reaction of Fig 4.6.



$$HO-\overset{\overset{O}{\|}}{C}-R + KOH \rightarrow K^{+}\,{}^{-}O-\overset{\overset{O}{\|}}{C}-R + H_2O$$

Fig 4.6 - Free fatty acids reaction [Van Gerpen, 2005]

Up to about 5% FFAs, the reaction can still be catalyzed with an alkali catalyst but additional catalyst must be added to compensate for that lost to soap. The soap created during the reaction is either removed with the glycerol or is washed out during the water wash. When the FFA level is above 5%, the soap inhibits separation of the glycerol from the methyl esters and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulphuric acid can be used to esterify the FFAs to methyl esters as shown in the reaction of Fig 4.7.



$$HO-\overset{\overset{O}{\|}}{C}-R + CH_3OH \xrightarrow{(H_2SO_4)} CH_3-O-\overset{\overset{O}{\|}}{C}-R + H_2O$$

Fig 4.7- Esterification of FFAs [Van Gerpen, 2005]

4.4 Technological Overview

There are three basic chemical processes used to produce biodiesel from oils and fats industrially. These processes can either be batch or continuous and are the following:

- Base catalyzed transesterification of the oil with alcohol (methanol).
- Direct acid catalyzed esterification of the oil with methanol.

- Conversion of the oil to fatty acids (acid pretreatment) and then to alkyl esters with acid catalysis.

The base catalyzed transesterification of oil with methanol is the most common currently in used process. It utilizes oils and animal fats with low free fatty acids quantities and is considered the most cost effective due to the following reasons:

1. Occurs at low temperatures (up to 65^{o} C) and low pressure (atmospheric up to 1,4 bars);
2. Has a high conversion (>98%) with minimal side reactions and reasonable reaction times;
3. Presents direct conversion to methyl ester with no intermediate steps;
4. Unconventional or exotic materials of construction are not necessary.

Notwithstanding, the selection of the specific process and technology to be used for biodiesel production depends on a variety of factors including the size of the plant, feedstock type and quality, requirements regarding feedstock flexibility(multiple feedstocks), and others.

According to the feasibility study undertaken for British Columbia, the three main methods that are being commercially used to produce biodiesel from low to high FFA feedstock are the following:

4.4.1 Straight base catalyzed transesterification.

- Simple inexpensive process as no pre-processing is used
- Low to high yield losses due to the formation of soaps from non-reacted free fatty acids
- Increased waste costs
- Difficult quality control issues
- Limit on amount of allowable free fatty acids in the feed

4.4.2 Free fatty acids removal (caustic washing) followed by straight base catalyzed transesterification:

- Purifies feedstock allowing for efficient processing and good quality control
- An equal amount of clean oil tends to be lost with free fatty acids in the form of soap, resulting in a significant loss in yield (depending on free fatty acids content)

- Free fatty acids must be sold (can be difficult to find market), or straight acid esterified into methyl esters (additional process equipment) in order to be viable

4.4.3 Acid esterification followed by base transesterification with low or high free fatty acids greases and fats (see Fig 4.8)

- Results in high yields as acid esterification pre-process converts free fatty acids to methyl esters
- Requires simple additional pre-processing equipment
- Good quality control
- Process can be adjusted to suit free fatty acids content
- Requires high ratios of methanol that must be recovered to be viable
- Process produces water that must be continuously removed to ensure complete reaction

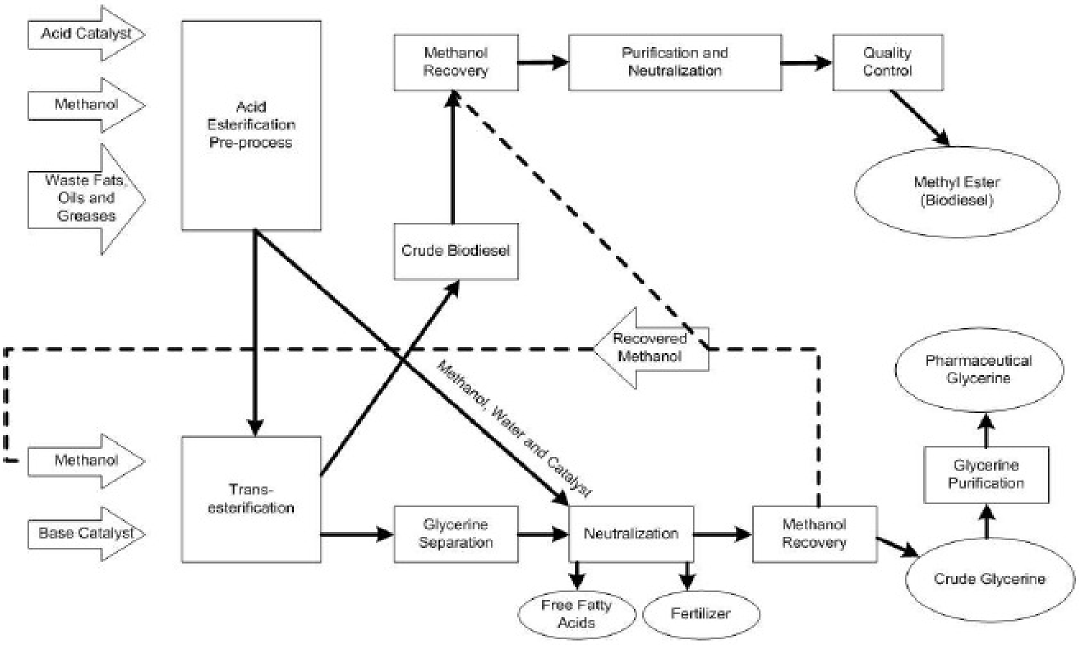


Fig 4.8 Biodiesel process flow diagram using low-high FFAs feedstock

It is evident that the amount of oilseed currently produced annually in Greece is insufficient to cover the Greek biodiesel targets. Furthermore, it is questionable whether in the near future a considerable increase of oilseed production could be expected. This therefore implies that alternative sources must be examined. Due to its high yields, oil imports like crude palm oil presents an attractive option. Also, locally, oils like the crude olive kernel oil which has the potential to be produced in significant quantities can also be examined. As mentioned earlier this feeds are characterized by their high content in FFAs. Of the three processes described above, the last one is more suitable for these feedstocks. Generally, it is more adoptable to different feedstock than the other two, and as such it can be considered as the most suitable for biodiesel production in Greece.

4.4.4 Batch Vs continuous process technology

The process of biodiesel production can be performed either in a batch or a continuous system.

i. Batch Systems

A batch reactor is basically a discontinuous process reactor in which all reactants are loaded at once. Straight batch systems usually consist of a series of tanks in which each phase of production is completed before being pumped to the next phase. This implies that batch systems require more space for the extra processing vessels. These systems offer the flexibility of a varied feedstock source as each batch can be altered depending on the level of the FFA level of the feedstock. They also offer the flexibility of troubleshooting during the processing stage. The technology is simple and less automated than the continuous flow process. However, it conveys the disadvantage of high labor cost per batch and also the difficulty of large scale production. The main characteristics of a batch reactor are that the total mass of each batch is fixed; each batch is a close system; and the reaction time for all the elements of the fluid are the same. Batch systems typically require one 8-hour shift per day.

ii. Continuous Systems

Continuous flow systems are highly efficient and quick at processing high quality feedstock with a low level of FFA (less than 0.5%). They are best suited to more centralized, large capacity facilities, producing well over 10 million L/yr where the economies of scale begin to take effect. These systems are highly automated and with excellent quality control. Continuous systems require operations 24 hrs/day in order to maintain efficiencies.

iii. Hybrid Systems

There are many new companies that are using hybrid systems that utilize a batch acid esterification pre-process for low to high FFA content feedstock (5-30%). This creates a consistent feedstock that can then be fed into a continuous transesterification system.

Another version of a “hybrid” type system involves the use of continuous esterification, followed by batch transesterification reaction, and the resulting ester/glycerine processed continuously in downstream processing equipment. In this instance, only the transesterification reactor is batch, and overall continuous response is achieved via the use of surge tanks ahead of and following the transesterification reactor. Depending on the size of the facility, this approach can be as cost effective as a fully continuous system, for example, plants in the range of 10 million to 30 million L per year production rates should carefully evaluate this approach from an overall economic comparison standpoint (compared to full continuous).

