ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

MSc THESIS

Hasan PEKER

THE COMPARISON OF ALTERNATIVE FUELS PRODUCED FROM SUNFLOWER AND HAZELNUT OILS BY THERMAL CRACKING AND TRANSESTERIFICATION METHODS

DEPARTMENT OF MECHANICAL ENGINEERING

ADANA, 2015

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We certify that the thesis titled above was reviewed and approved for the award of degree of the Master of Science by the board of jury on 12/01/2015

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ABSTRACT

MSc THESİS

THE COMPARİSON OF ALTERNATİVE FUELS PRODUCED FROM SUNFLOWER AND HAZELNUT OİLS BY THERMAL CRACKİNG AND TRANSESTERİFİCATİON METHODS

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ÇUKUROVA UNİVERSİTY
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Supervisor : Asst. Prof. Dr. Hasan SERİN
Year: 2015, Pages: 131
Jury : Asst. Prof. Dr. Hasan SERİN
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The overall objective of this study was to explore the utility of two different oils as a potential source of diesel fuel. Sunflower oil and hazelnut oil were selected as samples to produce alternative diesel fuel with thermal cracking and transesterification methods. İn the cracking method, sunflower oil and hazelnut oil were degraded thermally. The oil collected at optimum conditions (430-490 °C range and 1 h reaction time) was fractionated at different temperatures and fuel properties of the fractions were measured. The second method is a production facility that uses the transesterification process, methanol as an alcohol and sodium methoxide as the catalyst. Products were prepared in order to investigate fuel specifications according to ASTM and EN standards. Density, cetane number, flash point, pour point and kinematic viscosity values were determined. Fuel properties of products are found comparable with those of diesel fuel within the EN 590 Diesel Fuel standard and they were also been used as fuel in compression ignition engines.

Key Words: Engine performance, Emissions, Fuel properties, Thermal cracking, Transesterification

ÖZ

YÜKSEK LİSANS TEZİ

AYÇİÇEK VE FİNDİK YAĞİLARİNDAN İSİL PARÇALAMA VE ESTER DÖNÜŞÜM METODU İLE ÜRETİLEN ALTERNATİF YAKİTLARİN KARŞİLAŞTİRİLMASİ

Hasan PEKER

ÇUKUROVA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ
MAKİNA MÜHENDİSLİĞİ ANABİLİMDALİ

Danişman : Yrd. Doç. Dr. Hasan SERİN
Yil: 2015, Sayfa: 115
Jüri : Yrd. Doç. Dr. Hasan SERİN
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Bu çalişmanin genel amaci 2 farkli yağin dizel yakit olarak kullanim potansiyelini keşfetmektir. Çalişmada ayçiçek ve findik yağlari'na transesterifikasyon ve termal cracking metodlari uygulanmiştir. Cracking metodunda yağlar yüksek sicakliklarda parçalanmiş, transesterifikasyon metodunda ise alkol ve katalizör ile tepkimeye girdirilmiştir. Sonuçlar ASTM ve EN standartlarina göre değerlendirilmiş. Çalişmada ürünlerin; setan sayisi, parlama noktasi, akma noktasi ve kinematik viskoziteleri ölçülmüştür. Çalişma sonunda ürünlerin EN590 Dizel Yakit standartlarina göre uygunluğu bulunmuş olup ayrica elde edilen alternatif yakitlar dizel bir motorda denenmiştir.

Anahtar Kelimeler: Motor performansi, Emisyonlar, Yakit özellikleri, Termal parçalanma, Transesterifikasyon

ACKNOWLEDGEMENTS

İ gratefully thank to my supervisor Assistant. Prof. Dr. Hasan SERİN, for his supervision guidance, encouragements, patience, motivation, useful suggestions and his valuable time spared for the development of this work.

İ would like to thank all my research assistant Ceyla GÜNGÖR and Automotive Laboratory staff of Çukurova University for their continuous support.

Last, special thanks to my family for their absolute support.

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LIST OF ABBREVIATIONS AND NOMENCLATURE

MSW : Municipal Solid Waste
ESCAP : United Nations Economicand Social Commission for Asia and Pasific
ASEAN : Association of Southeast Asian Nations
MOEF : Ministry of Environment and Forestry
SWMP : Solid Waste Master Plan (SWMP)
UNEP : United Nations Environmental Programme
WHO : World Health Organization
AFR : Africa Region
EAP : East Asia and Pacific Region
ECA : Europe and Central Asia Region
LCR : Latin America and the Caribbean Region
MENA : Middle East and North Africa Region
OECD : Organisation for Economic Co-operation and Development
SAR : South Asia Region
GHG : Greenhouse Gas
ASTM : American Society for Testing and Materials
MUNWP : Municipal Waste Plastic Fuel
MEDWP : Medical Waste Plastic Fuel
PET : Polyethylene terephthalate
HDPE : High Density Polyethylene
LDPE : Low Density Polyethylene
PP : Polypropylene
PS : Polystyrene
PVC : Polyvinyl Chloride
GC/MS : Gas Chromatography and Mass Spectrometer
FT-IR : Furrier Transform İnfrared Spectroscopy
DSC : Differential Scanning Calorimeter
EPA : US Environmental Protection Agency
PE : Polyethylene

US-Y : Zeolite catalyst of ultrastable Y-type

LDO : Light Diesel Oil

HSD : High Speed Diesel

AV : Acid Value

GL : Gas-Liquid Chromatography

FİD : Flame Ionization Detector

Tc(t) : The incineration cycle time

Do(t) : Total diesel oil consumed per cycle

WPE : Waste polyethylene

LP : Light phase

HP : Heavy phase

D : Diesel fuel

EN : European standards

GC/MS : Gas Chromatography/Mass Spectrometry

C&D : Construction and Demolition waste

SOC : Sunflower oil's experimental result's by using thermal cracking method

SOT : Sunflower oil's experimental result's by using transesterification method

HOC : Hazelnut oil's experimental result's by using thermal cracking method

HOT : Hazelnut oil's experimental result's by using transesterification method

1. INTRODUCTION

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial. One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine. With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as fuel and diesel fuels and diesel engines evolved together. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations. Recently, because of increases in crude oil prices, limited resources of fossil oil and environmental concerns there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by CO2. In a particular case, such as the emission of pollutants in the closed environments of underground mines, biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens.

Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides. Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats contain small amounts of free fatty acids and water. The free fatty acid and water contents have significant efectson the transesterification of glycerides with alcohols using alkaline or acid catalysts. They also interfere with the separation of fatty acid esters and glycerol. Considerable research has been done on vegetable oils as diesel fuel. That research included palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil and tung oil. Animal fats, although mentioned frequently, have not been studied to the same extent as vegetable oils. Some methods applicable to vegetable oils are not applicable to animal fats because of natural property differences. Oil from algae, bacteria and fungi also have

been investigated. Microalgae have been examined as a source of methyl ester diesel fuel. Terpenes and latexes also were studied as diesel fuels. Some natural glycerides contain higher levels of unsaturated fatty acids. They are liquids at room temperature. Their direct uses as biodiesel fuel is precluded by high viscosities. Fats, however, contain more saturated fatty acids.

They are solid at room temperature and cannot be used as fuel in a diesel engine in their original form.

Because of the problems, such as carbon deposits in the engine, engine durability and lubricating oil contamination, associated with the use of oils and fats as diesel fuels, they must be derivatized to be compatible with existing engines. Four primary production methodologies for producing biodiesel have been studied extensively. This paper reviews the technologies starting with the direct use or blending of oils, continuing with microemulsion and pyrolysis and finishing with an em- phasis on the current process of choice, transesterification.

In petroleum geology and chemistry, cracking is the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of catalysts. Cracking is the breakdown of a large alkane into smaller, more useful alkanes and alkenes. Simply put, hydrocarbon cracking is the process of breaking a long-chain of hydrocarbons into short ones. More loosely, outside the field of petroleum chemistry, the term "cracking" is used to describe any type of splitting of molecules under the influence of heat, catalysts and solvents, such as in processes of destructive distillation or pyrolysis. Fluid catalytic cracking produces a high yield of gasoline and LPG, while hydrocracking is a major source of jet fuel, Diesel fuel, naphtha, and LPG .

Since the early 1980s, the demand for heavy oil fuels from petroleum has decreased steadily. The rise of demand for the light fuels particularly gasoline is important to extract much useful materials from crude oil.

About 94% of the projected growth in petroleum consumption stems from increased consumption of light products, including gasoline, diesel, kerosene, jet fuel, and liquefied petroleum gas, which are more difficult and costly to produce than heavy products. Refined product prices are expected to increase and are determined by crude oil costs, refining process costs, marketing costs, and taxes. The thermal cracking process which subjected heavy fuels to both pressure and intense heat is physically breaking the large molecules into smaller ones to produce additional gasoline and distillate fuels by the use of high temperature without the aid of a catalyst. Thermal cracking processes are commonly used to convert petroleum residual oil into distillable products, although thermal cracking processes as used in the early refineries.

In assessing the effect of operating conditions on thermal cracking product, the use of an adequate experimental design is particularly important. The primary goal in scientific research is usually to show the statistical significance of an effect that a particular factor exerts on the dependent variables of interest.

A very fundamental part of statistics is concerned with the design of experiments to determine cause-effect relationship, the relationship with some response of the system is very important. For solving the problem by statistical methods, a plan of experiment must be set up that includes the method of collecting the data, the size of sample and the method of solution of problem. Response surface methodology (RSM), fractional factorial design, provides a systematic and efficient experimental strategy for studying the parameters effect using statistical methods. It is well suited for the study of main and interaction effects of factors on the products. The three level factorial design is certainly a possible choice by an experimenter who is concerned about curvature in the response function.

The basic of this study is comparing emission performance values of the sunflower oil and hazelnut oil produced by thermal cracking method and biodiesel sunflower oil and hazelnut oil. In the study same amount of products are used for both process and in the different reactors for processes.

2. LITERATURE REVIEW

Transesterification of a vegetable oil was conducted as early as 1853 by E. Duffy and J. Patrick, four decades before the first diesel engine became functional. Rudolf Diesel's prime model, a single 10 ft (3 m) iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany, on 10 August 1893 running on nothing but peanut oil. In remembrance of this event, 10 August has been declared "International Biodiesel Day". It is often reported that Diesel designed his engine to run on peanut oil, but this is not the case. Diesel stated in his published papers, "at the Paris Exhibition in 1900 (*Exposition Universelle*) there was shown by the Otto Company a small Diesel engine, which, at the request of the French government ran on arachide (earth-nut or pea-nut) oil (see biodiesel), and worked so smoothly that only a few people were aware of it. The engine was constructed for using mineral oil, and was then worked on vegetable oil without any alterations being made. The French Government at the time thought of testing the applicability to power production of the Arachide, or earth-nut, which grows in considerable quantities in their African colonies, and can easily be cultivated there." Diesel himself later conducted related tests and appeared supportive of the idea. In a 1912 speech Diesel said, "the use of vegetable oils for engine fuels may seem insignificant today but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time." Despite the widespread use of petroleum-derived diesel fuels, interest in vegetable oils as fuels for internal combustion engines was reported in several countries during the 1920s and 1930s and later during World War II. Belgium, France, Italy, the United Kingdom, Portugal, Germany, Brazil, Argentina, Japan and China were reported to have tested and used vegetable oils as diesel fuels during this time. Some operational problems were reported due to the high viscosity of vegetable oils compared to petroleum diesel fuel, which results in poor atomization of the fuel in the fuel spray and often leads to deposits and coking of the injectors, combustion chamber and valves.

Attempts to overcome these problems included heating of the vegetable oil, blending it with petroleum-derived diesel fuel or ethanol, pyrolysis and cracking of the oils.

On 31 August 1937, G. Chavanne of the University of Brussels (Belgium) was granted a patent for a "Procedure for the transformation of vegetable oils for their uses as fuels" (fr. "Procédé de Transformation d'Huiles Végétales en Vue de Leur Utilisation comme Carburants") Belgian Patent 422,877.

This patent described the alcoholysis (often referred to as transesterification) of vegetable oils using ethanol (and mentions methanol) in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols. This appears to be the first account of the production of what is known as "biodiesel" today.

More recently, in 1977, Brazilian scientist Expedito Parente invented and submitted for patent, the first industrial process for the production of biodiesel. This process is classified as biodiesel by international norms, conferring a "standardized identity and quality. No other proposed biofuel has been validated by the motor industry." As of 2010, Parente's company Tecbio is working with Boeing and NASA to certify bioquerosene (bio-kerosene), another product produced and patented by the Brazilian scientist.

Research into the use of transesterified sunflower oil, and refining it to diesel fuel standards, was initiated in South Africa in 1979. By 1983, the process for producing fuel-quality, engine-tested biodiesel was completed and published internationally.[44] An Austrian company, Gaskoks, obtained the technology from the South African Agricultural Engineers; the company erected the first biodiesel pilot plant in November 1987, and the first industrial-scale plant in April 1989 (with a capacity of 30,000 tons of rapeseed per annum).

Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, Germany and Sweden. France launched local production of biodiesel fuel (referred to as *diester*) from rapeseed oil, which is mixed into regular diesel fuel at a level of 5%, and into the diesel fuel used by some captive fleets (e.g. public transportation) at a level of 30%.

Renault, Peugeot and other manufacturers have certified truck engines for use with up to that level of partial biodiesel; experiments with 50% biodiesel are underway.

During the same period, nations in other parts of the world also saw local production of biodiesel starting up: by 1998, the Austrian Biofuels Institute had identified 21 countries with commercial biodiesel projects. 100% biodiesel is now available at many normal service stations across Europe.

The first thermal cracking process was developed around 1913. Distillate fuels and heavy oils were heated under pressure in large drums until they cracked into smaller molecules with better antiknock characteristics.

However, this method produced large amounts of solid, unwanted coke. This early process has evolved into the following applications of thermal cracking: visbreaking, steam cracking, and coking [13].

HOSSAIN, A.B.M.S. and A.N. BOYCE, studied on comparison of the optimum conditions of alkaline-catalyzed transesterification process for biodiesel production from pure sunflower cooking oil (PSCO) and waste sunflower cooking oil (WSCO) through transesterification process using alkaline catalysts.

To obtain a high quality biodiesel fuel that comply the specification of standard methods (ASTM D 6751 & EN 14214), some important variables such as volumetric ratio, types of reactants and catalytic activities were selected. The highest approximately 99.5% biodiesel yield acquired under optimum conditions of 1:6 volumetric oil-to-methanol ratio, 1% KOH catalyst at 40ºC reaction temperature and 320 rpm stirring speed. Result showed that the biodiesel production from PSCO and WSCO exhibited no considerable differences. The research demonstrated that biodiesel obtained under optimum conditions from PSCO &WSCO was of good quality and could be used as a diesel fuel which considered as renewable energy and environmental recycling process from waste oil after frying. The optimum conditions for biodiesel production from WSCO & PSCO have been studied. Result shows optimal condition of sunflower oil biodiesel productions are 1:6 volumetric oil-to-methanol molar ratio, 1 wt. %KOH at 400C reaction temperature.

This study has provided evidence that waste cookin sunflower oil may be employed as a substantial source of biodiesel as fuel in diesel engines. Because, the produced biodiesel is of good quality within the array of standard method specifications and the production yield is apt. up to approximately 99% under optimum conditions.

Moreover, this research represented that the production of biodiesel from PSCO & WSCO has no significant differences. Advance research is ongoing to reduce the production cost by developing a method to decrease the emulsification during base catalytic transesterification and aqueous-washing of the product and readily recovery of glycerin byproduct. Biodiesel from used cooking sunflower oil could be used as a diesel fuel which considered as renewablenergy and environmental recycling process from waste oil after frying [14].

Mojtaba Mansourpoor and Dr. Ahmad Shariati studied on the sunflower oil. The batch reaction kinetic experiments were employed to optimize various parameters in the production of the methyl esters. The transesterification reactions are performed in various conditions to determine the optimum conditions of transesterification. Two liter of sunflower oil poured in the reactor and allowed to equilibrate to the temperature of reaction at 290 rpm. Hot water circulated in the jacket of the reactor provided the necessary heat for the reaction.

Variable quantities of catalyst were dissolved in various amount of methanol as described in each test. After attaining a required temperature, the potassium methoxide was added to the reactant and was maintained for 2 hours for completion of the reaction.

After 2 hours the transesterification reaction was completed and mixture was withdrawn from the reactor and poured in the funnel separator to separates biodiesel from glycerol. Separation of two phases which is performed by gravity requires at least 4 hours. Glycerol and biodiesel have a deep red and bright yellow color. After separation of biodiesel, it should be washed out from impurities and unreacted agents. The biodiesel was washed out 10 times. At the first time, washing of the biodiesel should be done slowly and carefully to avoid soap formation. One liter of warm distillated water was used per 1 liter of biodiesel.