CHAPTER 5: EXPERIMENTAL EVALUATION

5.1 introduction

Crude vegetable oils generally contain high amounts of free fatty acids and a procedure for converting them to biodiesel is very much required. This chapter discusses the experimental procedures carried out to optimize the pretreatment process for reducing the FFA of Crude Palm Oil (CPO), Crude Palm Kernel Oil (CPKO), and Crude Olive Kernel (COKO) oil below 1% for maximum biodiesel production. Also the transesterification process for the production of biodiesel is discussed.

5.2 Reactants and Equipments

5.2.1 Reactants

The reactants that were used as well as their purity are presented on Table 5.1. All the reactants were supplied by (or purchased from) Riedel-de Haen.

Table 5.1 – Reactants used for biodiesel production process

Reactants	Purity (%)
Methanol	>99.8
Isopropyl	>99.8
Sulfuric acid	95-97
Phosphoric acid	95
Sodium hydroxide pellets	Min 99

Phenolphthalein (indicator)	98-101

5.2.2 Equipments

- 250 cc glass bottles with airtight plastic covers
- Magnetic stirrer bar
- Magnetic hotplate stirrer
- Electronic thermometer
- Stopwatch
- 1000cc glass beaker

5.2.3 Characterization of the feedstocks

The three crude vegetable oils used as feedstock for this study are CPO, CPKO and COKO.

Fig 5. 1 Crude vegetable oil samples used for experiments (CPO, CPKO and COPO)

The CPO and CPKO were obtained from a local market in Cameroon. These oils are extracted by a local method from freshly harvested fruits and kernels. The CPO is reddish yellow in color and has a high viscosity which causes it to solidify at room temperature. CPKO is golden yellow in color and presents a lower viscosity than CPO, though it also solidifies at low temperatures. COKO is extracted by means of a solvent from olive-pomace which is a by-product from virgin olive oil processing. It is black in color and has a strong smell. Large quantities of this sample were provided by A.B.E.A (www.abea.gr). The fatty acid profiles of these oils are given in Table 5.2.

Table 5.2- Fatty acid composition of CPO, CPKO and COPO (EU, 2006; Leray, 2008)

Fatty Acid	CPO	CPKO	COKO
Caprylic acid $C_{8:0}$	-	3-4	-
Capric acid $C_{10:0}$	-	3-7	-
Lauric Acid $C_{12:0}$	<0,4	46-52	-
Myristic acid $C_{14:0}$	1-4	15-17	<0,05
Palmitic acid $C_{16:0}$	40,9-47,5	6-9	7,5-20
Stearic acid $C_{18:0}$	3,8-4,8	1-3	0,5-5
Oleic acid $C_{18:1}$	36,4-41,2	11-19	55-83
Linoleic acid $C_{18:2}$	9,2-11,6	0,5-2	3,5-21
Linolenic acid $C_{18:3}$	<0,5		<0,9
Arachidic acid $C_{20:0}$	<0,8		<0,6

The free fatty acid content of the oil was determined by a standard titrimetry method (see appendix II). Specifically, the CPO and the CPKO had FFA levels of 8.28% (acid value = 16.56) and 19.80% respectively, while that of COKO was 22.11%. All the oil samples had FFA levels far above the 1% limit required to achieve satisfactory transesterification by alkaline catalysts. This implies that the FFAs have to be first converted to esters in a pretreatment process using an acid catalyst (H_2SO_4) to reduce the acid value of the vegetable oil to the required levels.

5.3 Experimental Procedures

5.3.1 Esterification procedure

The objective of this study is to develop a process for producing biodiesel from feedstocks with high FFAs contents like CPO, CPKO and COKO The process consists of two steps namely, acid esterification and alkaline esterification.

a) Acid esterification: the first step reduces the FFA value of the crude vegetable oils to values less than 1% using acid catalyst.
b) Alkaline esterification: After removing the impurities of the product of first step, it is transesterified to mono-esters of fatty acids using alkaline catalyst.

In this study, parameters affecting the process such as alcohol to oil molar ratio, catalyst amount, reaction temperature and duration are analyzed for the acid esterification step.

5.3.2 Esterification setup

The following setup is used in the laboratory to carry out esterification reactions:

- The 250mL (cc) reaction bottles with airtight caps to retain any vaporized methanol to the reacting mixture are used as a lab scale reactor for these experimental purposes.
- The reaction bottle is immersed in the 1000mL beaker containing water maintained at 60°C below the melting point of methanol.
- The hot plate with magnetic stirrer arrangement is used for heating the mixture in the reaction bottle.
- The mixture is stirred at the same rate for all reaction runs with the use of a plastic magnetic stirrer.
- A temperature range of 58-62°C is maintained throughout and for all the experiments as shown in Fig 5. 2.
- Progress of the reaction was monitored by measuring the free fatty acid content by titration.

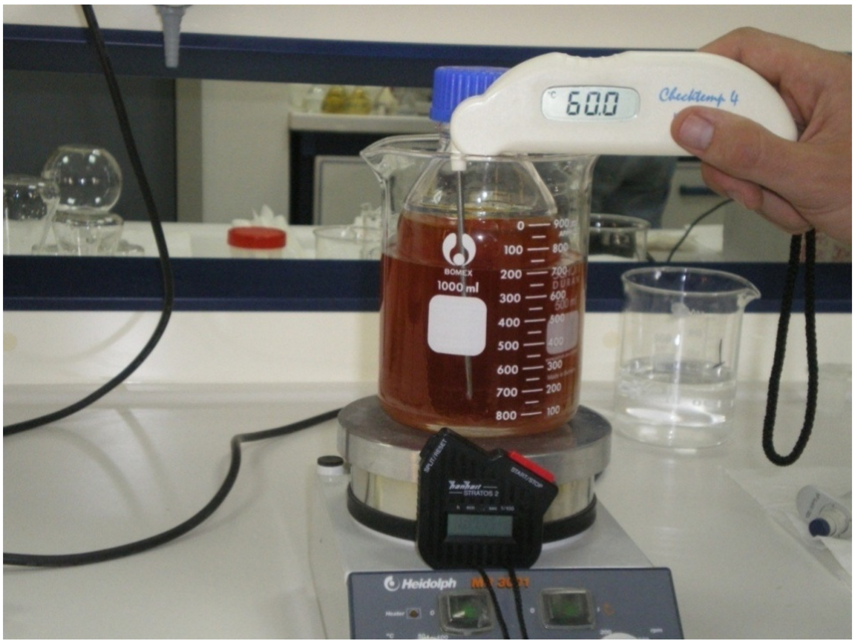


Fig 5. 2 – Laboratory Setup used for esterification reaction

5.4 Acid Esterification

In this step, 75 g of crude vegetable oil was used for all reactions. The oil was poured into the bottle and heated to about 60°C. Different solutions of concentration H_2SO_4 acid (0.5% and 1% v/v based on oil weight) in methanol was then added into the reaction bottle. Different methanol to oil ratios by weight, namely at 0.15, 0.20, 0.25, 0.30, 0.35, and 0.40 were used to investigate for the optimization and their influence on the acid value of the oil samples. The FFA values of the reaction were measured at intervals of 0, 15, 30 and 60 minutes. Heating and stirring is maintained for 60 min at atmospheric pressure while titration measurements are made at the indicated time intervals to monitor the progress of the reaction. The sample that presented the lowest FFA content in the shortest reaction time and lowest methanol to oil ratio was chosen as the optimum condition and was used for the next step (alkaline-catalyzed-transesterification reaction).

5.5 Alkaline Transesterification

The transesterification reaction was carried out with 0.25v/v methanol (6:1 molar ratio) and 1% w/v NaOH/oil as an alkaline catalyst. The NaOH amount is the common catalyst amount to be used for feedstocks having FFA level less than 1% (Van Gerpen et al, 2004).

When FFA levels are above 1%, it is possible to add extra alkaline catalyst. This allows part of the catalyst to neutralize the FFAs forming soap, while still leaving enough to act as the reaction catalyst. According to Van Gerpen, the amount of additional catalyst needed to neutralize to the extra FFA can be calculated by the following formula (Van Gerpen et al, 2004):

$$\text{Amount of NaOH catalyst} = \left(\left[\%\text{FFA}\right]\left(0.144\right) + 1\%\right) * \text{weight of oil} \qquad (1)$$

The reaction was carried out at 50^{o}C for half an hour and was stirred with a magnetic stirrer. The mixture was allowed to settle before removing the glycerol layer from the bottom to get the ester layer on the top, separated as biodiesel.