At the next times, the washing procedure can be done more quickly until the color of water shifts to white. Finally, biodiesel was dried completely by silica jell. Physical properties of the biodiesel which were produced in the optimum conditions were measured in the Abadan's oil refinery lab and shown in Table 1. These results are tabulated and compared with ASTM standard and petro-diesel. It is found which results are drawn on the ASTM standard and compared well with petro-diesel. It was seen that the flash point of biodiesel is 170 when that of petro-diesel is about 60 which helps the transportation of biodiesel but it should be blend with petro-diesel for better combustion in engine.

Kinematic viscosity of biodiesel at 40, were higher than that of petro-diesel and is 3.6 cSt. This biodiesel has a copper strip corrosion of 1a which indicate that this fuel is not corrosive. Heating value of biodiesel was 39.58 MJ/Kg which is less than that of petro-diesel but only 9 percent. The reason for the lower heating value of biodiesel is the presence of chemically bound oxygen in vegetable oils which lowers their heating values.In this work, biodiesel has a cetane index 49.2 which is higher than that of ASTM.

It was found that biodiesel had a cloud point higher than petro-diesel because biodiesel produced from vegetable oils which have FFA that these free fatty acids cause a higher cloud point of biodiesel than Petro diesel. Whatever saturated fatty acids be higher in the oil, the produced biodiesel has a poorer cloud point. Carbon residue of biodiesel was lower than that of petro-diesel which is about 0.002 wt%. Biodiesel has a negligible amount of sulphur relative to petro-diesel. Methanol was produced from corn and corn has sulphur; hence, biodiesel has a negligible amount of sulphur [15].

M.Thirumarimurugan studied process Conditions Preheating of oil 50 C, Pressure 1 atm, The commencement of the production process depends upon the type of oil employed, and whether it is fresh oil used oils from the catering industry. In the case of the latter, a titration process takes place, the result of which determines the proportions of methanol to potassium hydroxide used in the preparation of the reaction catalyst. The following are the steps required for the production of Biodiesel. Dissolve 1 gram of KOH in 1 liter of distilled water.

Dissolve 1 ml of waste vegetable oil into 10ml isoprophyl alcohol. With an eyedropper, set the pH of WVO to 8-9 by adding NaOH one milliliter at a time. You will see an eventual rise in the ph level. Record the quantity of KOH solution added until the colour of the oil changes pink and holds for at least 5 seconds (This represents a pH of between 8 and 9). Burette solution: KOH solution - 1000ppmPipette solution: 1 ml of used vegetable Solvent: 10 ml iso propyl alcohol Indicator: Phenolphthalein. End point: Appearance of pink color. Carefully pour the KOH solution into 100 ml methanol. Agitate the mixture until the KOH is completely dissolved in the methanol. The potassium methoxide solution prepared is mixed with oil. The residue is heated in between 120F to 130F after which it is mixed well using a stirrer at 300 rpm. Continue mixing the contents. Carefully pour the potassium methoxide and shake vigorously for 15 minutes. After mixing the liquid, it is allowed to cool down.

After the cooling process, the bio fuel is found floating on the top while the heavier glycerine is found at the bottom. The glycerine is easily separated by allowing it to drain out from the bottom. In this way pure Bio Diesel is prepared. Allow the glycerin to settle Settle the mixture overnight. The successful chemical reaction between the oil, alcohol, and the catalyst will have broken down the oil into several layers.

The top layer will be biodiesel, chemically called an Ester, the next layer may contain soap, and the bottom layer will be glycerine. Biodiesel and glycerin will separate due to density difference. Glycerin and unreacted catalyst will sink to the bottom and can be easily drained. After separation of biodiesel it must be washed with hot water to remove unreacted methanol and potassium hydroxide. In this process, the waste vegetable oil is filtered to remove all the food particles. This process generally involves warming up the liquid a little. After warming up the liquid, it is filtered with the use of a cotton cloth. All the water contained in the residual gangue is removed which makes thenreaction faster. The water is easily removed by boiling the liquid at 50 C for sometime. Fuel properties analysis was carried out according to ASTM Biodiesel Standards.

Fuel characteristics of biodiesel which were tested include dynamic viscosity at 40°C (eta), kinematic viscosity at 40°C (ny), density at 40°C (Rho), , flash point (°C), cloud point (°C), specific gravity at 60°F (kg/1), Carbon residue, Acid value and Calorific value. Thus Bio Diesel was prepared from used vegetable oil, the properties resembled closely to that of commercial Diesel. Hence it can be used as an alternate for diesel. It is relatively economic than diesel and emits less pollutants.

It can be used for Vehicular use, Railway usage, as heating oil when blended with other fuel oil in proportion. The experimental work carried out in this project shows that bio-diesel of acceptable quality can be produced on a small scale from a number of low-cost raw materials. However, the search for alternative feed-stocks needs to be continued. More research on the esterification of used vegetable oil is needed, to establish process requirements for high yield and quality, and to find ways of improving its low-temperature properties so that a higher proportion could be included in bio-diesel blends. The ester yields obtained from all the oils used in these trials have been low in comparison with those obtained from refined vegetable oils in existing large-scale plants. Rising of yields has a significant effect on the economics of bio-diesel production.

Modern technology is giving very high yields; it needs to be demonstrated that the same can be achieved with other raw materials, whereas more information is required on alternative uses for small amounts of glycerol. On this scale, the investment required to produce pharmaceutical grade glycerine could not be warranted. Uses that require a minimum amount of additional plant investment, but add maximum value to the produce, need to be examined.

When a use for the glycerol has been decided a plant for the removal of methanol and any further processing of the glycerol can be specified. In this work, biodiesel was prepared using alkali catalyzed method where the raw material used was waste sunflower oil used for cooking. Biodiesel can also be manufactured using non-edible oil such as pongamia oil as raw material. Further studies can also be carried out by modifying the catalysis. i.e. by using either acid-base or algae as the catalyst. Increased utilization of renewable bio fuels results in significant microeconomic benefits to both the urban and rural sectors, and the balance of trade.

The chief advantage of Biodiesel for agriculture is cost minimisation. The expression "oil well on your farm" means in fact a higher local value added. Oil plants renew themselves every year. In any event, the focus is not only on providing emergency supplies but also to a large extent on reducing the pollution load produced by day-to-day operations. The flexibility of Biodiesel plants is also a response to another energy target: the creation of manageable regional supply systems. The production of biodiesel is relevant for developing countries where the demand of transport fuels is going to increase to a great extent. A high-quality research is promoted in support of a sustainable development of society covering subjects of strategic importance to economic and social development and aiming a greater energy self-sufficiency and security in addition to environmental (decreasing the air pollution from transportation and mitigating greenhouse gas emissions) benefits.

The biodiesel fuel production has gained importance for its ability to replace fossil fuels, its environmental benefits and the fact that it is a renewable source of energy. Since the direct usage of vegetable oils as biodiesel is impractical, many processes have been developed to convert them into a suitable form. Pyrolysis and microemulsification are not satisfactory and hence only the transesterification process is accepted for large scale production of biodiesel [16].

F. Behar * and M. Vandenbroucke were aimed to determine the apparent rate constants for the *n*-C_{25} thermal cracking and, then, to study pressure effect on these rate constants so as to evaluate *n*-alkane stability in high-pressure/high-temperature deep prospects. Pyrolyses were carried out in anhydrous closed system (gold vessels) during times ranging from 1 to 360 h under isothermal conditions (325−425 °C) and various pressures (120, 400, and 800 bar) in the range of those occurring in petroleum systems.

Results show that degradation of *n*-C_{25} follows a first-order kinetics under isothermal conditions at 120 bar. The main chemical class produced along increasing severity is the saturated hydrocarbons ranging from C_{10} to C_{22} (80 wt %). The gas contribution is very low (<2 wt %) up to 85 wt % conversion. On the basis of the linearity of the Arrhenius plot, accurate kinetic parameters were calculated (E = 68.2 kcal/mol and $A = 6.1 \times 10^{17}$ s^{-1}).

An extrapolation of these kinetic parameters to geological conditions shows that *n*-C_{25} begins to be measurably degraded above 180 °C for residence times higher than 10 million years. This means that a reservoired oil enriched in *n*-alkanes will be stable in very high temperature conditions. When this oil begins to degrade, condensate is mainly produced and will be measurably degraded only above 200°C during similar residence times.

Pressure effect increases the thermal degradation rate of *n*-C_{25} between 120 and 400 bar then decreases it between 400 and 800 bar down to its value at 120 bar. These results are in a good agreement with those already published (Fabuss, B. M.; *et al*. In *Advances in Petroleum Chemistry and Refining*; Mc Ketta, J., Jr., Ed.; Wiley and Sons: New York, 1964; Vol. 5, Chapter 4, pp 156−201) for thermal degradation of *n*-C_6 and *n*-C_7 saturated hydrocarbons in the same range of pressure. Nevertheless, the relative increase of the degradation rate for *n*-C_{25} reaching a maximum around 1.7 for 400 bar, i.e., for an average depth of 4000 m and a temperature of 140 °C, the pressure effect is not sufficient to allow a measurable degradation in these geological conditions [17].

M. Cooper and J.E. Shepherd were studied on storable liquid hydrocarbon fuels such as JP-10 or Jet A. However, without significant advances in initiation technology, such fuels are not optimal for PDE operation due to the high energy input required for direct initiation of a detonation and the long de∞agration to detonation transition times associated with low-energy initiators.

In an effort to utilize such conventional liquid fuels and still maintain the performance of the lighter and more sensitive hydrocarbon fuels, various fuel modification schemes such as thermal cracking, catalytic cracking, and partial oxidation have been investigated. We have examined the decomposition of JP-10 through thermal and catalytic cracking mechanisms at elevated temperatures using a benchtop reactor system. The system hasthe capability to vaporize liquid fuel at precise ∞ow rates while maintaining the flow path at elevated temperatures and pressures for extended periods of time.

The catalytic cracking tests were completed utilizing common industrial zeolite catalysts installed in the reactor. A gas chromatograph with a capillary column and ∞ame ionization detector, connected to the reactor output, is used to speciate the reaction products. The conversion rate and product compositions were determined as functions of the fuel metering rate, reactor temperature, system backpressure, and zeolite type. An additional study was carried out to evaluate the feasibility of using pre-mixed rich combustion to partially oxidize JP-10. A mixture of partially oxidized products was initially obtained by rich combustion in JP-10 and air mixtures for equivalence ratios between 1 and 5. Following the first burn, air was added to the products, creating an equivalent stoichiometric mixture. A second burn was then carried out. Pressure histories and schlieren video images were recorded for both burns. The results were analyzed by comparing the peak and final pressures to idealized thermodynamic predictions [18].

JOHN F. GEYER and S. NEMAT-NASSER were studied, a free edge of a glass plate heated to a uniform temperature, was brought in contact with a liquid bath cooled by dry ice. The thermal contraction of the boundary layer produced interacting tension cracks. When no initial cracks existed, a large amount of potential energy was released in the formation of a few cracks which extended in a dynamic manner beyond the thermal layer. To prevent this type of cracking, initial cracks were formed before thermally inducing crack growth. This resulted in stable crack growth which qualitatively agreed well with the previously developed theory. The quantitative comparison was also reasonably good [19].

Kumar and Singh involved that waste high density polyethylene was pyrolyzed in a batch reactor at a temperature of 400 ºC to 550 ºC at a heating rate of 20 ºC/min. The effect of pyrolytic temperature and holding time on the reaction time and yield of liquid product, char, and gaseous product were studied. The fuel properties of the oil (obtained at a temperature of 450 ºC from pyrolysis of waste HDPE) such as kinematic viscosity, flash point, fire point, cloud point, pour point, specific gravity, and water content were determined using standard test methods. The chemical compositions of the waste HDPE pyrolytic oil were investigated using FT-IR and GC/MS. The liquid yield is highest at 450 °C.

Highly volatile products are obtained at low temperature. The products obtained at 500 °C and 550 °C are viscous liquid and wax and the product obtained at 600 °C is only wax. Liquid yield increases as the holding time increases from 1 hr to 4 hr at temperatures from 400 °C to 450 °C, but as the holding time increases from 4 hr to 6 hr, the liquid yield decreases. Reaction time decreases with an increase in temperature. It has been shown that a simple batch pyrolysis method can convert waste HDPE to liquid hydrocarbon products with a significant yield, which varies with temperature [20].

3. MATERIAL AND METHOD

3.1. Bıodıesel

3.1.1. Introductıon

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting vegetable oil or animal fat with alcohol and the catalyst. Biodiesel is miscible in diesel fuel, and can be easily blended with diesel fuel with minor or no modifications to the engine and fuel system. According to EU guidelines the consumption of bio-fuels for road transportation should represent 20% of the total fuel consumption by 2020 and the use of bio-fuels will be stimulated by environmental aspects. For these reasons, biodiesel has become a popular topic in energy sources. The most common way to produce biodiesel is the transesterification method, which refers to a catalyzed chemical reaction involving vegetable oil and alcohol to yield fatty acid alkylesters (i.e., biodiesel) and glycerol. The reaction requires a catalyst, usually a strong base, such as sodium and potassium hydroxide or sodium methylate. A catalyst is usually used to improve the reaction rate and the yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. Especially methanol is used as alcohol because of its low cost and its physical and chemical advantages. Methanol can quickly react with vegetable oil and NaOH can easily dissolve in it. To complete a transesterification reaction stoichiometrically, a 3:1 molar ratio of alcohol to
triglycerides is necessary. In practice, the ratio needs to be higher to drive the equilibrium to amaximum ester yield. The transesterification conditions and biodiesel properties of RC oil were studied. It has been concluded that the blends of RC biodiesel and diesel fuel up to approximately 40% of RC biodiesel meet most of the specifications of EN590. An optimization of transesterification of RC oil using central composite rotational design (CCRD) and response surface modeling method (RSM) has been reported by authors.

On the other hand, technical process and production cost of biodiesel plants from castor bean oil through a transesterification reaction using ethanol was studied. It has been concluded that the castor bean oil is more expensive than the conventional ones used to produce biodiesel.

RC is cultivated for the seeds which yield fast-drying, non-yellowing oil, used mainly in industry and medicine. RC oil is critical to many industrial applications because of its unique ability to withstand high and low temperatures.

It is used in coating fabrics and other protective coverings, in the manufacture of highgrade lubricants, transparent typewriter and printing inks, in textile dyeing (when converted into sulfonated Castor Oil or Turkey-Red Oil, for dyeing cotton fabrics with alizarine), in leather preservation.

Hydrogenated oil is utilized in the manufacture of waxes, polishes, carbon paper, candles and crayons. 'Blown Oil' is used for grinding lacquer paste colors, while when it is hydrogenated and sulfonated it can be used for preparation of ointments. Castor Oil Pomace, the residue after crushing, is used as a high-nitrogen fertilizer. Previous studies on castor oil suggest that its uniquely high level of the hydroxy fatty acid ricinoleic acid may impart increased lubricity to the oil and its derivatives as compared to other vegetable oils.

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3.1.2. Advantages Of Bıodıesel

3.1.2.1. Cost Benefit

As of now, biofuels cost the same in the market as gasoline does. However, the overall cost benefit of using them is much higher. They are cleaner fuels, which means they produce fewer emissions on burning. Biofuels are adaptable to current engine designs and perform very well in most conditions. This keeps the engine running for longer, requires less maintenance and brings down overall pollution check costs. With the increased demand of biofuels, they have a potential of becoming cheaper in future as well. So, the use of biofuels will less of a drain on the wallet.

3.1.2.2. Easy To Source

Gasoline is refined from crude oil, which happens to be a non-renewable resource. Although current reservoirs of gas will sustain for many years, they will end sometime. Biofuels are made from many different sources such as manure, waste from crops and plants grown specifically for the fuel.

3.1.2.3. Renewable

Most of the fossil fuels will expire and end up in smoke one day. Since most of the sources like manure, corn, switchgrass, soyabeans, waste from crops and plants are renewable and are not likely to run out any time soon, making the use of biofuels efficient in nature. These crops can be replanted again and again.

3.1.2.4. Reduce Greenhouse Gases

Fossil fuels, when burnt, produce large amount of greenhouse gases i.e. carbon dioxide in the atmosphere. These greenhouse gases trap sunlight and cause planet to warm. The burning of coal and oil increases the temperature and causes global warming. To reduce the impact of greenhouse gases, people around the world are using biofuels. Studies suggests that biofuels reduces greenhouse gases up to 65 percent.

3.1.2.5. Economic Security

Not every country has large reserves of crude oil. For them, having to import the oil puts a huge dent in the economy. If more people start shifting towards biofuels, then the dependence on the imports will decrease. More jobs will be created with a growing biofuel industry, which keeps our economy secure.

3.1.2.6. Reduce Dependance on Foreign Oil

While locally grown crops has reduce the nation's dependance on fossil fuels, many experts believe that it will take a long time to solve our energy needs. As prices of crude oil is touching sky high, we need some more alternative energy solutions to reduce our dependance on fossil fuels.