Chapter 6: Results and Discussion

The two-step process (Acid-Catalyzed esterification followed by alkaline-catalyzed transesterification) was adopted for processing the oils into biodiesel because of their high FFA content.

6.1 Acid-Catalyzed esterification

The objective of this pretreatment stage was to reduce the FFA contents of CPO, CPKO and COPO. Important parameters affecting the acid value in the esterification process was the methanol to oil ratio, the acid to oil ratio, reaction time. According to reports, to get completely FFA esterification in some vegetable oils, could be done in the reaction temperature of 50^{o}C, with a reaction time of one hour, and the acid H_2SO_4 to oil ratio 1% w/w (Ghadge and Raheman, 2005; Veljkovic et al, 2006). Therefore these conditions were selected with slight modifications to investigate the effect of methanol to oil ratios and reaction time on the FFA contents of the crude vegetable oil. For the optimization experiments, two acid-to-oil ratios (0.5% v/v and 1%v/v) were tested at a temperature of 60±2^{o}C and for reaction times 0, 15, 30, 60 minutes.

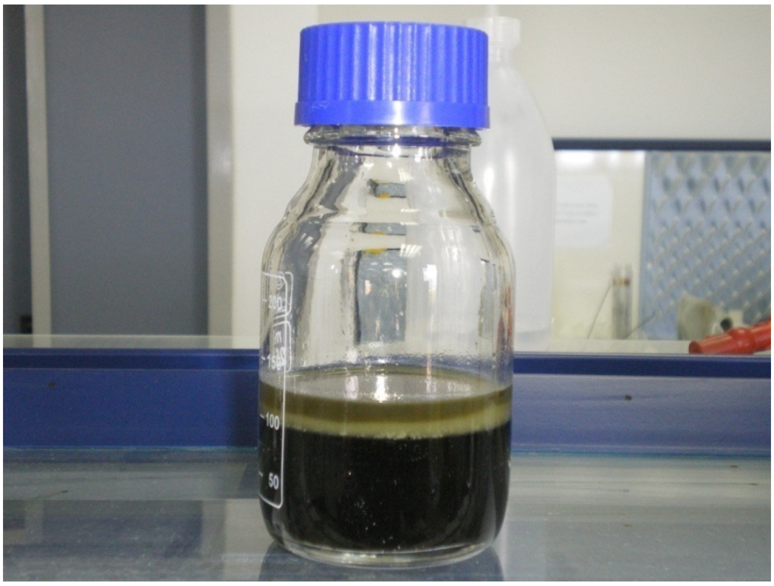


Fig 6. 1 - COPO mixture after pretreatment (upper layer is methanol, acid and impurities mixture while lower layer is pretreated oil)

The vegetable oils tested during these experiments were CPO(FFA = 8.28%), CPKO (FFA = 19.80%) and COKO (FFA = 22.11%). The effect of methanol amount and reaction time on the FFA contents of the mixtures after one hour reaction is shown in Fig 6. 2 to Fig 6.7 for the reaction conditions.

6.1.1 Crude Palm Oil

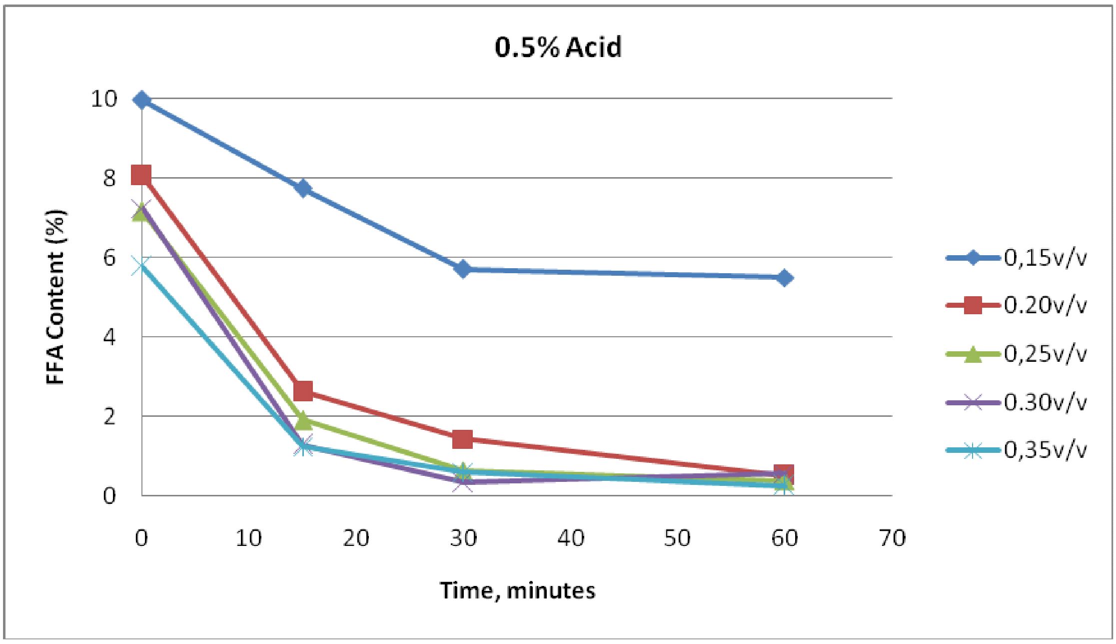


Fig 6. 2- Effect of reaction time and methanol quantity on reduction of FFA value of palm oil for 0.5% v/v, acid-to-oil ratios during pretreatment for biodiesel production (initial FFA value = 8.28%)

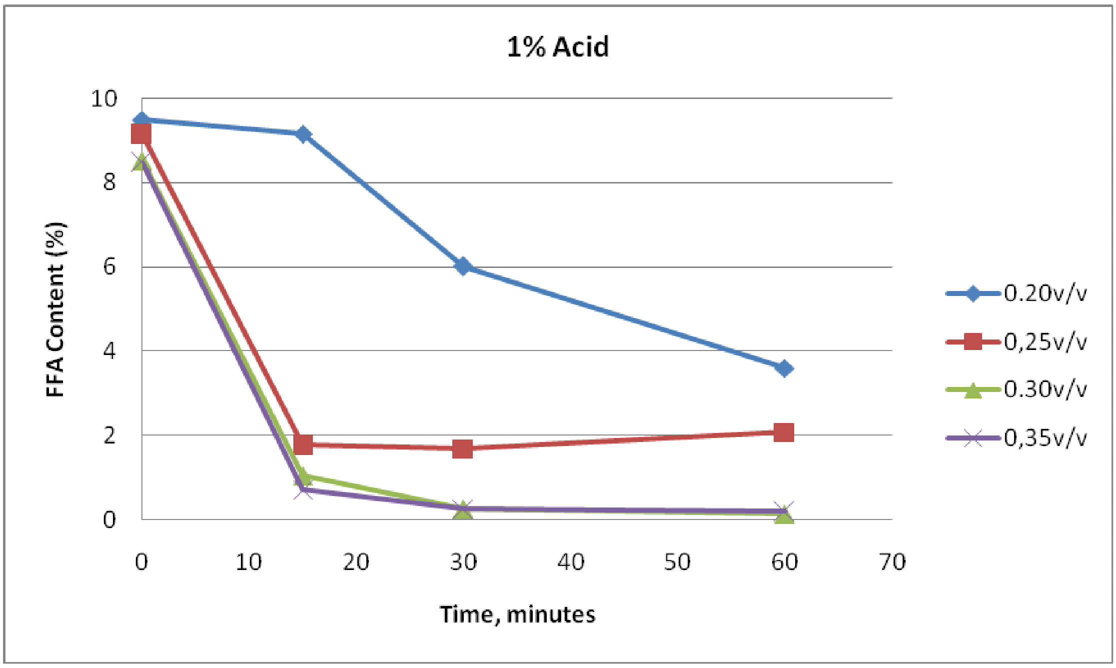


Fig 6. 3- Effect of reaction time and methanol quantity on reduction of FFA value of palm oil for 1.0 % v/v, acid-to-oil ratios during pretreatment for biodiesel production (initial FFA value = 8.28%)

The changes in FFA concentration for the pretreatment of CPO at 0.5%v/v and 1%v/v catalyst ratios are shown in Fig 6. 2 and Fig 6. 3, respectively. From these figures, it can be seen that the rate of reaction was greatly influenced by both the quantity of methanol and the reaction time.

- Specifically, the reaction progressed rapidly during the first 15 minutes showing over 70% reduction in FFA values at high-methanol ratios for both catalyst values. After 30 minutes, there was no significant reduction in the acid value. This was attributed to the effect of water produced during the esterification of FFAs, which prevented further reaction.
- For lower methanol-to-oil ratios (0.15 v/v and 0.2 v/v), FFA value could not go below 1% after 60 minutes reaction time for both the 0.5% v/v and 1% catalyst to oil ratios. However, increasing the methanol-to-oil ratio to values above 0.20v/v, the FFA value could be lowered to a desirable range of 0.52% for 0.5% catalyst-to-oil ratio in 60 minutes. While for methanol-to-oil ratio 0.25 v/v and above the reaction was completed in 30 minutes. On the other hand, at 1.0% catalyst-to-oil ratio, the desirable range for the FFA value was obtained in only 15 minutes for 0.30v/v and above methanol-to-oil. Increasing the methanol amount beyond 0,25v/v and 0,3v/v, for 0.5% v/v and 1%v/v catalyst, respectively, showed no significant effect on the FFA concentration. Therefore, there was an optimum

quantity of methanol required to complete the esterification process of all FFA in CPO;

- As can be seen, the amount of acid catalyst used in the process also affects the conversion efficiency of the process. Specifically, for catalyst amount 0.5%, lowest reaction duration was 30mins (0.25v/v MeOH/oil) while for catalyst amount 1%, the lowest duration was 15mins (0.35v/v MeOH/oil);
- The combination of 0.25 v/v methanol-to-oil ratio and 30minutes reaction time for 0.5% catalyst-to-oil ratio, which reduced FFA value from 8.28% to 0.62%, was selected as optimum conditions for the pretreatment of CPO.

6.1.2 Crude Palm Kernel Oil

The changes in FFA concentration for the pretreatment of CPKO at 0.5%v/v and 1%v/v catalyst ratios are shown in Fig 6. 4 and Fig 6. 5, respectively. From these figures, it can be seen that the rate of reaction was greatly influenced by both the quantity of methanol and the reaction time.

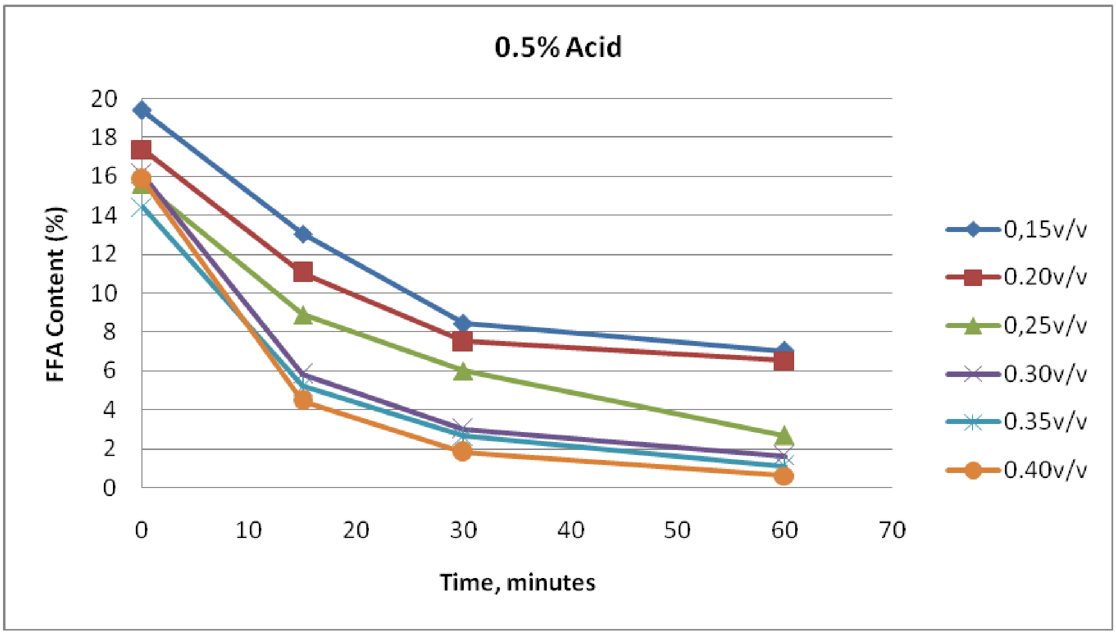


Fig 6. 4 - Effect of reaction time and methanol quantity on reduction of FFA value of palm oil for 0.5% v/v, acid-to-oil ratios during pretreatment for biodiesel production(initial FFA value = 19.80%)

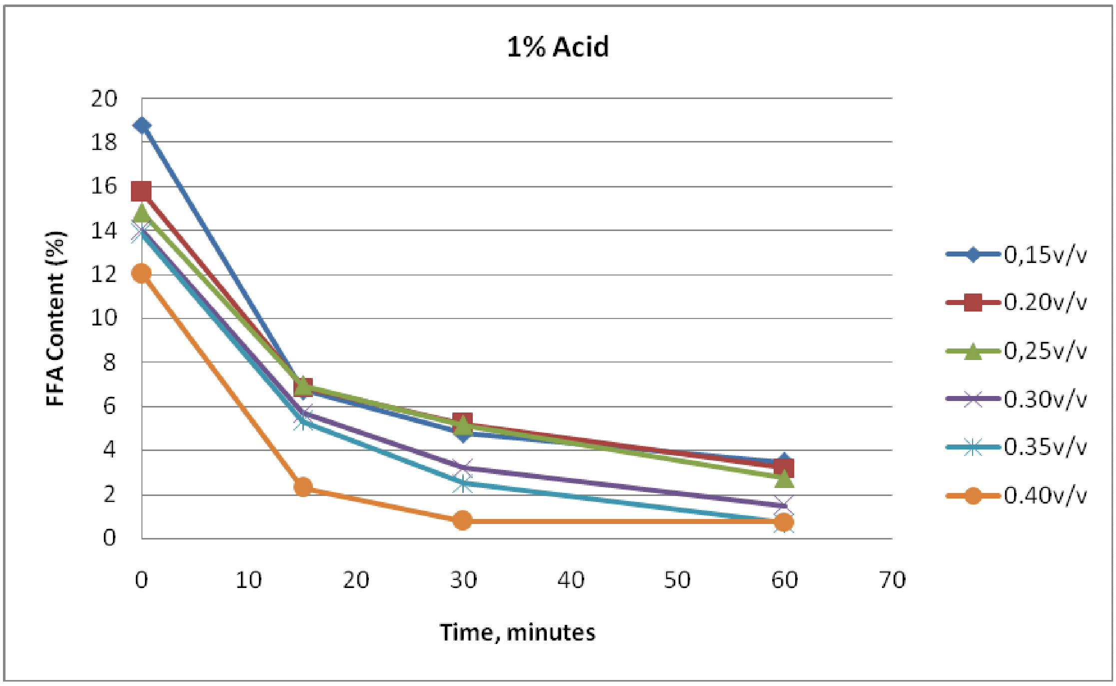


Fig 6. 5 - Effect of reaction time and methanol quantity on reduction of FFA value of palm oil for 1.0 % v/v, acid-to-oil ratios during pretreatment for biodiesel production(initial FFA value = 19.80%)

- The reaction progressed rapidly during the first 30 minutes showing over 50% reduction in FFA values at low-methanol ratios and over 80% reduction for high-methanol ratios for both catalyst values. Generally, after 30 minutes, the decrease in FFA concentration was more gradual. This might be due to the effect of water produced during the esterification of FFAs, which prevented further reaction.
- Increasing the methanol amount of the reaction clearly led to an increase in process efficiency. For the 0.5% catalyst-to-oil ratio, the desirable reduction (0.62% FFA) was attained only after a one hour reaction and at 0.40v/v MeOH/Oil. While at 1% catalyst-to-oil ratio, it was attained after one hour reaction at 0.35v/v MeOH/Oil. It implies that the acid amount also plays an important role in the conversion efficiency of the CPKO pretreatment process.
- The combination of 0.4 v/v methanol-to-oil ratio and 30minutes reaction time for 1% catalyst-to-oil ratio, which reduced FFA value from 19.8% to 0.79%, was selected as optimum conditions for the pretreatment of CPKO.