3.1.2.7. Lower Levels of Pollution

Since biofuels can be made from renewable resources, they cause lesser pollution to the planet. However, that is not the only reason why the use of biofuels is being encouraged. They release lower levels of carbon dioxide and other emissions when burnt, which means they pollute the environment in lesser amounts. Although the production of biofuels creates carbon dioxide as a byproduct, it is frequently used to grow the plants that will be converted into the fuel. This allows it to become something close to a self sustaining system.

3.1.3. Dısadvantages Of Bıodıesel

3.1.3.1. High Cost of Production

Even with all the benefits associated with biofuels, they are quite expensive to produce in the current market. As of now, the interest and capital investment being put into biofuel production is fairly low but it can match demand. If the demand increases, then increasing the supply will be a long term operation, which will be quite expensive. Such a disadvantage is still preventing the use of biofuels from becoming more popular.

3.1.3.2. Monoculture

Monoculture refers to practice of producing same crops year after year, rather than producing various crops through a farmer's fields over time. While, this might be economically attractive for farmers but growing same crop every year may deprive the soil of nutrients that are put back into the soil through crop rotation.

3.1.3.3. Use of Fertilizers

As biofuels are produced from crops and these crops need fertilizers to grow better. The downside of using fertilizers is that they can have harmful effects on surrounding environment and may cause water pollution. Fertilizers contain nitrogen and phosphorus. They can be washed away from soil to nearby lake, river or pond.

3.1.3.4. Shortage of Food

Biofuels are extracted from plants and crops that have high levels of sugar in them. However, most of these crops are also used as food crops. Even though waste material from plants can be used as raw material, the requirement for such food crops will still exist. It will take up agricultural space from other crops, which can create a number of problems. Even if does not cause an acute shortage of food, it will definitely put pressure on the current growth of crops. One major worry being faced by farmers is that the growing use of biofuels may just mean a rise in food prices as well.

3.1.3.5. Industrial Pollution

The carbon footprint of biofuels is lesser than traditional forms of fuel when it is burnt. However, the process with which they are produced makes up for that. Production is largely dependent on lots of water and lots of oil.

Large scale industries meant for churning out biofuel are known to emit large amounts of emissions and cause small scale water pollution as well. There is also heavy soil erosion caused in areas that are meant only for growth of raw materials. Unless more efficient means of production are put into place, the overall carbon emission does not get a very big dent in it.

3.1.3.6. Water Use

Large quantities of water are required to irrigate the biofuel crops and it may impose strain on local and regional water resources, if not managed wisely. In order to produce corn based ethanol to meet local demand for biofuels, massive quantities of water are used that could put unsustainable pressure on local water resources.

3.1.3.7. Future Rise in Price

Current technology being employed for the production of biofuels is not as efficient as it should be. Scientists are engaged in developing better means by which we can extract this fuel. However, the cost of research and future installation means that the price of biofuels will see a significant spike. As of now, the prices are comparable with gasoline and are still feasible. Constantly rising prices may make the use of biofuels as harsh on the economy as the rising gas prices are doing right now.

3.1.4. Applıcatıons

Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most injection pump diesel engines. New extreme high-pressure (29,000 psi) common rail engines have strict factory limits of B5 or B20, depending on manufacturer.

Biodiesel has different solvent properties than petrodiesel, and will degrade natural rubber gaskets and hoses in vehicles (mostly vehicles manufactured before 1992), although these tend to wear out naturally and most likely will have already been replaced with FKM, which is nonreactive to biodiesel. Biodiesel has been known to break down deposits of residue in the fuel lines where petrodiesel has been used. As a result, fuel filters may become clogged with particulates if a quick transition to pure biodiesel is made. Therefore, it is recommended to change the fuel filters on engines and heaters shortly after first switching to a biodiesel blend.

3.1.4.1. Distribution

Since the passage of the Energy Policy Act of 2005, biodiesel use has been increasing in the United States. In the UK, the Renewable Transport Fuel Obligation obliges suppliers to include 5% renewable fuel in all transport fuel sold in the UK by 2010. For road diesel, this effectively means 5% biodiesel (B5).

3.1.4.2. Vehicular use and manufacturer acceptance

In 2005, Chrysler (then part of DaimlerChrysler) released the Jeep Liberty CRD diesels from the factory into the American market with 5% biodiesel blends, indicating at least partial acceptance of biodiesel as an acceptable diesel fuel additive. In 2007, DaimlerChrysler indicated its intention to increase warranty coverage to 20% biodiesel blends if biofuel quality in the United States can be standardized.

The Volkswagen Group has released a statement indicating that several of its vehicles are compatible with B5 and B100 made from rape seed oil and compatible with the EN 14214 standard. The use of the specified biodiesel type in its cars will not void any warranty.

Mercedes Benz does not allow diesel fuels containing greater than 5% biodiesel (B5) due to concerns about "production shortcomings".

Any damages caused by the use of such non-approved fuels will not be covered by the Mercedes-Benz Limited Warranty.

Starting in 2004, the city of Halifax, Nova Scotia decided to update its bus system to allow the fleet of city buses to run entirely on a fish-oil based biodiesel. This caused the city some initial mechanical issues, but after several years of refining, the entire fleet had successfully been converted. In 2007, McDonalds of UK announced it would start producing biodiesel from the waste oil by product of its restaurants. This fuel would be used to run its fleet.

The 2014 Chevy Cruze Clean Turbo Diesel, direct from the factory, will be rated for up to B20 (blend of 20% biodiesel / 80% regular diesel) biodiesel compatibility.

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3.1.4.3. Railway usage

British train operating company Virgin Trains claimed to have run the UK's first "biodiesel train", which was converted to run on 80% petrodiesel and 20% biodiesel.

The Royal Train on 15 September 2007 completed its first ever journey run on 100% biodiesel fuel supplied by Green Fuels Ltd. His Royal Highness, The Prince of Wales, and Green Fuels managing director, James Hygate, were the first passengers on a train fueled entirely by biodiesel fuel. Since 2007, the Royal Train has operated successfully on B100 (100% biodiesel).

Similarly, a state-owned short-line railroad in eastern Washington ran a test of a 25% biodiesel / 75% petrodiesel blend during the summer of 2008, purchasing fuel from a biodiesel producer sited along the railroad tracks. The train will be powered by biodiesel made in part from canola grown in agricultural regions through which the short line runs.

Also in 2007, Disneyland began running the park trains on B98 (98% biodiesel). The program was discontinued in 2008 due to storage issues, but in January 2009, it was announced that the park would then be running all trains on

biodiesel manufactured from its own used cooking oils. This is a change from running the trains on soy-based biodiesel.

In 2007, the historic Cog Railways added the first biodiesel locomotive to its all-steam locomotive fleet. The fleet has climbed up the Mount Washington in New Hampshire since 1868 with a peak vertical climb of 37.4 degrees.

3.1.4.4. Aircraft use

A test flight has been performed by a Czech jet aircraft completely powered on biodiesel. Other recent jet flights using biofuel, however, have been using other types of renewable fuels. On November 7, 2011 United Airlines flew the world's first commercial aviation flight on a microbially derived biofuel using Solajet™, Solazyme's algae-derived renewable jet fuel. The Eco-skies Boeing 737-800 plane was fueled with 40 percent Solajet and 60 percent petroleum-derived jet fuel. The commercial Eco-skies flight 1403 departed from Houston's IAH airport at 10:30 and landed at Chicago's ORD airport at 13:03.

3.1.4.5. As a heating oil

Biodiesel can also be used as a heating fuel in domestic and commercial boilers, a mix of heating oil and biofuel which is standardized and taxed slightly differently from diesel fuel used for transportation. It is sometimes known as "bioheat" (which is a registered trademark of the National Biodiesel Board [NBB] and the National Oilheat Research Alliance [NORA] in the U.S., and Columbia Fuels in Canada). Heating biodiesel is available in various blends. ASTM 396 recognizes blends of up to 5 percent biodiesel as equivalent to pure petroleum heating oil.

Blends of higher levels of up to 20% biofuel are used by many consumers. Research is underway to determine whether such blends affect performance. Older furnaces may contain rubber parts that would be affected by biodiesel's solvent properties, but can otherwise burn biodiesel without any conversion required. Care

must be taken, however, given that varnishes left behind by petrodiesel will be released and can clog pipes- fuel filtering and prompt filter replacement is required. Another approach is to start using biodiesel as a blend, and decreasing the petroleum proportion over time can allow the varnishes to come off more gradually and be less likely to clog. Thanks to its strong solvent properties, however, the furnace is cleaned out and generally becomes more efficient. A technical research paper describes laboratory research and field trials project using pure biodiesel and biodiesel blends as a heating fuel in oil-fired boilers. During the Biodiesel Expo 2006 in the UK, Andrew J. Robertson presented his biodiesel heating oil research from his technical paper and suggested B20 biodiesel could reduce UK household CO_2 emissions by 1.5 million tons per year.

A law passed under Massachusetts Governor Deval Patrick requires all home heating diesel in that state to be 2% biofuel by July 1, 2010, and 5% biofuel by 2013. New York City has passed a similar law.

3.1.4.6. Cleaning oil spills

With 80-90% of oil spill costs invested in shoreline cleanup, there is a search for more efficient and cost-effective methods to extract oil spills from the shorelines. Biodiesel has displayed its capacity to significantly dissolve crude oil, depending on the source of the fatty acids. In a laboratory setting, oiled sediments that simulated polluted shorelines were sprayed with a single coat of biodiesel and exposed to simulated tides. Biodiesel is an effective solvent to oil due to its methyl ester component, which considerably lowers the viscosity of the crude oil. Additionally, it has a higher buoyancy than crude oil, which later aids in its removal. As a result, 80% of oil was removed from cobble and fine sand, 50% in coarse sand, and 30% in gravel. Once the oil is liberated from the shoreline, the oil-biodiesel mixture is manually removed from the water surface with skimmers. Any remaining mixture is easily broken down due to the high biodegradability of biodiesel, and the increased surface area exposure of the mixture.

3.1.4.7. Biodiesel in generators

In 2001, UC Riverside installed a 6-megawatt backup power system that is entirely fueled by biodiesel. Backup diesel-fueled generators allow companies to avoid damaging blackouts of critical operations at the expense of high pollution and emission rates. By using B100, these generators were able to essentially eliminate the by products that result in smog, ozone, and sulfur emissions. The use of these generators in residential areas around schools, hospitals, and the general public result in substantial reductions in poisonous carbon monoxide and particulate matter.

3.1.5. Properties

Biodiesel has better lubricating properties and much higher cetane ratings than today's low sulfur diesel fuels. Biodiesel addition reduces fuel system wear, and in low levels in high pressure systems increases the life of the fuel injection equipment that relies on the fuel for its lubrication. Depending on the engine, this might include high pressure injection pumps, pump injectors (also called unit injectors) and fuel injectors.

The calorific value of biodiesel is about 37.27 MJ/kg. This is 9% lower than regular Number 2 petrodiesel. Variations in biodiesel energy density is more dependent on the feedstock used than the production process. Still, these variations are less than for petrodiesel. It has been claimed biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petrodiesel.

Biodiesel is a liquid which varies in color —between golden and dark brown —depending on the production feedstock. It is slightly miscible with water, has a high boiling point and low vapor pressure. *The flash point of biodiesel (>130 °C, >266 °F) is significantly higher than that of petroleum diesel (64 °C, 147 °F) or gasoline (−45 °C, -52 °F). Biodiesel has a density of ~ 0.88 g/cm³, higher than petrodiesel (~ 0.85 g/cm³).

Biodiesel has virtually no sulfur content, and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel to aid with lubrication, as the sulfur compounds in petrodiesel provide much of the lubricity.

3.1.5.1. Fuel Efficiency

Biodiesel will have a varying amount of power output depending on its: blend, quality, and load conditions under which the fuel is burnt. The thermal efficiency for example of B100 as compared to B20 will vary due to the BTU content of the various blends. Thermal efficiency of a fuel is based in part on fuel characteristics such as: viscosity, specific density, and flash point; these characteristics will change as the blends as well as the quality of biodiesel varies. The American Society for Testing and Materials has set standards in order to judge the quality of a given fuel sample.

A study on the brake thermal efficiency of varied biodiesel blends were tested under a series of load conditions as well as compression ratios. A part of the trial was comparing the thermal efficiency of B40 to traditional petrodiesel, as well as varying blends of biodiesel; as a result it was found that B40 performed at greater levels of efficiency over its traditional counterpart at higher compression ratios (this higher brake thermal efficiency was recorded at compression ratios of 21:1. It was noted that as the compression ratios increased the efficiency of all fuel types as well as blends being tested increased; though it was found that a blend of B40 was the most economical at a compression ratio of 21:1 over all other blends. The study implied that this increase in efficiency was due to fuel density, viscosity, and heating values of the fuels.

3.1.5.2. Combustion

Fuel systems on the modern diesel engine were not designed to accommodate biodiesel. Traditional direct injection fuel systems operate at roughly 3,000 psi at the injector tip while the modern common rail fuel system operates upwards of 30,000 PSI at the injector tip. Components are designed to operate at a great temperature range, from below freezing to over 1,000 degrees Fahrenheit. Diesel fuel is expected to burn efficiently and produce as few emissions as possible.

As emission standards are being introduced to diesel engines the need to control harmful emissions is being designed into the parameters of diesel engine fuel systems. The traditional inline injection system is more forgiving to poorer quality fuels as opposed to the common rail fuel system. The higher pressures and tighter tolerances of the common rail system allows for greater control over atomization and injection timing. This control of atomization as well as combustion allows for greater efficiency of modern diesel engines as well as greater control over emissions. Components within a diesel fuel system interact with the fuel in a way to ensure efficient operation of the fuel system and so the engine. If a fuel is introduced to a system-that has specific parameters of operation-and you vary those parameters by an out of specification fuel you may compromise the integrity of the overall fuel system. Some of these parameters such as spray pattern and atomization are directly related to injection timing.

One study looked at these characteristics of biodiesel in a fuel system. It was found that during atomization biodiesel and its blends produced droplets that were greater in diameter than the droplets produced by traditional petrodiesel. The smaller droplets were attributed to the lower viscosity and surface tension of traditional petrol. It was found that droplets at the periphery of the spray pattern were larger in diameter than the droplets at the center this was attributed to the faster pressure drop at the edge of the spray pattern; there was a proportional relationship between the droplet size and the distance from the injector tip. It was found that B100 had the greatest spray penetration, this was attributed to the greater density of B100. Having a greater droplet size can lead to; inefficiencies in the combustion, increased

emissions, and decreased horse power. In another study it was found that there is a short injection delay when injecting biodiesel. This injection delay was attributed to the greater viscosity of Biodiesel. It was noted that the higher viscosity and the greater cetane rating of biodiesel over traditional petrodiesel lead to poor atomization, as well as mixture penetration with air during the ignition delay period. Another study noted that this ignition delay may aid in a decrease of NOx emission.

3.1.5.3. Emissions

There are a number of emissions that are inherent to the combustion of diesel fuels that are regulated by the Environmental Protection Agency, E.P.A. As these emissions are a byproduct of the combustion process in order to ensure E.P.A. compliance a fuel system must be capable of controlling the combustion of fuels as well as the mitigation of emissions.

There are a number of new technologies that are becoming phased in in order to control the production of diesel emissions. The exhaust gas recirculation system, E.G.R., and the diesel particulate filter, D.P.F., are both designed to mitigate the production of harmful emissions.

While studying the effect of biodiesel on a D.P.F. it was found that though the presence of sodium and potassium carbonates aided in the catalytic conversion of ash, as the diesel particulates are catalyzed, they may congregate inside the D.P.F. and so interfere with the clearances of the filter. This may cause the filter to clog and interfere with the regeneration process. In a study on the impact of E.G.R. rates with blends of jathropa biodiesel it was showed that there was a decrease in fuel efficiency and torque output due to the use of biodiesel on a diesel engine designed with an E.G.R. system. It was found that CO and CO2 emissions increased with an increase in exhaust gas recirculation but NOx levels decreased. The opacity level of the jathropa blends was in an acceptable range, where traditional diesel was out of acceptable standards. It was shown that a decrease in Nox emissions could be obtained with an E.G.R. system. This study showed an advantage over traditional diesel within a certain operating range of the E.G.R. system.

3.1.6. Bıodıesel Productıon

The conversion of the vegetable oil to biodiesel, i.e. the transesterification reaction of the triglycerides to fatty acid methyl esters was performed in a jacketed 1000-mL batch reactor equipped with a reflux condenser and a magnetic stirrer. Initially, heterogeneous solid catalyst and methanol were mixed in the reaction vessel, and canola oil was added to the reaction mixture. The system was heated to the desired temperature and the mixing rate was kept constant at 600 rpm during the reaction. During the experiments the alcohol to oil ratio, 15:1, temperature of 60°C, 3 wt. % of catalyst, and reaction time of 8 h were set constant, according to ourpreviously published results. After 8 h of the transesterification reaction, the reaction mixture was separatedfrom the catalyst via filtration under vacuum and then poured into a separator funnel in which it was keptconstant overnight. The biodiesel and glycerol layers had different densities and thus were easily separated. The upper layer was biodiesel and the bottom layer was, essentially, glycerol. Chemical analysis of the methylester content of the biodiesel phase was performed using an Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID) and with a Carbowax 20 M capillary column, according to European StandardEN 14103 (2003).

3.1.6.1. Kinematic viscosity

Biodiesel is much less viscous than the oil from which it is made. In diesel engines viscosity affects injector lubrication and fuel atomization.15 In the present study kinematic viscosity was determined using a COMECTA Cannon-Fenske viscometer, according to the ASTM D445 standard test method.

3.1.6.2. Density

Density is an important parameter for diesel fuel injection systems. Many performance characteristics, such as cetane number and heating value, are related to density.

This property influences the efficiency of fuel atomization. Density in the present study was measured using an Anton Paar DMA 35 N density meter at 15° C, according to the ASTM D941 standard test method.

3.1.6.3. Flash point

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will flash upon application of an ignition source. One of the most important advantages of biodiesel is that its flash point is greater than that of diesel fuel, which is reflected in the specifications in the standards. The flash point of biodiesel must be a minimum 120°C and 130°C, according to EN 14214 and ASTM 6751, respectively. This parameter was determined in the present study according to the ASTM D93 standard test method. Copper strip corrosion

Corrosion is a chemical action that destroys the surface of a metal by oxidation alone or in combination with a chemical process. It should be tested in fuels, especially for transportation and storage conditions. Free fatty acids and some sulphur compounds that exist in biodiesel may cause corrosion. In the present study corrosion level was measured according to the ASTM D130 standard test method.

3.1.6.4. Ester content

Biodiesel is the name of the ester generally defined as the mono alkyl ester made from renewable sources, such as vegetable oil and animal fat, through the transesterification process. Use of biodiesel with low conversion is a significant issue as the unconverted triglycerides could polymerize and eventually build up in fuel lines, causing partial clogging of these lines, which could cause significant power

loss. High ester content is a measurement of the completeness of the transesterification reaction.

In the present study, the conversion of canola oil to fatty acid methyl esters was measured using an Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID), and with a Carbowax 20 M capillary column, according to European Standard EN-14103 (2003).

3.1.6.5. Total and free glycerol

Glycerine is a by-product of the transesterification reaction. The stoichiometry of the transesterification reaction requires a 3:1 molar ratio to yield 3 mol of ester and 1 mol of glycerol. Total and free glycerol is used to determine the level of glycerine in the fuel and includes the free glycerine portion of any unreacted or partially reacted oil or fat. High levels of free glycerine can cause injector deposits as well as clogged fuelling systems, and can result in the build up of free glycerine at the bottom of storage and fuelling systems. In the present study this parameter was tested according to the A.O.C.S. Ca 14-56 method.

3.1.6.6. Acid value

The acid value measures the amount of unreacted acids remaining in the finished fuel, and is also an indicator of oxidized fuel. The acid value defines the number of milligrams of potassium hydroxide necessary to neutralize the free acids in 1 g of sample. A high acid value will damage fuel pumps and fuel filters. In the present study the free fatty acid of canola oil and biodiesel were determined according to the A.O.C.S. Cd 3a-64 method. The acid value was calculated according to Eq. (1).

$$\text{Acid value, mg KOH/g of sample} = [(A - B) \times N \times 56.1]/W \quad (3.1)$$

Where A= mL of standard alkali used in titrating to the middle of inflection in the titration curve of sample, B= mL of standard alkali used in titrating to the same pH meter reading as for the blank, N=normality of the standard alkali, and W =g of sample.

3.1.6.7. Distillation temperatures

Distillation is an indicator of the purity of finished fuel. Distillation includes determination of the range of boiling points for the fuel and is used to characterize the fuel in terms of the boiling temperatures of its components. In the present study distillation temperatures were determined according to the ASTM D86 standard test method.

3.1.6.8. Cetane index

The cetane index is a measure of the ignition quality of a fuel and influences white smoke and combustion roughness. The cetane index is based on specific gravity and the 10%, 50%, and 90% distillation temperatures of the fuel. This parameter was calculated according to the ASTM D4737 standard test method in the present study

3.1.6.9. Pour point and freezing point

Liquids have a characteristic temperature at which they turn into solids, known as their freezing point. On the other hand, pour points define the lowest temperature at which the fuel can still be moved, before it has gelled.26 The pour point and freezing point are used to characterize the cold flow operability of fuel, because the pour point and the freezing point of fuel affect the utility of a fuel, especially in cold climate conditions. The pour point and the freezing point were determined in the present study according to the ASTM D97 and ASTM D2386 standard test methods.

Table 3.1. ASTM D 6751 – 02 Requirements

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	mm²/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	D2500	Report to customer	°C
Carbon residue	D4530	0.050 max	wt. %
Acid number	D664	0.80 max	mg KOH/g
Free glycerin	D6584	0.020	wt. %
Total glycerin	D6584	0.240	wt. %
Phosphorus	D4951	0.0010	wt. %
Vacuum distillation end point	D1160	360 °C max, at %90 distilled	ºC
Storage stability	Determined	Determined	Determined

Table 3.2. European Committee for Standardization EN 14214 biodiesel fuel standard

Property	Test method(s)	Limits	Units
Ester content	EN 14103	96.5 min	% (mol/mol)
Density, 15°C	EN ISO 3675, EN ISO 12185	860–900	kg/m^3
Kinematic viscosity, 40°C	EN ISO 3104, ISO 3105	3.5–5.0	mm^2/s
Flash point	EN ISO 3679	120 min	°C
Sulfur content	EN ISO 20846, EN ISO 20884	10.0 max	mg/kg
Carbon residue (10% distillation residue)	EN ISO 10370	0.30 max	% (mol/mol)
Cetane number	EN ISO 5165	51 min	
Sulfated ash	ISO 3987	0.02 max	% (mol/mol)
Water content	EN ISO 12937	500 max	mg/kg
Total contamination	EN 12662	24 max	mg/kg
Copper strip corrosion (3 h, 50°C)	EN ISO 2160	1	Degree of corrosion
Oxidation stability, 110°C	EN 14112	6.0 min	h
Acid value	EN 14104	0.50 max	mg KOH/g
Iodine value	EN 14111	120 max	g I_2/100 g
Linolenic acid content	EN 14103	12.0 max	% (mol/mol)
Polyunsaturated (≥4 double bonds) methyl esters	EN 14103	1 max	% (mol/mol)
Methanol content	EN 14110	0.20 max	% (mol/mol)
MAG content	EN 14105	0.80 max	% (mol/mol)
DAG content	EN 14105	0.20 max	% (mol/mol)
TAG content	EN 14105	0.20 max	% (mol/mol)
Free glycerol	EN 14105 EN 14106	0.020 max	% (mol/mol)
Total glycerol	EN 14105	0.25 max	% (mol/mol)
Group I metals (Na, K)	EN 14108 EN 14109	5.0 max	mg/kg
Group II metals (Ca, Mg)	EN 14538	5.0 max	mg/kg
Phosphorous content	EN 14107	10.0 max	mg/kg

Table 3.3. ASTM D7467 biodiesel-petrodiesel blend (B6–B20) fuel standard

Property	Test method(s)	Limits	Units
Ester content	EN 14103	96.5 min	% (mol/mol)
Density, 15°C	EN ISO 3675, EN ISO 12185	860–900	kg/m^3
Kinematic viscosity, 40°C	EN ISO 3104, ISO 3105	3.5–5.0	mm^2/s
Flash point	EN ISO 3679	120 min	°C
Sulfur content	EN ISO 20846, EN ISO 20884	10.0 max	mg/kg
Carbon residue (10% distillation residue)	EN ISO 10370	0.30 max	% (mol/mol)
Cetane number	EN ISO 5165	51 min	
Sulfated ash	ISO 3987	0.02 max	% (mol/mol)
Water content	EN ISO 12937	500 max	mg/kg
Total contamination	EN 12662	24 max	mg/kg
Copper strip corrosion (3 h, 50°C)	EN ISO 2160	1	Degree of corrosion
Oxidation stability, 110°C	EN 14112	6.0 min	h
Acid value	EN 14104	0.50 max	mg KOH/g
Iodine value	EN 14111	120 max	g I_2/100 g
Linolenic acid content	EN 14103	12.0 max	% (mol/mol)
Polyunsaturated (≥4 double bonds) methyl esters	EN 14103	1 max	% (mol/mol)
Methanol content	EN 14110	0.20 max	% (mol/mol)
MAG content	EN 14105	0.80 max	% (mol/mol)
DAG content	EN 14105	0.20 max	% (mol/mol)
TAG content	EN 14105	0.20 max	% (mol/mol)
Free glycerol	EN 14105 EN 14106	0.020 max	% (mol/mol)
Total glycerol	EN 14105	0.25 max	% (mol/mol)
Group I metals (Na, K)	EN 14108 EN 14109	5.0 max	mg/kg
Group II metals (Ca, Mg)	EN 14538	5.0 max	mg/kg
Phosphorous content	EN 14107	10.0 max	mg/kg

3.1.7. Types Of Bıodıesel Productıon Processes

3.1.7.1. Introduciton

This module provides an overview of the steps in the production of biodiesel from preparation of the feedstock to the recovery and purification of the fatty acid esters (biodiesel) and the co-product glycerol (also called glycerin). We will review several chemistries used for esterification and different approaches to product preparation and purification. The emphasis throughout the module will be the choices to be made in matching feedstock selection, capacity, and operating mode with the selection of the basic process chemistry and layout for a specific location. While no specific process technology is favored in this description, an effort has been made to describe the major approaches currently in use in the industry.

3.1.7.2. Feedstocks Used in Biodiesel Production

The primary raw materials used in the production of biodiesel are vegetable oils, animal fats, and recycled greases. These materials contain triglycerides, free fatty acids, and other contaminants depending on the degree of pretreatment they have received prior to delivery. Since biodiesel is a mono-alkyl fatty acid ester, the primary alcohol used to form the ester is the other major feedstock. Most processes for making biodiesel use a catalyst to initiate the esterification reaction. The catalyst is required because the alcohol is sparingly soluble in the oil phase. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate. The most common catalysts used are strong mineral bases such as sodium hydroxide and potassium hydroxide. After the reaction, the base catalyst must be neutralized with a strong mineral acid. Typical proportions for the chemicals used to make biodiesel are:

Reactants
•Fat or oil (e.g. 100 kg soybean oil)
•Primary alcohol (e.g. 10 kg methanol)
Catalyst
•Mineral base (e.g. 0.3 kg sodium hydroxide)
Neutralizer
•Mineral acid (e.g. 0.25 kg sulfuric acid)
Fats and Oils:

Choice of the fats or oils to be usedin producing biodieselis both a process chemistry decision and an economic decision.

Withrespect to process chemistry, the greatest difference among the choices of fats and oils is the amount of free fatty acids that are associated with the triglycerides. Other contaminants, such as color and odor bodies can reduce the value of the glycerin produced, and reduce the public acceptance of the fuel if the color and odor persist in the fuel. Most vegetable oils have a low percentage of associated free

fatty acids. Crude vegetable oils contain some free fatty acids and phospholipids. The phospholipids are removed in a “degumming” step and the free fatty acids are removed in a “refining” step. Oil can be purchased as crude, degummed, or refined. The selection of the type of oil affects the production technology that is required. Animal tallows and recycled (yellow) grease havemuch higher levels of free fatty acids.

Yellow grease is limited to 15% free fatty acids and is a traded commodity that is typically processed into animal and pet food. Specifications for yellow grease are described in the chapter on Feedstock Preparation. Trap greases come from traps under kitchen drains and these greases can contain between 50 and 100% free fatty acids. There is no market for these greases at this time and most are landfilled. Trap grease is not yet used for biodiesel production and may have some technical challenges that have notbe fully resolved such as difficult to break emulsifications (gels), fine silt that will cause equipment wear, high water contents, and very strong color and odor bodies that affect biodieseland glycerin products. There are also unresolved questions about small quantities of other contaminants such aspesticides that might be present in the fuel. The options for the triglyceride choice are many. Among the vegetable oils sources are soybean, canola, palm, and rape. Animal fats are products of rendering operations. They include beef tallow, lard, poultry fat, and fish oils. Yellow greases can be mixtures of vegetable and animal sources. There are other less desirable, but also less expensive triglyceridesources such as brown grease and soapstock. The free fatty acid content affects the type of biodiesel process used, and the yield of fuel from that process. The other contaminants present can affect the extent of feedstock preparation necessary touse a given reaction chemistry.

3.1.7.4. Alcohol

The most commonly used primary alcohol used in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. A key quality factor for the primary alcohol is the water content. Water

interferes with transesterification reactions and can result in poor yields and high levels of soap, free fatty acids, and triglycerides in the final fuel.

Unfortunately, all the lower alcohols are hygroscopic and are capable of absorbing water from the air. Many alcohols have been used to make biodiesel. Other issues such as cost of the alcohol, the amount of alcohol needed for the reaction, the ease of recovering and recycling the alcohol, fuel tax credits, and global warming issues influence the choice of alcohol. Some alcohols also require slight technical modifications to the production process such as higher operating temperatures, longer or slower mixing times, or lower mixing speeds.

Since the reaction to form the esters is on a molar basis and we purchase alcohol on a volume basis, their properties make a significant difference in raw material price. It takes three moles of alcohol to react completely with one mole of triglyceride.

The reason for using extra alcohol is that it “drives” the reaction closer to the 99.7% yield we need to meet the total glycerol Standard for fuel grade biodiesel. The unused alcohol must be recovered and recycled back into the process to minimize operating costs and environmental impacts. Methanol is considerably easier to recover than the ethanol. Ethanol forms an azeotrope with water so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions. Methanol recycles easier because it doesn’t form an azeotrope.

These two factors are the reason that even though methanol is more toxic, it is the preferred alcohol for producing biodiesel. Methanol has a flash point of 10 °C, while the flash point of ethanol is 8°C, so both are considered highly flammable.

The alcohol quality requirements are that it be un-denatured and anhydrous. Since chemical grade ethanol is typically denatured with poisonous material to prevent its abuse, finding undenatured ethanol is difficult. Purchase ethanol that has been denatured with methanol if possible.

3.1.7.5. Catalysts and Neutralizers

Catalysts may either be base, acid, or enzyme materials. The most commonly used catalyst materials for converting triglycerides to biodiesel are sodium hydroxide, potassium hydroxide, and sodium methoxide. Most base catalyst systems use vegetable oils as a feedstock. If the vegetable oil is crude, it contains small amounts (<2%) of free fatty acids that will form soaps that will end up in the crude glycerin. Refined feedstocks, such as refined soy oil can also be used with base catalysts.

The base catalysts are highly hygroscopic and they form chemical water when dissolved in the alcohol reactant. They also absorb water from the air during storage. If too much water has been adsorbed the catalyst will perform poorly and the biodiesel may not meet the total glycerin standard.

Although acid catalysts can be used for transesterification they are generally considered to be too slow for industrial processing. Acid catalysts are more commonly used for the esterification of free fatty acids. Acid catalysts include sulfuric acid and phosphoric acid. Solid calcium carbonate is used as an acid catalyst in one experimental homogeneous catalyst process. The acid catalyst is mixed with methanol and then this mixture is added to the free fatty acids or a feedstock that contains high levels of free fatty acids. The free fatty acids convert into biodiesel. The acids will need neutralization when this process is complete, but this can be done as base catalyst is added to convert any remaining triglycerides.

There is continuing interest in using lipases as enzymatic catalysts for the production of alkylfatty acid esters. Some enzymes work on the triglyceride, converting them to methyl esters; and some work on the fatty acids. The commercial use of enzymes is currently limited to countries like Japan, where energy costs are high, or for the production of specialty chemicals from specific types of fatty acids. The commercial use of enzymes is limited because costs are high, the rate of reaction is slow, and yields to methyl esters are typically less than the 99.7% required for fuel-grade biodiesel. Enzymes are being considered for fatty acid conversion to biodiesel as a pretreatment step, but this system is not commercial at this time.

Neutralizers are used to remove the base or acid catalyst from the product biodiesel and glycerol. If you are using a base catalyst, the neutralizer is typically an acid, and visa versa. If the biodiesel is being washed, the neutralizer can be added to the wash water. While hydrochloric acid is a common choice to neutralize base catalysts, as mentioned earlier, if phosphoric acid is used, the resulting salt has value as a chemical fertilizer.

3.1.8. Catalyst Selectıon

Base catalysts are used for essentially all vegetable oil processing plants. The initial free fatty acid content and the water content are generally low. Tallows and greases with free fatty acid contents greater than about 1% must be pretreated to either remove the FFA or convert the FFA to esters before beginning the base catalyzed reaction.