6.1.3 Crude Olive Kernel Oil

The changes in FFA concentration for the pretreatment of COPO at 0.5%v/v and 1%v/v catalyst ratios are shown in Fig 6.6 and Fig 6.7 respectively. From these figures, it can be seen that the rate of reaction was greatly influenced by both the quantity of methanol and the reaction time.

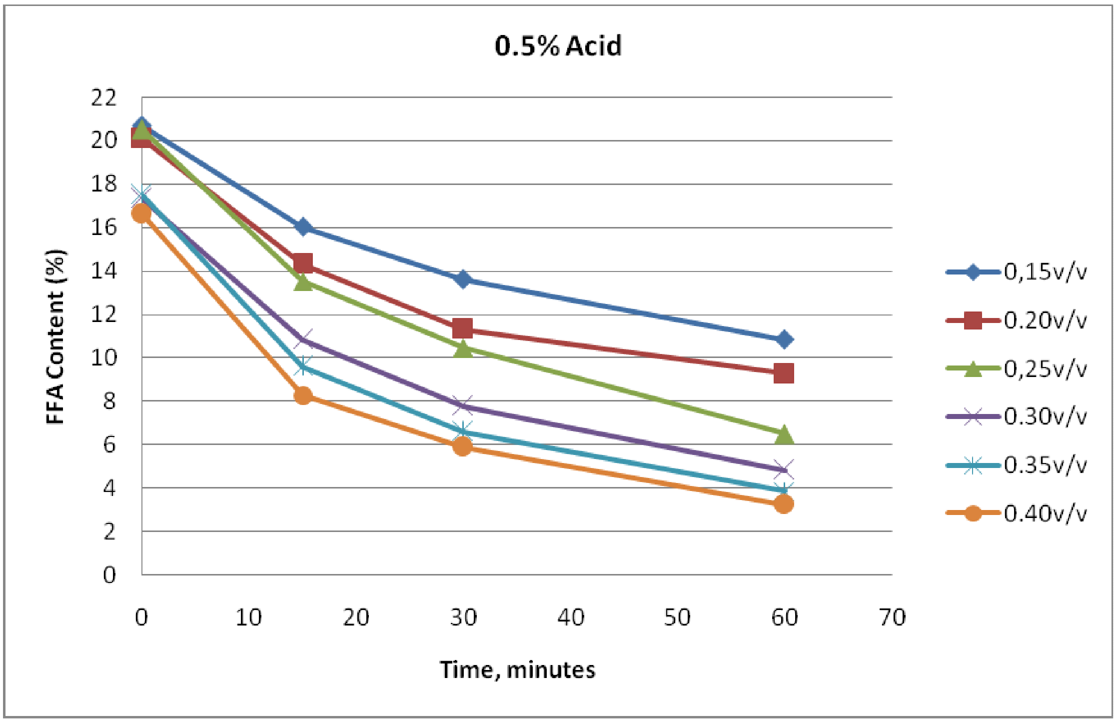


Fig 6.6 - Effect of reaction time and methanol quantity on reduction of FFA value of palm oil for 0.5% v/v, acid-to-oil ratios during pretreatment for biodiesel production (initial FFA value = 22.11%)

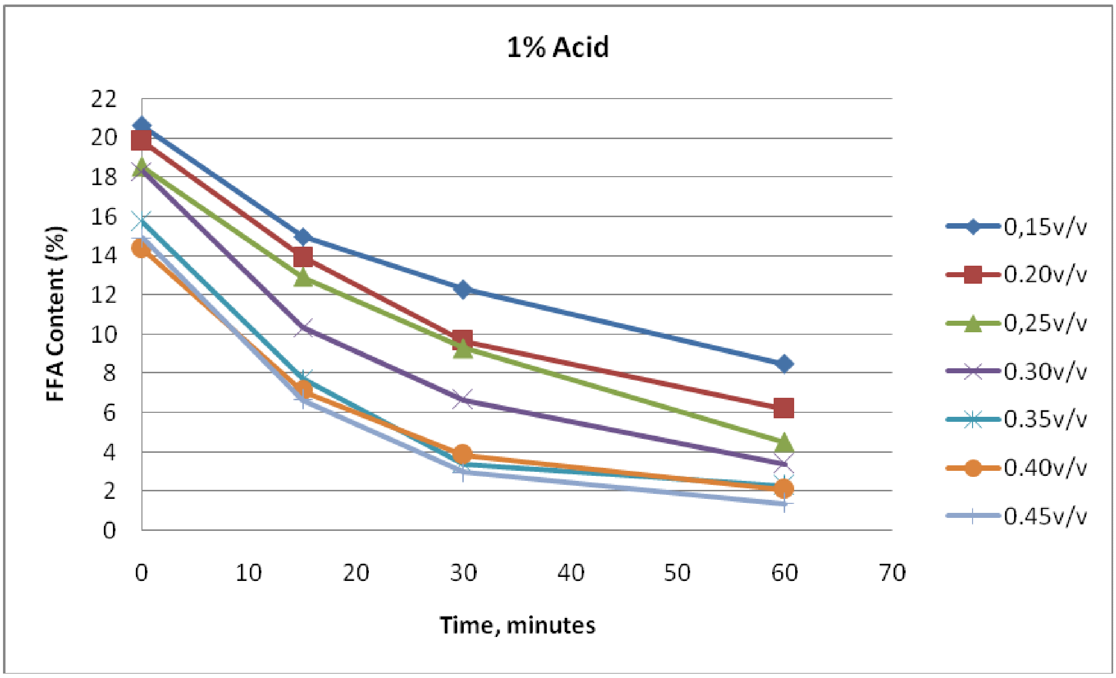


Fig 6.7 - Effect of reaction time and methanol quantity on reduction of FFA value of palm oil for 1.0 % v/v, acid-to-oil ratios during pretreatment for biodiesel production (initial FFA value = 22.11%)

- The FFA concentration reduced gradually during the reaction duration. The effect of methanol-to-oil ratio was very important as after 60 minutes reaction time, the FFA concentration decreased from 10.85% at 0.15v/v MeOH/oil to 3.22% at

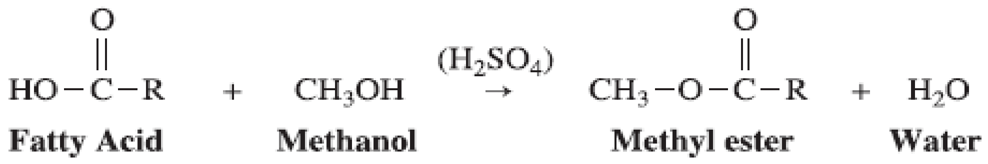
0.4v/v MeOH/oil at 0.5% v/v acid amount. For 1% acid amount, the decrease was8.47% at 0.15v/v MeOH/oil to 2.1% at 0.4v/v MeOH/oil, after 1h reaction.

- The lowest FFA value obtained was 1.38% at of 0.45 v/v methanol-to-oil ratio, 1% catalyst-to-oil ratio and 60minutes reaction time. Clearly this value is not satisfactory because it is higher than the 1% limit needed for effective alkaline transesterification. The FFA value could be reduced by further increasing the MeOH/Oil ratio or by introducing a second pretreatment step. However, a more feasible and economical solution might be to use an extra amount of alkaline catalyst during the transesterification process.

6.1.4 Rate Reaction Analysis of Pretreatment Process

Acid Pre-treatment of FFA

The acid esterification reaction for the pre-treatment of FFAs is given in the figure below.



$$\underset{\text{Fatty Acid}}{HO-\overset{\overset{\displaystyle O}{\|}}{C}-R} + \underset{\text{Methanol}}{CH_3OH} \xrightarrow{(H_2SO_4)} \underset{\text{Methyl ester}}{CH_3-O-\overset{\overset{\displaystyle O}{\|}}{C}-R} + \underset{\text{Water}}{H_2O}$$

Fig 6.1- Esterification of FFAs (Van Gerpen, 2005)

This reaction can be simplified as follows:

$$FFA + MeOH \xrightarrow{H_2SO_4} ME + H_2O \tag{1}$$

This reaction can be described by a first order reaction with respect to FFA concentration

$$r = -\frac{d[FFA]}{dt} = k[FFA] \tag{2}$$

Where by k is the first order rate constant, which has units of 1/time.

The integrated first-order rate law is:

$$\ln[FFA] = -kt + \ln[FFA]_0 \tag{3}$$

$$y = -bx + c \tag{4}$$

Plots of ln[FFA] against t gives a straight line with a slope of –k.

The aim of this experiment was to determine the optimum conditions for the reduction of the FFA value of the crude vegetable oils to values less than 1% using the acid catalyst.

$$[FFA]=1 \Rightarrow \ln[FFA]=0 \tag{5}$$

$$\Rightarrow -kt+\ln[FFA]_0=0 \tag{6}$$

$$\Rightarrow t=\frac{-\ln[FFA]_0}{-k}=\frac{\ln[FFA]_0}{k} \tag{7}$$

Where t is the time required to reduce the FFA concentration to 1%.

The tables in appendix I give the values of the intercept $[FFA]_0$, rate constant k, and t , for the feedstocks: CPO, CPKO and COPO.

Table 6.1 gives the conditions of the pre-treatment stage for the reactions that were completed in 60 minutes.

Table 6.1 Rate reaction Analysis of pretreatment (t<60)

Oil	Acid/Oil ratio (%v/v)	MeOH/Oil ratio (v/v)	Duration (minutes)
CPO	0.5	0.2	42.77
	0.5	0.25	32.70
	0.5	0.3	29.74
	0.5	0.35	27.17
	1	0.3	21.97
	1	0.35	21.28
CPKO	0.5	0.35	59.41
	0.5	0.4	47.52
	1	0.35	51.02
	0.01	0.4	42.56
COPO	0.01	0.5	64.95

6.2 Alkali-catalyzed transesterification (ACT)

In the second step, a test case of alkaline-catalyzed transesterification was run using the oil samples that had been pretreated from the first step. This process uses the experimental setup of the pretreatment process. 300g (i.e. 384mL) of sample was used all time. The oil sample is heated to the required reaction temperature (50^oC) in the reaction bottle. Meanwhile, 3g NaOH is dissolved in 96 mL methanol and is poured in the reaction bottle. The mixture is heated and stirred for 30mins. The reaction is stopped and the products are allowed to separate into two layers. The lower layer contains impurities and glycerol while the upper layer which is the biodiesel is removed.

Fig 6. 8 - Alkali transesterification (lower layer contains glycerin, soapstock and impurities while upper layer is CPO methyl ester)

Following this process, the yield of biodiesel obtained was much better than that obtained on samples which had not been pretreated (one step alkali-catalyzed transesterification). For this one-step process, the conditions used were similar to those described in section ***5.5*** (i.e. 1% w/v NaOH catalyst, 0.25v/v MeOH/oil, for 30 mins at 50^oC).

Generally, the ACT process will have to be optimized with respect to alcohol amount, catalyst amount, reaction temperature and time to get the best yield of biodiesel of the pretreated oil.

6.2.1 Crude Palm Oil

- Before pretreatment, very little (less than 5%) biodiesel was produced and little change was recorded even when catalyst and alcohol as well as reaction time and temperature were increased. The main product was a solid mass of soapstock. This result could be attributed to the high contents of gums, phospholipids, moisture and FFA contained in the crude palm oil. These impurities react with the alkali catalyst to form soap, thus lowering the yield of the oil.

- After pretreatment, the biodiesel yield was about 80% while the remaining 20% which settled at the bottom was soapstock and glycerine. One way to improve the yield of this step is to degum the CPO so as to remove the gums and the phospholipids. The degumming process is described in the appendix.

6.2.2 Crude Palm Kernel Oil

- Before pretreatment, the yield in biodiesel after the one-step alkaline transesterification process was about 40% while the remaining 60% of the sample was unreacted oil and glycerine. The result is attributed to the fact that the CPKO content in gums and phospholipids is very small compared to that of CPO
- After pretreatment, about 90% biodiesel and 10% glycerine and soapstocks was produced.

6.2.3 Crude Olive Kernel Oil

- Before pretreatment, only a very tiny layer (about 1%) of biodiesel appeared on the surface of the mixture during the alkali transesterification process. The rest of the mixture was unreacted oil.
- After pretreatment, the yield in biodiesel was greater than 90%, while the remaining 10% was mainly glycerine and other impurities.

The above results therefore show that the acid-catalyzed transesterification results not only in significant reduction of the FFA in the oil samples but also leads to improve yields in biodiesel production.

Chapter 7: Conclusion and Recommendations

7.1 Conclusion

As it has been presented on this thesis, Greece, like countries all over the world is responding to the urgent need to reduce petroleum dependency by developing strategies to help the biodiesel market grow. This is being done in the framework of the EU directive 2003/30/CE to reduce petroleum dependency in the transport sector, in which the EU countries have proposed to use the 5.75% of biofuel in transport at 2010 and 8% at 2020.

On this work, it has been shown that the production of biodiesel from oilseeds in Greece can be successfully carried out, but only after having taken into consideration all the technical, socio-economical and experimental aspects.

Looking at the social aspect, it is shown that biodiesel coming from vegetable oils contributes in a significant way to the sustainable power provision, and to reduce the dependency of petroleum; to increase the security and diversity in the provisions; and to increase the socioeconomic development of the rural area, and thus the conservation of local environments.

From the technical point of view, nowadays some technologies are available in the market, but the most widely used are large scale factories producing via a transesterification process. Some improvements are under studies, but previsions are that the technology will not be able to reduce in a significant range biodiesel production costs due to the fact that they are highly dependent on feedstock prices. This implies that for biodiesel to compete economically with fossil diesel, less expensive feedstocks must be used. These feedstocks are usually characterized by their high free fatty acid contents which make biodiesel production difficult thus requiring alternative processes.

From an experimental point of view, biodiesel production from CPO, CPKO and COKO with a high content of FFA has been investigated. In alkali base catalyzed transesterification process, the presence of high concentration of FFA reduced the yield of methyl esters of fatty acids significantly. A two-stage esterification process was selected to improve the methyl ester yield. The first stage was the acid pretreatment process, which was aimed to reduce the FFA level of the feedstocks to less than 1%.The optimum conditions were determined to be:

Table 7.1: Optimum conditions to reduce FFA content to values below 1% (see appendix I)

Oil	Acid/Oil ratio (%v/v)	MeOH/Oil ratio (v/v)	Duration (minutes)
CPO	0.5	0.2	45
	1	0.3	22
CPKO	0.5	0.35	48
	1	0.35	52
COKO	0.5	0.4	102
	1	0.45	65

This pretreatment stage product having FFA level less than 1% was then used for the final alkali-catalyzed (1% w/v NaOH) transesterification reaction with methanol (0.25v/v). The second stage, alkali base catalyzed transesterification process gave methyl ester yields greater than 80% for the 3 oil samples.

7.2 Recommendations

Some important areas for additional research into biodiesel are outlined below.

- Potential land required to grow indigenous oilcrops: As highlighted earlier 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 requirements, the distribution around the country, the competition with food crops, and eventually the different prices and market balance for a truly global analysis.
- Optimization of alkali-catalyzed process: The variables affecting transesterification such as catalyst concentration (0.25-1.5%), alcohol/oil ratio, temperature (37-65^{o}C) and reaction can be studied in subsequent studies to get higher conversion under optimal reaction condition.

- Determination of fuel quality: This involves the experimental evaluation of the physico-chemical properties of the biodiesel fuel produced as per the ASTM specification. This is to determine whether the fuel produced is within the prescribed range in the ASTM 6751 specifications for use as alternative for conventional diesel.

Bibliography

Agarwal, A. K. (2007). Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science* , 233-271.

Ali, Y., Hanna, M. (1994). Alternative Diesel fuels from Vegetable oils. *Bioresource Technology* , 153-163.

Barnwal, B. K., Sharma, M. P. (2005). Prospects of biodiesel production from vegetable oils in India. *Renewable and Sustainable energy review* , 363-378.

Boukis, I., al. (2008). Policy plan for the use of biomass and biofuels in Greece Part 1: Available biomass and methodology. *Renewable and Sustainable Energy Reviews* , in press.

BRAC. (2006). *Biofuels in the European Union: A Vision for 2030 and Beyond.* Biofuels Research Advisory Council.

CIA. (2008, June 19). *Greece*. Ανάκτηση June 30, 2008, από World Fact Book: https://www.cia.gov/library/publications/the-world-factbook/geos/gr.html

COM. (2007). *Biofuels Progress Report.* Brussels: Commission of the European Communities.

Dalianis, D., Petassis, D. (1993). *HIGH ECONOMIC COST FOR IMPACTS OF CLIMATE CHANGE IN GREECE.* Ανάκτηση May 31, 2008, από GREENPEACE Climate Impacts Database: http://archive.greenpeace.org/climate/database/records/zgpz0399.html

Demirbas, A. (2005). Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science 31* , 466-487.