Otherwise, the base catalyst will react with the free fatty acids to form soap and water. The soap formation reaction is very fast and goes to completion before any esterification begins. Essentially all of the current commercial biodiesel producers use base catalyzed reactions. Base catalyzed reactions are relatively fast, with residence times from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol:triglyceride ratio.

Most use NaOH or KOH as catalysts, although glycerol refiners prefer NaOH. KOH has a higher cost but the potassium can be precipitated as K3PO4, a fertilizer, when the products are neutralized using phosphoric acid. This can make eating water effluent standards a bit more difficult because of limits on phosphate effluents. Sodium methoxide, usually as a 25 % solution in methanol, is a more powerful catalyst on a weight basis than the mixture of NaOH and methanol. This appears to be, in part, the result of the negative effect of the chemical water produced in situ when NaOH and methanol react to form sodium methoxide.

Acid catalyst systems are characterized by slow reaction rates and high alcohol:TG requirements (20:1 and more). Generally, acid catalyzed reactions are

used to convert FFAs to esters, or soaps to esters as a pretreatment step for high FFA feedstocks. Residence times from 10 minutes to about 2 hours are reported.

Counter current acid esterification systems have been used for decades to convert pure streams of fatty acids into methyl esters at yields above 99%. These systems tend to force yields to 100% and wash water out of the system at the same time because the feedstock and the sulfuric acid/methanol mix are moving in opposite directions. Acid esterification systems produce a byproduct of water. In batch systems, the water tends to accumulate in the vessel to the point where it can shut the reaction down prematurely. The sulfuric acid tends to migrate into the water, out of the methanol, rendering it unavailable for the reaction. All acid esterification systems need to have a water management strategy. Good water management can minimize the amount of methanol required for the reaction. Excess methanol (such as the 20:1 ratio) is generally necessary in batch reactors where water accumulates. Another approach is to approach the reaction in two stages: fresh methanol and sulfuric acid is reacted, removed, and replaced with more fresh reactant. Much of the water is removed in the first round and the fresh reactant in the second round drives the reaction closer to completion. Acid-catalyzed esterification is discussed in more detail in the chapter on Pretreatment of High FFA Feedstocks.

Lipase catalyzed reactions have the advantage reacting a room temperature without producing spent catalysts. The enzymes can be recycled for use again or immobilized onto a substrate. If immobilized, the substrate will require replacement when yields begin to decline. The enzyme reactions are highly specific. Because the alcohol can be inhibitory to some enzymes, a Typical strategy is to feed the alcohol into the reactor in three steps of 1:1 mole ratio each.

The reactions are very slow, with a three step sequence requiring from 4 to 40 hours, or more. The reaction conditions are modest, from 35 to 45 °C. Transesterification yields generally do not meet ASTM standards, but esterification yields can occur relatively quickly and yields are good. Excess free fatty acids can be removed as soaps in a later transesterification or caustic stripping step.

3.1.9. Biodiesel Production Process Options

3.1.9.1. Batch Processing

The simplest method for producing alcohol esters is to use a batch, stirred tank reactor. Alcohol to triglyceride ratios from 4:1 to 20:1 (mole:mole) have been reported, with a 6:1 ratio most common. The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually about 65°C, although temperatures from 25°C to 85°C have been reported.

The most commonly used catalyst is sodium hydroxide, with potassium hydroxide also used. Typical catalyst loadings range from 0.3 % to about 1.5%. Thorough mixing is necessary at the beginning of the reaction to bring the oil, catalyst and alcohol into intimate contact. Towards the end of the reaction, less mixing can help increase the extent of reaction by allowing the inhibitory product, glycerol, to phase separate from the ester – oil phase. Completions of 85% to 94 % are reported. Some groups use a two-step reaction, with glycerol removal between steps, to increase the final reaction extent to 95+ percent. Higher temperatures and higher alcohol: oil ratios also can enhance the percent completion. Typical reaction times range from 20 minutes to more than one hour.

The oil is first charged to the system, followed by the catalyst and methanol. The system is agitated during the reaction time. Then agitation is stopped. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other processes the reaction mixture is pumped into a settling vessel, or is separated using a centrifuge.

The alcohol is removed from both the glycerol and ester stream using an evaporator or a flash unit. The esters are neutralized, washed gently using warm, slightly acid water to remove residual methanol and salts, and then dried. The finished biodiesel is then transferred to storage. The glycerol stream is neutralized and washed with soft water. The glycerol is than sent to the glycerol refining section.

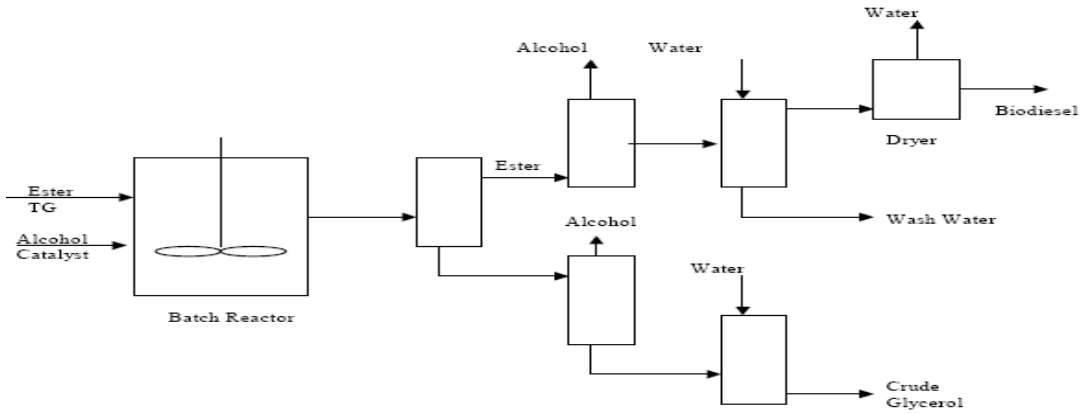


Figure 3.1. Batch Reaction Processing

For yellow grease and animal fats, the system is slightly modified with the addition of an acid esterification vessel and storage for the acid catalyst.

The feedstock is sometimes dried (down to 0.4% water) and filtered before loading the acid esterification tank. The sulfuric acid and methanol mixture is added and the system is agitated.

Similar temperatures to transesterification are used and sometimes the system is pressurized or a cosolvent is added. Glycerol is not produced. If a two-step acid treatment is used, the stirring is suspended until the methanol phase separates and is removed. Fresh methanol and sulfuric acid is added and the stirring resumes. Once the conversion of the fatty acids to methyl esters has reached equilibrium, the methanol/water/acid mixture is removed by settling or with a centrifuge. The remaining mixture is neutralized or sent straight into transesterification where it will be neutralized using excess base catalysts. Any remaining free fatty acids will be converted into soaps in the transesterification stage. The transesterification batch stage processes as described above.

3.1.9.2. Continuous Process Systems

A popular variation of the batch process is the use of continuous stirred tank reactors (CSTRs) in series. The CSTRs can be varied in volume to allow for a longer residence time in CSTR 1 to achieve a greater extent of reaction. After the initial

product glycerol is decanted, the reaction in CSTR 2 is rather rapid, with 98+ completions not uncommon.

An essential element in the design of a CSTR is sufficient mixing input to ensure that the composition throughout the reactor is essentially constant. This has the effect of increasing the dispersion of the glycerol product in the ester phase. The result is that the time required for phase separation is extended.

There are several processes that use intense mixing, either from pumps or motionless mixers, to initiate the esterification reaction. Instead of allowing time for the reaction in an agitated tank, the reactor is tubular. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. This type of reactor, called a plug-flow reactor (PFR), behaves as if it were a series of small CSTRs chained together.

The result is a continuous system that requires rather short residence times, as low as 6 to 10 minutes, for near completion of the reaction. The PFRs can be staged, as shown, to allow decanting of glycerol. Often this type of reactor is operated at an elevated temperature and pressure to increase reaction rate.

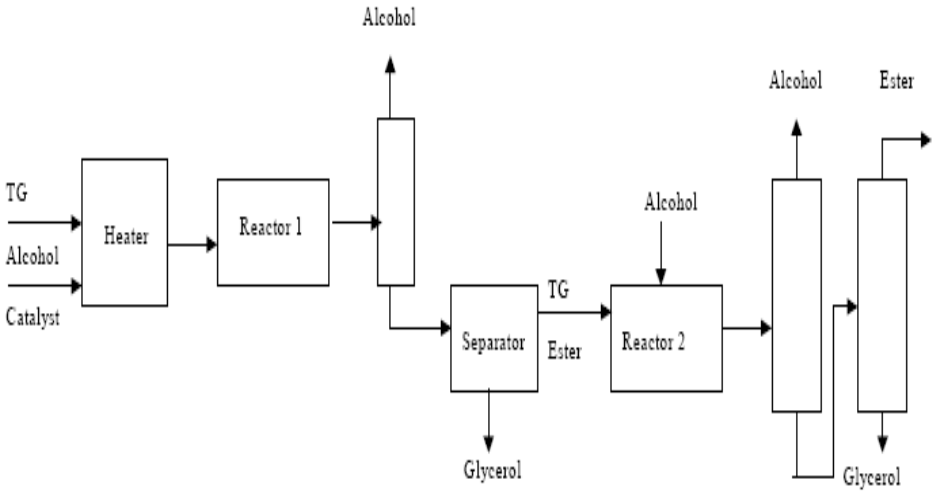


Figure 3.2. Plug Flow Reaction System

3.1.9.3. High Free Fatty Acid Systems

High free fatty acid feedstocks will react with the catalyst and form soaps if they are fed to a base catalyzed system. The maximum amount of free fatty acids acceptable in a base catalyzed system is less than 2 percent, and preferably less than 1 percent. Some approaches to using high free fatty acid feedstocks use this concept to “refine” the free fatty acids out of the feed for disposal or separate treatment in an acid esterification unit. The caustic is added to the feedstock and the resulting soaps are stripped out using a centrifuge. This is called caustic stripping

Some triglycerides are lost with the soaps during caustic stripping. The soap mixture can be acidulated to recover the fatty acids and lost oils in a separate reaction tank. The refined oils are dried and sent to the transesterification unit for further processing. Rather than waste the free fatty acids removed in this manner, they can be transformed into methyl esters using an acid esterification process. As described earlier, acid catalyzed processes can be used for the direct esterification of free fatty acids in a high FFA feedstock. Less expensive feedstocks, such as tallow or yellow grease, are characteristically high in free fatty acids (FFA). The standard for tallow and yellow grease is ≤ 15 percent FFA. Some lots may exceed this standard.

Direct acid esterification of a high free fatty acid feed requires water removal during the reaction, or the reaction will be quenched prematurely. Also, a high alcohol to FFA ratio required, usually between 20:1 and 40:1. Direct esterification may also require rather large amounts of the acid catalyst depending on the process used.

The esterification reaction of FFAs with methanol produces byproduct water that must be removed, but the resulting mixture of esters and triglyceride, can be used directly in a conventional base catalyzed system. The water can be removed by vaporization, settling, or centrifugation as a methanol-water mixture. Counter-current continuous-flow systems will wash out the water with the exiting stream of acidic methanol.

One approach to the acid catalyst system has been to use phosphoric acid as the initial catalyst, neutralize with an excess of KOH for the base step, and then

neutralize with phosphoric acid upon completion. The insoluble potassium phosphate is recovered, washed, and dried for use as a fertilizer. Figure 3.3 shows a typical acid catalyzed, direct esterification process.

An alternative approach to utilization of high FFA feedstocks is to use a base catalyst to deliberately form soap from the FFAs. The soap is recovered, the oil dried, and then used in a conventional base catalyzed system.

This strategy can lead to a false sense of economy. If the soapstock is discarded, the effective price of the feedstock is increased in inverse proportion to the percentage of remaining oil. The soapstock can, however, be converted into esters by using an acid catalyzed reaction. The problem with this strategy is that the soapstock system contains a large amount of water that must be removed before the product esters can meet the biodiesel standard. The soapstock process is shown in Figure 3.3

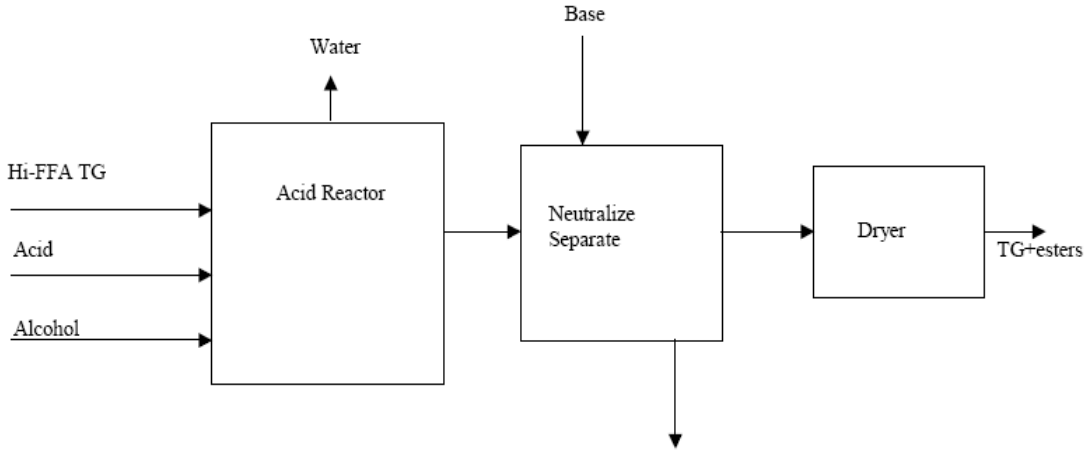


Figure 3.3. Acid Catalyzed Direct Esterification Process

An alternative procedure for processing high FFA feeds is to hydrolyze the feedstock into pure FFA and glycerine. Typically this is done in a counter current reactor using sulfuric/sulfonic acids and steam. The output is pure free fatty acids and glycerin. Any contaminates in the feedstock partition mostly into the glycerin and some may leave with the steam/water effluent. Some contaminants continue with the FFA and can be removed or left in, depending on the processes and product specifications. The pure FFA are then acid esterified in another counter current

reactor to transform them into methyl esters. The methyl esters are then neutralized and dried. Yields can exceed 99%. Equipment needs to be acid resistant but generally feedstock costs are extremely low.

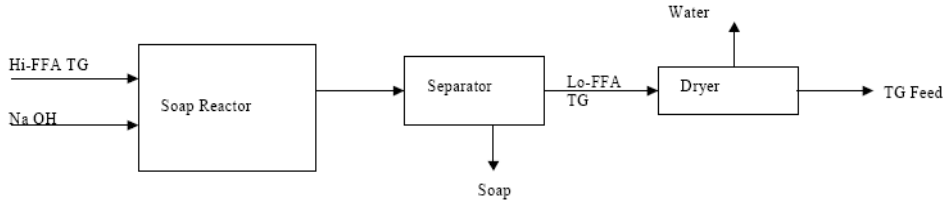


Figure 3.4. Preparation of Soapstock from a High FFA Feed

A variation of the base-catalyzed system that avoids the problem of high FFAs is the use of a fixed bed, insoluble base. An example of this system, using calcium carbonate as the catalyst, has been demonstrated at the bench-scale. This process is depicted in Figure 3.5.

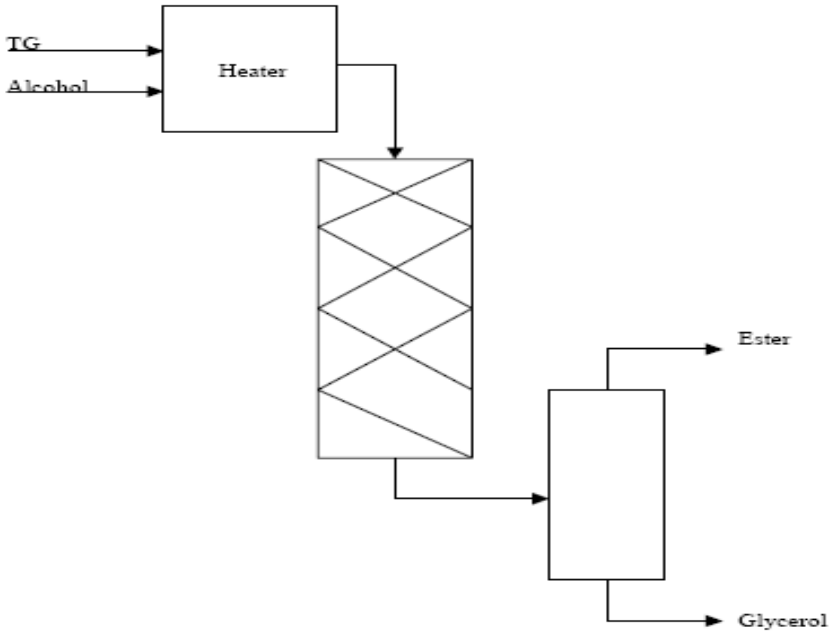


Figure 3.5. Fixed-Bed, Base Catalyzed Reactor

3.1.9.4. Non-Catalyzed Systems

3.1.9.5. Biox process

Cosolvent options are designed to overcome slow reaction time caused by the extremely low solubility of the alcohol in the TG phase. One approach that is nearing commercialization is the Biox Process. This process uses a co-solvent, tetrahydrofuran, to solubilize the methanol. The result is a fast reaction, on the order of 5 to 10 minutes, and no catalyst residues in either the ester or the glycerol phase. The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol.