DOE. (1998). *A Look Back at the U.S. Department of Enegy's Aquatic Species Program - Biodiesel from Algae".*

DOE. (2006). *Biomass Energy Data Book: Edition 1.* Tennessee: U.S. Department of Energy.

EBB. (2008, May 30). *Biodiesel*. Ανάκτηση June 2, 2008, από European Biodiesel Board: http://www.ebb-eu.org/biodiesel.php ebio. (2008, April 10). *European ethanol production improves*. Ανάκτηση June 9, 2008, από biofuel review: http://www.biofuelreview.com/content/view/1105/5/

EU. (2006). *COMMUNIQUÉ ON OLIVE OIL AND POMACE OIL.* Ανάκτηση 07 22, 2008, από http://ec.europa.eu/enterprise/tris/pisa/cfcontent.cfm?vFile=120068019EN.DOC

Fadiloglu, S., al. (2003). Reduction of Free Faty Acid Content of Olive-Pomace Oil by Enzymatic Glycerolysis. *Food Science and Technology International* .

FAOSTAT. (2004). *ANNEX B- Area, Production and Oil Production.* FAOSTAT DATA.

Friedrich, S. (2001). *World wide review production of biodiesel.* Wrtshaffts University.

Fukuda, H., al. (2001). Biodiesel fuel production by transesterification of oils. *Journal of Biosciences and Bioengineering* , 405-416.

Ghadge, S. V., Raheman, H. (2005). Biodiesel Production from mahua (Madhuca indica) oil having high free fatty acids. *Biomass and bionergy 28* , 601-605.

GPBE. (2006, August 18). *EU Biofuel Production in 2005*. Ανάκτηση June 9, 2008, από greenprice bio energy: www.greenprices.com

HL. (2006). *The EU Strategy on Biofuels: from field to fuel, Volume 1: Report.* London: House of Lords.

IEA. (2004). *Biofuels for Transport-An International Perspective.* Paris: OECD.

IEA. (2006). *Energy Policies of IEA Countries, Greece 2006 Review.* Paris: OECD.

IFEU. (2003). Ανάκτηση από Institut für Energie- und Umweltforschung Heidelberg GmbH: www.ifeu.de

Leray, C. (2008). *Main World Sources of Oil and Seven Important Oils* . Ανάκτηση 4 4, 2008, από Cyberlipids: http://www.cyberlipid.org

Ma, F., Hanna, M. (1999). Biodiesel production: a review. *Bioresource Technology* , 1-15.

Meher, L., al. (2006). Technical aspects of biodiesel production by transesterification—a review. *Renewable and Sustainable Energy Reviews* , 248-268.

NBB. (1996). *Biodiesel Report.* National Biodiesel Board.

Nylund, N. O., al. (2008). *Status and outlook for biofuels, other alternative fuels and new vehicles.* Helsinki: Bioenergy NoE.

Panoutsou, C., al. (2007). Biodiesel options in Greece. *Biomass and Bioenergy* .

Putt, R. (2007). *"Algae as a Biodiesel Feedstock: A Feasibility Assessment –DRAFT"* . Alabama: Center for Microfibrous Materials Manufacturing (CM3),Auburn University, Alabama 36849-5127.

Scotland, F. (2006). *Feasibility Report: Small Scale Biodiesel Production.* Glasgow, UK.

Sekliziotis, S. (2007). *Greece Bio-Fuels, Biofuel Activity in Greece 2007.* Voluntary Report - Public distribution.

Shay, E. G. (1993). Diesel fuel from vegetable oils: Status and opportunities. *Biomass and Bioenergy* , 227-242.

Shumaker, G., al. (2003). *A Study on the Feasibility of Biodiesel Production in Georgia.* Georgia.

Srivastava, A., Prasad, R. (2000). Triglycerides-based diesel fuels. *Renewable and Sustainable Energy Reviews* , 111-133.

Strachan, P. A. (2003). *What is biodiesel.* Institute for Energy and Environment, University of Strathclyde, UK.

Tan, K., al. (2007). Palm oil: Addressing issues and towards sustainable development. *Renewable and Sustainable Energy Reviews* , Article in press.

Tyson, K. S., al. (2004). *Biomass: Oil Analysis: Research Needs and Recommendations,.* NREL TP-510-34796.

UNH. (2008). *About biodiesel*. Ανάκτηση June 18, 2008, από Propel: Fueling Change: http://propelbiofuels.com/content/about_biodiesel

Van Gerpen, J. (2005). Biodiesel processing and production. *Fuel Processing Technology, 86* , 1097-1107.

Van Gerpen, J., al. (2004). *Biodiesel Production Technology.* Golden, Colorado: NREL.

Veljkovic, V. b., al. (2006). Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids. *Fuel 85* , 2671-2675.

YPAN. (2004). *First report for promotion of the use of biofuels or other renewable fuels for the transport sector in Greece for the period 2005 to 2010.* Athens: Greek Ministry of Development.

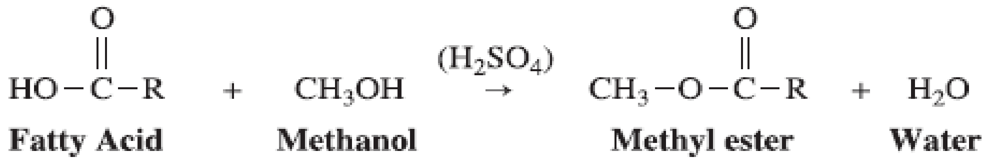
YPAN. (2006). *Second report for promotion of the use of biofuels or other renewable fuels for the transport sector in Greece for the period 2005 to 2010.* Athens: Greek Ministry of Development.

Zanzi, R., al. (2006). *Biodiesel fuel production.* Villa Clara-Cienfuegos, Cuba: Cubasolar.

Appendix I: Rate Reaction of Pretreatment Reaction

Acid Pretreatment of FFA

The acid esterification reaction for the pretreatment of FFAs is given in the figure below.



$$HO-\overset{O}{\overset{\|}{C}}-R + CH_3OH \xrightarrow{(H_2SO_4)} CH_3-O-\overset{O}{\overset{\|}{C}}-R + H_2O$$

Fig 1 - Esterification of FFAs (Van Gerpen, 2005)

This reaction can be simplified as follows:

$$FFA + MeOH \xrightarrow{H_2SO_4} ME + H_2O \tag{1}$$

This reaction can be described by a first order reaction with respect to FFA concentration

$$r = -\frac{d[FFA]}{dt} = k[FFA] \tag{2}$$

Where by k is the first order rate constant, which has units of 1/time.

The integrated first-order rate law is:

$$\ln[FFA] = -kt + \ln[FFA]_0 \tag{3}$$

$$y = -bx + c \tag{4}$$

Plots of ln[FFA] against t gives a straight line with a slope of –k.

The aim of this experiment was to determine the optimum conditions for the reduction of the FFA value of the crude vegetable oils to values less than 1% using the acid catalyst.

$$[FFA] = 1 \ \Rightarrow \ln[FFA] = 0 \tag{5}$$

$$\Rightarrow -kt + \ln[FFA]_0 = 0 \tag{6}$$

$$\Rightarrow t = \frac{-\ln[FFA]_0}{-k} = \frac{\ln[FFA]_0}{k} \tag{7}$$

Where t is the time required to reduce the FFA concentration to 1%.

The following tables give the values of the intercept $[FFA]_0$, rate constant k, and t , for the feedstocks, CPO, CPKO and COPO.

1. *Crude Palm Oil*

Table 3: 1st order rate reaction of the esterification reaction of CPO for catalyst /oil ratios 0.5%v/v and 1.0%v/v

CPO					
0.5%v/v acid					
MeOH/Oil (w/w)	**c = ln FFAo**	**k**	**$FFA_o = e^c$**	**r^2**	**$t_{y=0}$**
0,15	2,2040	0,009	9,061186	0,807	244,89
0,2	1,8390	0,043	6,290245	0,96	42,77
0,25	1,5370	0,047	4,650617	0,866	32,70
0,3	1,3980	0,047	4,047098	0,83	29,74
0,35	1,3040	0,048	3,684003	0,898	27,17
1%v/v acid					
MeOH/Oil (w/w)	**c = ln FFAo**	**k**	**$FFA_o = e^c$**	**r^2**	**$t_{y=0}$**
0,2	2,338	0,017	10,36049	0,955	137,53
0,25	1,514	0,019	4,544874	0,372	79,68
0,3	1,428	0,065	4,17035	0,838	21,97
0,35	1,213	0,057	3,36356	0,736	21,28

The following observations can be made from Table 3

- The reaction rate of the pretreatment process increased with the increase in the methanol ratio.
- The reaction rate becomes constant at higher methanol ratios.

2. *Crude Palm Kernel Oil*

Table 4: 1st order rate reaction of the esterification reaction of CPKO for catalyst /oil ratios 0.5%v/v and 1.0%v/v

CPKO					
0.5%v/v acid					
MeOH/Oil (w/w)	**c = ln FFAo**	**k**	**$FFA_o = e^c$**	**r^2**	**$t_{y=0}$**
0,15	2,8420	0,016	17,15003	0,886	177,63
0,2	2,7010	0,015	14,89462	0,847	180,07
0,25	2,6840	0,028	14,64355	0,994	95,86
0,3	2,4970	0,036	12,146	0,919	69,36
0,35	2,4360	0,041	11,42724	0,957	59,41
0,40	2,471	0,052	11,83428	0,956	47,52
0,45					
1%v/v acid					
MeOH/Oil (w/w)	**c = ln FFAo**	**k**	**$FFA_o = e^c$**	**r^2**	**$t_{y=0}$**
0,15	2,587	0,025	13,28984	0,808	103,48
0,2	2,519	0,024	12,41617	0,896	104,96
0,25	2,518	0,026	12,40376	0,947	96,85
0,3	2,433	0,036	11,39301	0,957	67,58
0,35	2,5	0,049	12,18249	0,991	51,02
0,4	1,83	0,043	6,233887	0,724	42,56
0,45					

3. *Crude Olive Kernel Oil*

Table 5: 1st order rate reaction of the esterification reaction of COKO for catalyst /oil ratios 0.5%v/v and 1.0%v/v

COKO					
0.5%v/v acid					
MeOH/Oil (w/w)	**c = ln FFAo**	**k**	**$FFA_o = e^c$**	**r^2**	**$t_{y=0}$**
0,15	2,9720	0,01	19,53094	0,961	297,20
0,2	2,9040	0,012	18,24699	0,915	242,00

0,25	2,9490	0,018	19,08686	0,981	163,83
0,3	2,7590	0,02	15,78405	0,973	137,95
0,35	2,7300	0,024	15,33289	0,961	113,75
0,40	2,651	0,026	14,1682	0,955	101,96
0,45					
1%v/v acid					
MeOH/Oil (w/w)	**c = ln FFAo**	**k**	**FFA$_o$ = e^c**	**r^2**	**t$_{y=0}$**
0,15	2,972	0,014	19,53094	0,982	212,29
0,2	2,934	0,019	18,80269	0,983	154,42
0,25	2,918	0,023	18,50424	0,999	126,87
0,3	2,814	0,027	16,67649	0,983	104,22
0,35	2,549	0,031	12,7943	0,901	82,23
0,4	2,504	0,031	12,23132	0,954	80,77
0,45	2,533	0,039	12,59122	0,961	64,95

Appendix II: Titration and Degummation Experimental Procedures

Determination of the free fatty acid contents in the feedstocks:

Description:

The process used to determine the percent of FFA in oil is called titration. Titration is basically a reaction between a catalyst (NaOH) and oil in the presence of an alcohol (usually isopropyl). Isopropyl is preferred to methanol because it will not react with the oil.

In this process, the oil is first mixed with isopropyl. Next, a mixture of Sodium hydroxide and water is added until all the FFA has reacted. This is confirmed by checking the pH of the mixture. A pH of about 9 will indicate that all of the FFA has been reacted.

Requirements:

The following items are needed to perform accurate titration.

- Three flasks (beakers) (two 20mL and one 50 mL)
- A burette
- Two pipettes (1 mL and 10 mL)
- A 0.1% NaOH solution
- Phenolphthalein solution (pH indicator solution)

Procedure:

The NaOH solution in water is prepared by diluting 1 gram of NaOH in 1000mL (1l) of distilled water.

The process for titration is as follows:

- Fill the burette with the 0.1% NaOH solution
- Place 10mL of isopropyl in a 20mL flask
- Add 1mL of vegetable oil (mix the oil thoroughly prior to drawing 1mL)
- Mix the oil with the isopropyl (using a stirrer)
- Add the pH indicator solution (usually 3 drops)
- Add (drop by drop) the 0.1% NaOH solution (from burette) into the oil/isopropyl mixture (while stirring)
- Continue to add 0.1% NaOH until a pH of 9 (blue-green color) is reached. Note the amount in mL of NaOH that was required.
- Interpret the results as presented below.

Interpretation of the results:

If:

X = the number of milliliters of NaOH solution dropped into the oil, and

L = (X+3.5) is the number of grams of NaOH required to neutralize and react one liter of oil.

Table 1 can be used to determine the FFA content of the oil.

Table 1: Titration Information

mL titration	%FFA	NaOH grams/gallon	NaOH grams/L
0	0	13.25	2.9
0.5	0.357822	15.15	3.3

1	0.715645	17.03	3.7
1.5	1.073467	18.93	4.2
2	1.431289	20.83	4.6
2.5	1.789111	22.70	5.0
3	2.146933	24.60	5.4
3.5	2.504755	26.50	5.8
4	2.862578	28.39	6.2
4.5	3.2204	30.28	6.7
5	3.578222	32.17	7.1
5.5	3.936044	34.06	7.5
6	4.293866	35.96	7.9
6.5	4.651689	37.85	8.3
7	5.009511	39.74	8.7
7.5	5.367333	41.63	9.2
8	5.725155	43.52	9.6
8.5	6.082977	45.42	10.0
9	6.4408	47.31	10.4
9.5	6.798622	49.20	10.8
10	7.156444	51.09	11.2
10.5	7.514266	52.99	11.7
11	7.872088	54.88	12.1

Reference:

- WMRC, Feasibility Report, Small Scale Biodiesel Production
- Tickell, Joshua, 2003. “From the Fryer to the Fuel Tank”, Bookmasters: Ashland, OH.

Processing of feedstock

Introduction

The industrial processing of crude oil to food-grade oil generally consists of three steps: refining (degumming and caustic refining), bleaching, and deodorization. The oils obtained after this process are known as RBD oils (refined, bleached, and deodorized). However the only processing needed for our samples in order to produce biodiesel is refining.

Refining

The refining step is designed to remove the phospholipids and free fatty acids from the crude oil. Crude soybean oil typically contains 500-700 ppm of phosphorus which corresponds to 1.5% to 2.1% phospholipids [1]. The main reason to remove these phospholipids is that some of the compounds, particularly the calcium and magnesium salts of phosphatidic and lysophatidic acids, are strong emulsifiers. If these compounds are still present during the later alkali neutralization step, they will inhibit the separation of the soaps and lower the yield of neutral oil. Phospholipids (also called phosphotides) will also react with water to form insoluble sediments that are not desirable when cooking with the oil. Refining may consists of two steps:

Degumming

This is the first step of refining. In this step, the crude oil is mixed with 1% - 3% of water and the mixture is agitated mechanically for 30-60 minutes at 70º C (158º F). This hydrates the phospholipids and gums and these hydrates are insoluble in the oil.

They can be separated by settling, filtering, or centrifuging. The phosphorus content can be lowered to 12-170 ppm by this procedure. The byproduct of water degumming has value as a feedstock for lecithin production.

A portion of the phosphatides are not hydratable by contact with water alone. The addition of citric or phosphoric acid will hydrate those remaining. Citric acid is prefered if the byproduct is to be used for lecithin. The acid hydration is accomplished by adding 0.05-0.2 wt% of concentrated (85%) phosphoric acid to crude oil, which has been heated to 60 - 85 C. The residence time varies from a few seconds to 1-2 minutes depending on the type and quality of the oil. The extent of gum removal by these techniques is related to the strength of the acid treatment.

Experiment (water and acid degummation)

- Mix oil sample with 2% (wt) of distilled water
- Agitate mixture for 10 mins at 70^{o}C.
- Add 0.1 wt% of concentrated (85%) phosphoric acid to crude oil
- agitate intensely for 1min
- let mixture to rest for 5 min (reaction)
- proceed to caustic neutralisation