After the reaction is complete, the excess methanol and the tetrahydrofuran co-solvent are recovered in a single step. This system requires a rather low operating temperature, 30 °C. Other cosolvents, such as MTBE, have been investigated.

The ester-glycerol phase separation is clean and the final products are catalyst- and water- free. The equipment volume has to be larger for the same quantity of final product because of the additional volume of the co-solvent.

The Biox Process is depicted in Figure 3.6. Cosolvents that are subject to the hazardous and/or air toxic EPA list for air pollutants require special “leak proof” equipment the entire system including methanol/cosolvent recovery and recycling. Fugitive emissions are tightly controlled. The cosolvent must be completely removed from the glycerin as well as the biodiesel.

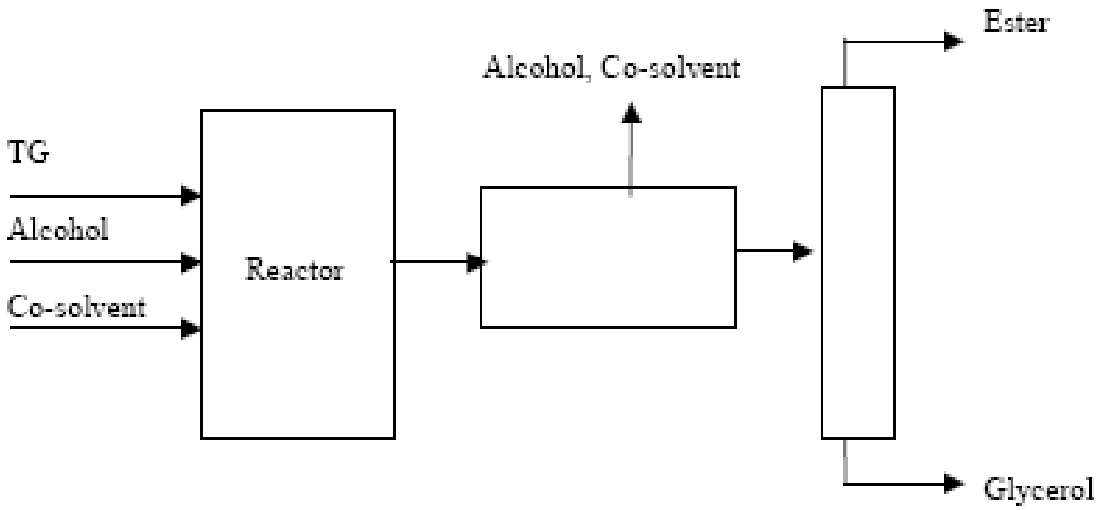


Figure 3.6. Biox Co-Solvent Process

3.1.9.6. Supercritical Process

When a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. There no longer is a distinct liquid and vapor phase, but a single, fluid phase present. Solvents containing a hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super-acids.

A non-catalytic approach is the use of a high (42:1) alcohol to oil ratio. Under supercritical conditions (350 to 400 °C and > 80 atm or 1200 psi) the reaction is complete in about 4 minutes. Capital and operating costs can be more expensive, and energy consumption higher.

An intriguing example of this process has been demonstrated in Japan, where oils in a very large excess of methanol have been subjected to very high temperatures and pressures for a short period of time. The result is a very fast (3 to 5 minute) reaction to form esters and glycerol. The reaction must be quenched very rapidly so that the products do not decompose. The reactor used in the work to date is a 5 ml cylinder that is dropped into a bath of molten metal, and then quenched in water.

Clearly, while the results are very interesting, the scale-up to a useful process may be quite difficult. Figure 3.7 depicts one conception of a configuration for a supercritical esterification process.

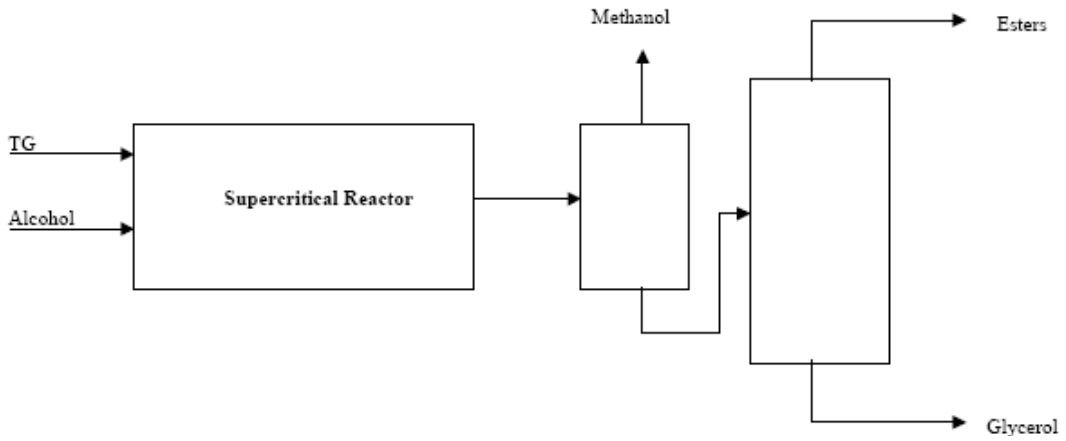


Figure 3.7. Supercritical esterification process

The refining of glycerol is discussed in a separate chapter, although it is a topic of great importance to the choice of biodiesel production process. Generally the quality of the glycerol produced and its value as a coproduct is an important economic variable.

The typical glycerol produced by a biodiesel plant is 50% glycerol or less and contains water, salts, methanol, methyl esters, and unreacted glycerides, color and odor bodies, dimers, timers, and other minor compounds. This is commonly referred to as "biodiesel crude" and is generally worth less than 5 cents per pound. Removing the water and methanol and bringing the glycerol content up to 88% can generate a credit based on the value of crude glycerol. Salts, and particularly sulfur salts or potassium salts reduces the value of the crude glycerol produced.

3.1.10. Treatment And Recovery Of Sıde Streams

3.1.10.1. Introduction

There are three non-ester side streams that must be treated as a part of the overall biodiesel process. These streams are:

1) The excess alcohol that is recycled within the process;
2) The glycerol co-product, and;
3) The wastewater stream from the process.

In this module it is assumed that methanol is the alcohol used in the process. Similar comments would apply to other alcohols. Methanol recycle is necessary because an excess of methanol is required for an effective transesterification reaction system. The recovery of the unused methanol saves input costs for the process and essentially eliminates the emissions of methanol to the surroundings.

The emissions reduction is needed because methanol is highly flammable and is toxic. Glycerol is recovered and partially refined as a co-product from biodiesel production. About 10 percent by weight of the input reactants are converted to glycerol in the transesterification reaction. On both a weight basis and a volume basis, partially refined glycerol is worth more than the biodiesel product. Wastewater constitutes an operating cost for the plant, both because of the water consumption and because of the water treatment costs to the plant.

3.1.10.2. Methanol Management

There are several physical parameters that are important to the recovery and recycle of methanol. Methanol's relatively low boiling point, 64.7 °C, means that it is fairly volatile and can largely be removed from the oil, ester and aqueous streams by flash evaporation and re-condensation. The low boiling point, along with a low flash point, 8 ° C, also mean the methanol is considered to be highly flammable. Methanol is fully miscible with water and with glycerol. However, it has a low solubility in fats and oils (approx. 10 % wt/wt at 65 °C in tallow). Methanol is more soluble in esters, but it is not fully miscible. The solubility in glycerol and water means that methanol will prefer these phases when there is a two-phase system present. The low solubility in fats and oils is the reason for the solubility-limited phase of the overall transesterification reaction.

When the two phases present are esters and glycerol, the methanol will distribute between the phases. At 90:10 % wt/wt ester and glycerol, the methanol distributes approximately 60:40 wt % between the phases. This fact is important, since the reaction is complete at 90:10 wt %.

If the methanol is allowed to remain in the system during phase separation, the methanol acts as a phase stabilizer, retarding the rate of gravity separation. It is advantageous to remove the methanol before phase separation. Methanol can be recovered using distillation, either conventional or vacuum, or partially recovered in a single stage flash. An alternative to distillation is a falling-film evaporator. Residual methanol in the ester phase can be removed in the water wash step in ester postprocessing. Product esters are typically washed with warm (140 °F), softened water to remove soaps and residual methanol.

3.1.10.3. Glycerol Refining

The recovered glycerol from the transesterification reaction contains residual alcohol, catalyst residue, carry-over fat/oil and some esters. The glycerol from rendered feedstocks may also contain phosphatides, sulfur compounds, proteins, aldehydes and ketones, and insolubles (dirt, minerals, bone, or fibers)

3.1.10.4. Glycerol Purification

The final purification of glycerol is completed using vacuum distillation with steam injection, followed by activated carbon bleaching. The advantages of this approach are that this is a well-established technology. The primary disadvantage is that the process is capital and energy intensive.

Vacuum distillation of glycerol is best suited to operations > 25 tons per day. Ion exchange purification of glycerol is an attractive alternative to vacuum distillation for smaller capacity plants. The ion exchange system uses cation, anion, and mixed bed exchangers to remove catalyst and other impurities. The glycerol is first diluted with soft water to a 15 to 35 percent glycerol-in-water solution. The ion exchange is followed by vacuum distillation or flash drying for water removal, often to an 85 percent partially refined glycerol. The advantage of this process is the fact that all purification takes place in the resin vessels so the system is suited to smaller

capacity operations. The disadvantages are that the system is subject to fouling by fatty acids, oils and soaps.

The system also requires regeneration of the beds producing large quantities of waste water. Regeneration requires parallel systems to operate and regenerate simultaneously.

3.1.10.5. Wastewater Considerations

Ester washing produces about 1 gallon of water per gallon of ester per wash. All process water must be softened to eliminate calcium and magnesium salts and treated to remove iron and copper ions. The ester wash water will have a fairly high BOD from the residual fat/oil, ester, and glycerol. The glycerol ion exchange systems can produce large quantities of low salt waters as a result of the regeneration process.

In addition, water softening, ion exchange and cooling water blowdown will contribute a moderate dissolved salts burden. The aggregate process waste waters should meet local municipal waste treatment plant disposal requirements, if methanol is fully recovered in the plant and not present in the wastewater. In many areas, internal treatment and recycle of the process water may lead to cost savings and easier permitting of the process facility.

3.1.11. Factors, Effected To Process

3.1.11.1. The Effect of Free Fatty Acids and Water

The presence higher level of free fatty acids and water in waste cooking oils has always negative effect on the reaction process. The presence water has a greater negative effect than that of the free fatty acids. Free fatty acids and water in oil causes saponification of reaction and reduces catalyst efficiency.

In addition to these, catalyst is required to neutralize waste oils. These factors causes, more catalyst is required than a normal process, the production process to be longer and decreased yield.

3.1.11.2. The Effect of Alcohol

Generally, short chain alcohols such as methanol, ethanol, propanol, and butanol are employed in the transesterification reaction. These alcohols present few differences with respect to the kinetics and final yield of esters. Freedman et al. investigated the effect of using methanol, ethanol, and butanol in a process of transesterification of soybean oil. They are obtained yields from 96 to 98% after an hour of reaction. Canakci and Van Gerpen, to investigate the effects of alcohols on acid-catalyzed transesterification, were prepared solution of sulfuric acid (3%) with methanol.

The solution was added soybean oil at 60, 45 and 25oC, respectively. The mixture was blended slightly at atmospheric pressure for 48 and 96 hours. They founded the effect of alcohol type on acid-catalyzed reaction. Although using butanol in reaction the temperature was highest level, ester conversion was not their expected level. They explained that this result obtained due to branched structure of alcohol.

3.1.11.3. The Effect of Catalyst Type

The transesterification reaction can be catalyzed by alkalis, acids, and or enzymes. Sulfuric, sulfonic, phosphorus and hydrochloric acids are usually used as acid catalysts; the alkali catalysts include NaOH, KOH, carbonates and alkoxides such as sodium methoxide, sodium ethoxide, and sodium propoxide. Lipases also can be used biocatalysts. Acid-catalyzed transesterification is much slower than alkali-catalyzed.

In general, although the transesterifications of refined and crude oils use direct alkali-catalyzed, the transesterifications of waste cooking oils use preliminary reaction with acid-catalyzed and then use alkali-catalyzed reaction. For an alkali-catalyzed transesterification, the glycerides and alcohol must be anhydrous. Because water makes the reaction partially change to saponification.

The catalyst consumes in producing soap and reduces catalyst efficiency. The soap causes an increase in viscosity, formation of gels and makes the separation of glycerol difficult.

3.1.11.4. The Effect of Molar Ratio

One of the most important parameter affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires 3 moles of alcohol and 1 mole of glyceride to yield 3 moles of fatty acid ester and 1 mole of glycerol.

Higher molar ratios result in greater ester conversion in a shorter time. Tomasevic and Siler- Marinkovic studied the effects of molar ratio and catalyst type on ester conversion.

They used waste frying oils and observed ester conversion with molar ratio 4.5:1, 6:1 and 9:1, using as catalyst 1.5%; %1; %0.5 (by weight of oil) of NaOH and KOH at 25oC and for 30 min. In that study, it was concluded that molar ratio is much more effective than catalyst on the reaction.

3.1.11.5. The Effect of Reaction Temperature

Transesterification can occur at different temperatures depending on the oil and alcohol used. Generally, the reaction temperature near the boiling point of the alcohol is recommended. Nevertheless, the reaction may be carried out at room temperature. They carried out same reaction time using 1% wt NaMeO (as catalyst), concentration of 15% in methanol at 25, 40, 55, and 60°C, respectively. In the result of this study, the ester conversions became 86%, 90%, 93%, and 94%, respectively. The ester conversion limited with the boiling point of the alcohol.

3.1.11.6. The Effect of Reaction Time

The conversion rate increases with reaction time. Canakci and Van Gerpen constructed a pilot plant to produce biodiesel from oil with high free fatty acids. They prepared solution of potassium hydroxide (1% of oil by weight) with methanol at room temperature, 6:1 molar ratio and the mixture was agitated for 8 hours. They observed glycerin ratio change. Samples of the mixture were extracted at one hour intervals and the glycerin level was measured. They found that ester conversion increased with decreasing glycerin ratio.

By collecting waste cooking oils and converting to biodiesel fuel provides important advantages such as hindering the destruction of these oils unsuitable manner with respect to environmental, recycling a waste energy resource and using in diesel engines without any modification. Waste cooking oils contain higher levels of free fatty acid and water.

Therefore, direct using alkalicatalyzed reaction causes saponification of and reduces catalyst efficiency. Biodiesel can be produced using numerous methods.

The most common method used is transesterification. The result of analysis of waste vegetable oils claims that between used and unused oils do not have an important difference. In most cases, heating and removal by filtration of solid particles suffice for subsequent transesterification. By adding 20% biodiesel to petroleum diesel fuel in the United State and Europe has gained big a potential resource. Using biodiesel as additive to petroleum diesel fuel is a remarkable reality to be considered for the countries such as Turkey.

3.1.12. Transesterıfıcatıon Methods

The transesterification of waste cooking oil can be performed using alkaline, acidic, and enzymatic catalysts. Depending on the undesirable compounds (especially FFA and water), each catalyst has its own advantages and disadvantages.

3.1.12.1. Alkali-Catalyzed Transesterification

Common alkaline catalysts (such as NaOH, KOH, and NaOCH3) are well-known for the transesterification reaction of edible oil. The rate of the alkaline-catalyzed transesterification reaction is fast, compared to that using acids, and it is reported that the rate could be as high as 4000 times, compared to that using an acidic catalyst. The application of an alkaline catalyst in the transesterification of waste cooking oil is somewhat limited, because the FFA in waste cooking oil reacts with the alkaline catalyst (KOH, NaOH) and forms soap. The soap formed during the reaction prevents the glycerol separation, which drastically reduces the ester yield. The water in waste cooking oil also affects the methyl ester yield by favoring a saponification reaction. Despite these two serious problems, many researchers have studied the transesterification of waste cooking oil using an alkaline catalyst.

Used sunflower oil (which has an acid value of 4) was transesterified with methanol, using alkaline catalysts such as KOH and NaOH and different molar ratios of methanol to oil (4.5:1, 6:1, 9:1).

The effects of various parameters such as the variation in oil quality, the molar ratio of methanol to oil, the type and amount of alkaline catalyst, the time and temperature of reaction on the yield, and the properties of esters were studied.

The optimum conditions developed for the production of good-quality biodiesel from used sunflower oil were as follows: molar ratio of methanol to oil, 6:1, with 1% of KOH; reaction temperature, 25^0C; and reaction time, 30 min. It was observed that, under the optimal conditions of methanolysis, the quality of the used frying oil did not have an essential effect on the quality of methyl esters produced.

An increase in the quantity of a catalyst and molar ratio of methanol to oil did not change the yield or quality of the esters. Of the two catalysts NaOH and KOH, 1% KOH has given the best yields and viscosities of the esters.

Similarly, a comparison of the catalytic activities of KOH and NaOH for the transesterification of waste cooking oil with an FFA content of 2.76 has been reported by Dorado et al. According to this study, the KOH-catalyzed transesterification proceeds quicker than the NaOH-catalyzed reaction.

The optimization of other reaction parameters (such as temperature, molar ratio of oil to alcohol, reaction time, and stirring) is also reported.

NaOH has been used by many researchers for the transesterification of waste cooking oil, despite its slower reaction rates. The transesterification of waste cooking oil that has an acid value in the range of 0.42-2.07, using NaOH as a catalyst, has been reported by Felizardo et al. The effects of the molar ratio of alcohol to oil (3.6-5.4), the acid value (0.4-2.07), and the sodium hydroxide/frying oil mass ratio (0.2-1.0) on the percentage of ester yield were studied. Oils with an acid value of 0.42 mg KOH/g gave a maximum yield of ester at methanolto- oil molar ratio of 4.8 and a catalyst/oil ratio of 0.6. Using the same type of catalyst (NaOH), the transesterification of waste cooking oil with an acid value of 1.24 was performed with methanol. The optimization of the reaction conditions and the effect of washing of ester with hot water on the glycerine content of biodiesel were also reported.

Three alternative reaction conditions, which included the molar ratio of oil to alcohol (1:6-1:5), catalyst amount (1%-2%), and time (30-120 min) at a reaction temperature of 55 □C to produce 100% ester, were suggested. In the above-reported cases, KOH and NaOH catalysts performed well, the probable reason being the very low FFA content in waste cooking oil. Hence, the problem of saponification was not serious. If the FFA content is >1% and if an alkaline catalyst must be used, then a greater amount of catalyst should be added to neutralize the FFA. The transesterification of processed waste cooking oil (with citric acid added to the waste cooking oil, to remove solids) and unprocessed waste cooking oil was performed with methanol using KOH (1.75 wt %) and 1:6 molar ratio of oil to alcohol at room temperature.

Excess catalyst was used to neutralize the FFA present in the waste cooking oil. The ester yield was 51 wt % with processed waste oil and 58 wt % with unprocessed waste cooking oil. The properties of the processed and unprocessed waste cooking oil methyl esters did not compare well with the canola and greenseed canola methyl esters. For example, these esters had poor cold-temperature properties and a poor lubricity number.

Using the same concept, hydrogenated soybean ethyl ester (HYSEE) was produced from used french fry oil and ethanol (1:6 molar ratio) using 1.43% of KOH as a main treatment catalyst. For each 1% of FFA, an excess of 0.197 g of KOH was added. To avoid an emulsion in the washing phase, 1-octanol and tannic acid were added, along with water.

The conversion to biodiesel was g92%.26 Similarly, Dorado et al. have reported the transesterification of waste cooking oils from different sources such as palm oil and hydrogenated fat from Brazil (5.12% FFA), olive oil from Spain (2.24% FFA), and a mixture of several vegetable oils from Germany (1.28% FFA), using KOH as a catalyst.

The transesterification was performed in two steps, using a stoichiometric amount of methanol and the necessary amount of KOH, supplemented with the additional amounts of KOH to neutralize the FFA. It was observed that a two-step transesterification process without any costly purification steps is a good method for biofuel production from waste cooking oils of different origins with FFA e3%. The conversion efficiency was in the range of 88%-95% after a two-step transesterification process using a basic catalyst.10 Apart from KOH and NaOH, sodium methoxide has been proven to be a very good alkaline catalyst for the transesterification of oils. The transesterification of three fatty materials such as soybean oil (acid index of 0.53%), waste cooking oil (acid index of 0.47%), and tallow (acid index of 6.8%) using sodium methoxide as a catalyst was reported by Alcantara et al. The optimized reaction conditions for the transesterification reaction were as follows: molar ratio of methanol to oil, 7.5.

Table 3.4. Effects of Various Treatments on the Physical and Chemical Properties of Waste Cooking Oil

	Batch 1			**Batch 2**		
Property	**Raw**	**T1**	**T2**	**Raw**	**T1**	**T2**
Moisture content (%)	1.1	0.5	0.4	1.4	0.6	0.4
Density (kg/m³)	0.937	0.925	0.921	0.39	0.929	0.922
Kinematic viscosity (mm²/s)	190.2	130.1	85.3	201.3	110.2	70.1
Acid value	5.3	4.4	3.9	6.3	4.9	4.3
Iodine value	104.3	103.7	105.2	115.3	117.2	116.2
PV (meq/kg)	5.6	5.3	4.6	6.3	5.7	4.4
Saponification number	204.3	194.2	184.2	195.1	194.3	193.9
Unsaponifiable matter (%w/w)	3.9	2.7	1.9	4.9	3.0	2.1
Energy value (kj/g)	37.2	38.8	38.6	37.9	38.3	39.1

Even though it is well-reported that the performance of the alkaline catalyst is not good in the presence of high FFA (>1%), these authors have reported that the acidity index of the fat was not a critical factor when using sodium methoxide as a catalyst. The reusability of a glycerine phase free of methanol, as a catalyst for the transesterification of fresh waste cooking oil, was also examined. It was reported that the used catalyst showed a slightly longer induction period, but after 1 h, the conversion obtained with used and fresh catalysts was almost the same. Catalytic activities of NaOH, KOH, sodium methoxide, and potassium methoxide were compared for the transesterification of used frying oil with methanol that had an FFA content of 1.15%. The effects of operation variables such as the molar ratio of alcohol to oil (3:1-9:1), the catalyst concentration (0.1%-1.5%), the temperature (25-65 °C), and the catalyst type on the ester yield were studied.

The biodiesel with the best properties was obtained using a methanol/oil molar ratio of 6:1, potassium hydroxide as the catalyst (1%), and temperature of 65°C. Two-stage transesterification with a separation of glycerol after the first stage was determined to be better than a onestage process.

The use of a liquid amine-based catalyst for the transesterification of neat vegetable and frying oil has been reported recently. Four amine-based catalysts (such as diethylamine (DEA), dimethylethanol amine (DMAE), tetramethyl diaminoethane (TEMED), and tertramethylammonium hydroxide (TMAH) (as 25% solution in methanol)) were screened for the transesterification reaction. The highest conversion of 98% was achieved with TMAH as a catalyst at 65 °C in 90 min. In this case, a large amount (13%) of liquid amine catalysts is required for the transesterification reaction. Amines used in the reaction not only act as a solvent for reactants but also for the products. Hence, the chemical equilibrium is shifted to the right side thus favoring more product. Also, when a solvent is used for both the oil and biodiesel, which has less solvent power for the glycerol, then it facilitates the glycerol formation in a separate phase.

As stated previously, the products of oil decomposition cause deterioration in oil quality, which can lead to reduced ester yield during biodiesel production and the formation of unwanted products. The negative effects of undesirable compounds can be avoided by pretreatment of the waste cooking oil.

Different types of pretreatments (such as steam injection, column chromatography, neutralization, and film vacuum evaporation) have been used for the purification of waste cooking oil prior to transesterification.

Steam injection and sedimentation treatment were performed on waste cooking oil, and the effects of such refining on the properties of the oil and the corresponding esters were studied by Supple et al. Some of the important changes observed in the oil after first and second treatment were:

1. Reduction in moisture content,
2. Reduction in FFA,
3. Substantial reduction in viscosity and increase in energy value with treatment

The treated raw oil, obtained after treatment 1 (referenced hereafter as T1) and after treatment 2 (referenced hereafter as T2) was transesterified with methanol (6:1 molar ratio of methanol to oil) using KOH (1%) as a catalyst at 60°C. Substantial increase in ester yield was observed after each treatment for both the batches. The decrease in moisture content from 1.4% to 0.4% and FFA from 6.3% to 4.3% corresponded with the increased yield of ester (from 67.5% to 83.5%).

Column chromatography is another efficient technique that is used for the purification of waste cooking oil. The effects of the purification of waste fryer grease (waste cooking oil) on the yield of methyl esters by column chromatography was studied. Restaurant grease that contained 10.6% free fatty acids and 0.2% water was purified by passing it through the column, which contained 50% magnesium silicate plus 50% aluminum oxide (basic).30 In this process, the FFA and water contents decreased from 10.6 to 0.23 wt % and from 0.2% to 0.02 wt %, respectively.

The conversion of crude grease before column chromatography was 25% after 24 h of reaction, which increased to 96% when purified grease was used.

The transesterification of pretreated waste cooking oil was performed in two different stages; using KOH as a catalyst at 65 °C for 90 min. various pretreatment methods were used for waste cooking oil to reduce its FFA, water, and polymer content. FFA was removed by neutralization with alkalis (such as KOH or NaOH) and removed as soaps. Also, waste cooking oil with higher polymer content was treated with activated charcoal, which was removed by adsorption. Of all these methods, film vacuum evaporation was more suitable for deacidification and drying.

Drying was performed under moderate conditions of 159°C and 20 mbar pressure. Deacidification required more severe conditions of 200-280°C and 0.1-8 mbar. The final yield of the methyl esters obtained for treated waste cooking oil was 96%.

Potassium hydroxide (KOH), and sodium hydroxide (NaOH), can act as effective catalysts for the transesterification of the waste cooking oil if the FFA content is <1%. The final product yield seems to be dependent on the FFA content of the waste cooking oil. Additional alkaline catalyst is required to neutralize the FFAs of the waste cooking oil, which would affect the cost of the biodiesel. The amount of liquid amine catalyst required (13%) for the transesterification is very high. Also, the removal of this catalyst from the ester phase is not cost-effective.

The removal of impurities such as FFA, water, and polymers prior to the alkali-catalyzed transesterification can improve the yield and the quality of the esters from waste cooking oil; however, it would increase the cost of pretreatment. Ultimately, this will lead to an increase in the cost of biodiesel.

Table 3.5. Effect of Various Parameters on Acid-Catalyzed Transesterification

Parameter	**Molar Ratio (Methanol : Oil)**	**Catalyst (H2SO4) (%)**	**FFA (%)**	**Temperature (ºC)**	**Time (hrs)**	**Water (%)**	**Conversion (%)**
Effect Of Temperature	6:1	3	0	25 45 60	48	0	10 55 85
Effect of Time of Reaction	6:1	3	0	60	48 96	0	88 95
Effect of Molar ratio	3.3:1 3.9:1 6:1 20:1 30:1	3	0	60	48	0	77 80 87 95 98
Effect of catalys Concentration	6:1	1 3 5	0	60	48	0	72 88 95
Effect of FFA	6.1	3	5 10 15 20 33	60	96	0	90 88 80 73 60
Effect of water	6:1	3	0	60	96	0.1 0.5 1 3 5	92 90 82 32 5

Table 3.6. Reaction Conditions for Transesterification of Used Oils and Yields of Liquid Fuels

Alcohol	**Molar Ratio (alcohol:oil)**	**Temperature (ºC)**	**Time (h)**	**Catalyst**	**Ester Yield (wt%)**	
					2 days at 25 ºC	**7 days at 5 ºC**
Methanol	3.6:1	65	40	0.1% H2SO4	79.3	64.0
		50	24	0.4% KOH	91.9	85.3
Ethanol	3.6:1	73	40	0.1% H2SO4	66.9	54.8
		50	24	0.4% KOH	28.9	
1-propanol	3.5:1	90	40	0.1% H2SO4	92.2	76.2
		50	24	0.4% KOH	42.7	
2-proponol	3.5:1	80	40	0.1% H2SO4	78.7	54.4
		50	24	0.4% KOH	51.2	
1-butanol	3.6:1	105	40	0.1% H2SO4	78.1	61.9
		50	24	0.4% KOH	59.5	
2-ethoxyethanol	4.2:1	125	40	0.1% H2SO4	53.5	39.2
		50	24	0.4% KOH	37.0	

3.1.12.2. Acid-Catalyzed Transesterification

One limitation in the alkali-catalyzed process is its sensitivity to the purity of reactants, especially to both water and FFA. The FFA and water make the use of an alkaline catalyst difficult, because of soap formation and then difficulty in product separation. Freedman et al. have reported that an acid catalyst is insensitive to FFA and is better than the alkaline catalyst for vegetable oil with >1% FFA. The only disadvantage of an acidic catalyst is a slower reaction rate.

The transesterification of edible oil using strong acids (Bro¨nsted acids) such as sulfuric and hydrochloric acid are available in literature reports. The acid-catalyzed transesterification of pure soybean oil was studied by Canakci and Gerpen. The effects of the molar ratio of oil to methanol (1:3.3 to 1:30), reaction temperature (25 to 60 °C), H2SO4 concentration (1%- 5%), reaction time (48 and 96 h), water content (0.1%-5%), and FFA amount (0%-33%) on the conversion of oil were studied. Results obtained are summarized in Table 7.2. The data showed that even 5% FFA or 0.5 wt % water decreased the conversion of oil to esters to <90%. The water formed by the reaction of FFA and methanol also inhibited the reaction. Higher alcohols increased the oil conversion when the reaction was conducted just below the boiling temperature of the alcohol.

The transesterification of used oils collected from the cafeterias at the University of Guelph, Canada, using an acidic catalyst (H2SO4) and an alkaline catalyst (KOH), was compared by Nye et al. Two types of used oils (partially hydrogenated soybean oil and margarine) were transesterified with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-ethoxyethanol. The ester yields were calculated when the product was allowed to settle for 48 h at 25 °C, followed by the removal of solids by gravity and filtration. The filtrate was then allowed to stand at 5 °C for 7 days and refiltered. Composition of the esters showed that fuel obtained at 5°C is richer in ester than those collected at 25 °C, because of better crystallization at lower temperature. Acid-catalyzed esters had higher yields, compared to the base-catalyzed reaction, except for methyl esters. However, more reaction time was required for the acid-catalyzed reaction. All the acid-catalyzed

esters had low viscosities (<13 cP), except for methyl ester. The performance of the best ester was examined in a high-speed diesel engine as fuel. No problems were observed with regard to starting, smoothness in running, and smokiness of the exhaust.

Table 3.7. Comparison of Two Catalysts for the Preparation of Methyl Esters from Waste Oils

Methanol / oil ratio	**Catalyst**	**Reaction time (h)**	**Conditions**	**Ester yield (wt% of fresh oil)**
0.2-0.8	0.01%-2% KOH	1-2	No heat	83-92
0.38	0.12% barium acetate and 0.34% calcium acetate	1-3	High temperature and high pressure	87-94

Catalytic activities of HCl and H2SO4 for the transesterification of waste palm oil was compared.34 Compared to HCl, H2SO4 was a better catalyst. The use of excess alcohol can reduce the longer reaction time that is required for the acidcatalyzed reaction. Thus, Bro¨nsted acid-catalyzed transesterification requires high catalyst concentration and a higher molar ratio to reduce the reaction time. Lewis acids can also act as a catalyst for the transesterification of vegetable oil. Basu et al.35 have developed a process to produce esters from feedstocks that have a high FFA content, diglycerides and monoglyerides, using calcium and barium acetate as a catalyst. This catalyst does not form soap with FFA. The optimized ratio of calcium to barium acetate was 3:1; however, ratios higher than 3:1 promote the formation of salts. The temperature (200-250°C) and pressure (400-600 psi) required for this reaction is quite high. Another disadvantage of this process is that barium compounds used in this reaction are highly toxic in nature. The solubility of barium compounds in methanol is quite high; therefore, data on the leaching of barium compounds in the ester phase would be very useful.

Recently, a method has been developed for the simultaneous esterification and transesterification of waste oils using homogeneous Lewis acids based on carboxylic salts of the metals (Cd, Mn, Pb, Zn). Catalytic activities of these catalysts are related to the Lewis acid strength of the metals (which must have an optimal intermediate value) and to the molecular structure of the anion.

Acetates and stearates of calcium, barium, magnesium, cadmium, manganese, lead, zinc, cobalt, and nickel were tested for their catalytic activity for the transesterification of waste oil at a molar ratio of oil to alcohol of 1:12 and a temperature of 200 °C for 200 min.

The influence of water and FFA on the catalyst activity has been studied. Stearates showed better performance than acetates, because of better solubility in the oil. This catalyst showed better performance than the Bro¨nsted acids at lower catalyst concentration and a lower molar ratio of oil to alcohol.

Hence, homogeneous acid catalysts are good for the transesterification of waste oil with a high FFA content. However, other than the slow reaction rate, and the requirement of high catalyst concentration and high temperature, separation of the catalyst and leaching of the catalyst can be serious issues with homogeneous acid catalysts.

Currently, the focus of the biodiesel research is on the use of a solid acid catalyst for the transesterification of the low-grade oils that have a high FFA content. The advantages of using a solid acid catalyst are (i) they are insensitive to FFA content, (ii) esterification and transesterification can be performed simultaneously, and (iii) removal of the catalyst is easy. Recently, a report has been published that emphasizes the use of a solid acid catalyst for the transesterification of oil with a high FFA content. The ideal solid acid catalyst for the transesterification of waste cooking oil should have characteristics such as an interconnected system of large pores, a moderate to high concentration of strong acid sites, and a hydrophobic surface.

3.1.12.3. Acid and Alkali Catalyzed Two-Step Transesterification

Acidic and alkaline catalysts have their own merits and demerits in the transesterification of waste cooking oil. Hence, looking at the characteristics of both the catalysts, many researchers have used both acidic and alkaline catalysts for the synthesis of biodiesel from waste cooking oil. An acidic catalyst can be used initially to convert FFA to the esters and to decrease the FFA level to e1%. In the second stage, the transesterification of oil can be performed using an alkaline catalyst.

A process was developed by Canakci et al., where the high FFA feedstock was initially treated using an acidic catalyst (H2- SO4) to reduce the FFA level to <1%.

The pretreated feedstock (with <1% FFA) was then transesterified with methanol, using an alkaline catalyst (KOH). The effects of the type of alcohol (methanol and ethanol), the amount of acid catalyst (0, 5, 15, and 25 wt %), and reaction time (1, 15, 30, and 60 min) on the reduction of the FFA level were studied with a synthetic mixture of 20% and 40% palmitic acid in soybean oil, as well with yellow grease (12% FFA) and brown grease (33% FFA) as a feedstock. Some of the important conclusions drawn from this study are given as follows:

1. Two-step acid-catalyzed esterification followed by an alkaline-catalyzed reaction, improved the methyl ester yield from waste cooking oil;
2. The reaction rate increased as the amount of acid catalyst increased;
3. When ethanol was used during the reaction, the rate of decrease in the FFA level of the synthetic mixture was faster than that observed with methanol.
4. The two-step acid-catalyst pretreatment process was successful in decreasing the acid value of yellow and Brown grease to <2 mg KOH/g. However, a higher molar ratio of methanol to FFA (40:1) and more reaction time (1 h) are required when yellow and brown grease are used for transesterification compared to synthetic mixture of virgin oil and FFA. This may be due to the presence of some unsapnifiable matter in yellow and brown grease.

Using the same two-stage transesterification, esters of waste cooking oil with methanol, ethanol, and different mixtures of methanol and ethanol have been prepared by Titipong et al. Mixtures of alcohols were used, to take the advantage of the better solvent properties of ethanol and the desired equilibrium conversion using methanol. An ester yield of >90% was obtained when the two-stage method was used. In the case of mixed alcohols, a small amount of ethyl esters was also formed along with methyl esters. Physical properties of mixed esters were similar to the diesel fuel.

Lepper and Friesenhagen have patented a two-stage acidic and basic catalytic process for the production of fatty acid esters of short-chain aliphatic alcohols from fats and/or oils with an FFA content of >1%.

The oil phase was subjected to esterification with monohydroxy alcohols in the presence of acidic catalyst (sulfuric acid, *p*-toluene sulfonic acid, alkyl benzene sulfonic acid) at temperatures of <120 °C, preferably in the range of 50-100 °C and under pressures no higher than 5 bar and in the presence of a liquid entraining agent (glycerol or ethylene glycol) that is substantially immiscible with the oil phase. The liquid entraining agent is useful to remove the water formed during the acid-catalyzed reaction. The treated oil with the reduced acid number was then transesterified using an alkaline catalyst (KOH or sodium methylate). The residue of the glycerol phase was successfully reused in nine successive reactions without any further addition of glycerol and catalyst. This procedure was found economical and efficient for the transesterification of waste cooking oils with a high FFA content. Thus, utilization of acid and alkaline catalysts in first and second stages, respectively, overcome the problem of a slow reaction rate with acid catalyst and formation of soap with an alkaline catalyst and ultimately increase the ester yield.

However, the two-stage method also faces the problem of catalyst removal in both stages. The problem of catalyst removal in the first stage can be avoided by neutralizing the acidic catalyst, using extra alkaline catalyst in the second stage. However, the use of extra catalyst will add to the cost of the biodiesel.

3.1.12.4. Enzyme-Catalyzed Transesterification

Chemical (acid or alkali)-catalyzed transesterification of waste cooking oil has problems, such as pretreatment of feedstock, recovery of glycerol, removal of the catalyst, and the energy-intensive nature of the process (high stirring speed, and temperature required for good conversions). Enzyme (such as lipase)-catalyzed reactions have advantages over traditional chemical-catalyzed reactions: the generation of no byproducts, easy product recovery, mild reaction conditions, and catalyst recycling. Also, enzymatic reactions are insensitive to FFA and water content in waste cooking oil. The enzymatic alcoholysis of pure triglycerides with or without solvent has been well-documented in the literature. Generally, in the presence of organic solvents, high yields of alkyl esters could be obtained. However, the alcoholysis of long-chain and branched alcohols proceeds efficiently in an organic-solvent-free system. However, the organic-solvent-free methanolysis does not give high conversion, because of inactivation of the enzyme by methanol.

Synthesis of biodiesel using enzymes such as Candida antarctica (SP-435), Mucor meihei (Lipozyme), Geotrichum candidum, Pseudomonas cepacia (PS-30), and Burkhoderias cepacia (IM-BS-30) is well reported in the literature. Nelson et al. screened four lipasessM. meihei (Lipozyme IM 60), C. antarctica (SP 435), G. candidum, and P. cepacia (PS 30)sas catalysts for the transesterification of olive oil, soybean oil, and tallow with short-chain alcohols. The reaction conditions developed for tallow were proved to be effective for the transesterification of waste cooking oil. The optimized reaction conditions developed for the transesterification of tallow were as follows: temperature, 45 °C; stirring speed, 200 rpm; enzyme concentration, 12%-25%, based on triglycerides; molar ratio of alcohol to oil, 3:1, and reaction time, 4-8 h (for primary alcohols) and 16 h (for secondary alcohols). M. meihei was most effective for the transesterification of tallow using primary alcohols (95% conversion) and lipase from C. antarctica and P. cepacia (PS-30) were most efficient using secondary alcohols (90% conversion). In the case of methanol, the reaction was very sensitive to the amount of water added to the reaction mixture, because water reduced the yield of ester that was formed.

A similar case was observed with 95% ethanol when M. meihei was used as a catalyst. In the case of secondary alcohols, the small amount of water (3-100 uL) improved the conversions when C. antarctica and P. cepacia were used as catalysts. The probable reason might be that, in the presence of water and secondary alcohols, the enzyme was not inhibited and gave more conversion. Hexane was used as a solvent for primary alcohols; however, for branched-chain alcohols, beter conversions were obtained without solvents.

Because organic-solvent-free methanolysis does not give high conversions, Watanbe et al. have conducted the transesterification of waste cooking oil via the stepwise addition of methanol, which prevented inactivation of the lipase (C. antarctica). Another major advantage of stepwise methanolysis is that the contaminants (FFA and water) in waste vegetable oil have little or no effect on the efficiency of a stepwise methanolysis and the reusability of an immobilized biocatalyst. The transesterification of waste vegetable oil was performed in a three-step flow methanolysis with three fixed-bed bioreactors, a three-step batch methanolysis, and a one-step flow methanolysis. Methanol was divided equally for all the three steps in fixed-bed reactors. Ninety percent of the waste oil was converted to the corresponding methyl esters by feeding the substrate mixture into the first, second, and third reactors at flow rates of 6, 6, and 4 mL/h, respectively.

In the one-step methanolysis of waste oil, a mixture of waste oil and 90% methyl ester that contained eluate (1:3 w/w) and an equimolar amount of methanol, relative to total fatty acids in the waste oil, was fed into a reactor that was packed with 3 g of immobilized C. antarctica lipase at a flow rate of 4 mL/h, and the methyl ester content in the eluate reached a value of 90%. The products of oxidation and hydrolytic reactions in the vegetable oil did not inhibit the methanolysis of acylglycerols.

Although Nelson et al. have reported that P. cepacia is not a good catalyst for the transesterification of waste cooking oil with primary alcohols, many researchers have tried different ways to get maximum conversion using this lipase. Transesterification of the waste cooking oil has been performed with 95% ethanol using P. cepacia.

The optimized conditions (temperature of 38.4 °C, time of 2.47 h, a lipase PS-30 content of 13.12 wt %, and a molar ratio of ethanol to waste cooking oil of 6.6:1) obtained by factorial design and response surface methodology gave a maximum yield of 85 wt %. The addition of PS-30 after 1 h of the reaction did not significantly improve the conversion of ethyl ester above the value predicted by the model (85 wt %). However, the addition of supported lipase SP435 (5 wt %) from C. antarctica after 1 h of reaction with PS-30 increased the ester yield to 96 wt %. The addition of PS-30 lipase in the first step and the addition of SP 435 in the second step increased the ester yield from 85 wt % to 96 wt %.

The effect of immobilization on the catalytic activity of P. cepacia lipase was examined by Hsu et al.48 P. cepacia lipase (PS-30) was immobilized within a phyllosilicate sol-gel matrix (IM PS-30) and then used for the transesterification of waste fryer grease with primary and secondary alcohols. The reaction was conducted under solvent-free conditions but in the presence of molecular sieves (0.4%), to eliminate water using both free and immobilized PS-30 lipase. The solvent-free condition did not give good conversions with methanol. This process gave poor conversion (47%-89%) when free lipase was used. However, immobilized lipase gave better conversions (84%- 94%) for both primary and secondary alcohols. In the case of 95% ethanol, high ester yields of 81 and 94 wt % were obtained with free and immobilized lipases, respectively. Nelson et al. have observed that the ethyl ester yield was low (68%) in the case of M. meihei lipase with 95 wt % alcohol, compared to that with absolute alcohol (98%), when reaction was conducted with tallow in the presence of hexane.

However, according to Wu et al.,41 85% conversion of recycled restaurant grease was obtained using 95% ethanol and PS-30 lipase in 2.47 h, using 13.7 wt % of PS-30 lipase at 38.4 °C. Using the same lipase (PS-30) immobilized within an phyllosilicate, a sol-gel matrix (IM PS-30) effectively converted grease and tallow to ethyl esters in a yield of >95%. The final conversion of grease or tallow to alkyl esters was aided by the addition of molecular sieves (0.4 wt % of substrates) to the reaction mixture.

Immobilized lipase can be used six times without a significant loss of activity, whereas free lipase lost 50% of its initial activity after second cycle and all activity after the third cycle.

Table 3.8. Yield of Esters Obtained from Restaurant Grease Using Different Alcohols and Enzymes

Alcohol	**GranT.I**	**Gran-C.a.**	**SP435**	**IM PS-30**	**Free[a] IM PS-30**	**IM PS-30[a]**
Methanol	4	27	60	88	47	94
Ethanol	87	76	70	88	81	88
Ethanol (95%)	64	41	30	86	81	94
Propanol	87	79	52	87	87	87
2-propaonol	61	59	87	46	75	90
Butanol	90	56	88	97	89	94
Isobutanol	97	89	94	72	87	84

Reaction conditions were as follows (unless noted otherwise): molar ratio of grease to alcohol, 1:4; enzyme loading, 10 wt %; reaction time, 24 h; reaction temperature, 40 °C; and no solvent. [a] Reaction conditions were as follows: molar ratio of grease to alcohol, 1:4; 100 mg immobilized lipase or 10 mg free lipase powder; reaction temperature, 50 °C; reaction time, 18 h; and 0.4% molecular sieves.

The performance of different lipases for the solvent-free transesterification of restaurant grease with a single-step addition of normal alcohols and branched-chain alcohols was compared with that using IM PS-30 lipase by Hsu et al.49 Lipases used in this study included

Thermomyces ianuginose and C. Antarctica supported on granulated silica (denoted hereafter as Gran-T.I., and Gran C.a., respectively), C. antarctica supported on macroporous acrylic resin (SP435), and P. cepacia immobilized within phyllosillicate sol-gel matrix (IM PS-30). The ester yields with different alcohols and lipases are shown in Table 3.8.

In this study, Gran-T.I., Gran-C.a., and SP435 produced low ester yields when methanol and 95% ethanol were used, as these lipases were deactivated with a single-step addition of alcohols. Similar observation was made by Nelson et al. However, IM PS-30 did not deactivate (98% ester yield in 48 h) with the single-step addition of alcohols, because the lipase was constrained in the matrix. SP435 was a good catalyst for branched alcohols. Similar observation was also made by Nelson et al. and Hsu et al. Gran-T.I. was good for all alcohols except for methanol and 2-propanol. IM PS-30 was an excellent enzyme for normal alcohols but was not good for branched alcohols. Reaction media with a water concentration of <0.5 wt %, in the case of lipase, resulted in highest conversions. The addition of molecular sieves improved the methyl ester yield by 20%, using IM PS-30. However, reactions that were catalyzed by granulated lipases were not affected by molecular sieves.

Hsu et al. have studied the continuous transesterification of waste cooking oil with ethanol using immobilized lipase from Burkholderias cepacia (IM-BS-30) as a catalyst in a recirculating packed-column reactor. The effects of feed flow rate (5- 50 mL/min), temperature (40-60 °C), reaction time (8-48 h), and reusability of the enzyme on the product yield was studied. The optimized conditions for 96 wt % ester yield were as follows: feed flow rate, 30 mL/min; temperature, 50 °C; molar ratio of substrates (ethanol to grease), 4:1; and reaction time, 48 h.

Thus, immobilization has a substantial effect on the catalytic activity of lipase, especially when feedstock with high FFA and water contents is used for the transesterification. Immobilized enzymes such as *P. cepacia* and *B. cepacia* are efficient enzymes for the transesterification of waste cooking oil that is contaminated with FFA and water.

3.1.12.5. Catalyst-Free Technology for Transesterification

Novel methanolysis processes are being developed for the synthesis of biodiesel from vegetable oils using noncatalytic methods. The disadvantages that result from the use of a catalyst and its removal from the products are eliminated if a noncatalytic transesterification reaction of vegetable oils with alcohol is realized. The use of supercritical methanol for the production of biodiesel is one such emerging technology.

In the case of a supercritical fluid process, the reactor pressure and temperature are manipulated to influence the thermophysical properties of solvent (methanol), such as dielectric constant, viscosity, specific gravity, and polarity. Liquid methanol is a polar solvent and has hydrogen bonding between the hydroxide oxygen and the hydroxide hydrogen to form methanol clusters. In supercritical methanol, with increasing temperature, the degree of hydrogen bonding decreases, which helps to reduce the polarity of methanol in a supercritical state? The decrease in the polarity of methanol increases the solubility of oil in it. Because of the hydrophobic nature of nonpolar triglycerides, they are well-solvated in supercritical methanol to form a singlephase oil/methanol mixture. The higher solubility of oil in methanol increases the rate of formation of methyl esters dramatically in the supercritical state. The ionic product, which is an important parameter for chemical reactions, can also be improved by increasing the pressure. Therefore, in the supercritical methanol treatment of vegetable oil, methanol not only acts as a solvent but also as an acid catalyst.

The biodiesel production from pure vegetable oil such as rapeseed using supercritical methanol has been performed by Saka and Kusdiana. It was demonstrated that preheating to a temperature of 350 °C and treatment for 240 s in supercritical methanol were sufficient to convert rapeseed oil to methyl esters. Although the properties of the methyl esters prepared by this method were similar to those prepared by the common method with a basic catalyst, the yield of methyl ester obtained by the supercritical method was higher.

Kinetic analysis of the transesterification reaction of rapeseed oil in subcritical and supercritical methanol revealed that the rate of formation of methyl esters from rapeseed oil increased dramatically in the supercritical state. At subcritical temperatures (<239 °C), the reaction rates are low, but at the supercritical state (at 350 °C), the rate constant increased by a factor of _85.

The optimized reaction conditions developed for the synthesis of methyl esters from rapeseed oil were a temperature of 350 °C and a molar ratio of oil to methanol of 1:42.53.

Although the use of supercritical alcohol for the transesterification of pure vegetable oil is well reported in the literature, the application of this technique for the transesterification of waste cooking oil is not well-documented.

Table 3.9. Comparison of the Yields of Methyl Esters in Supercritical Methanol and via Alkaline-Catalyzed and Acid-Catalyzed Methods

Vegetable oil	**FFA content (wt%)**	**Water content (wt%)**	**Alkaline-catalyzed**	**Acid-catalyzed**	**Supercritical methanol**
Rapeseed oil	2.0	0.02	97.0	98.4	98.5
Palm oil	5.3	2.1	94.4	97.8	98.9
Used frying oil	5.6	0.2	94.1	97.8	96.9
Waste palm oil	>20.0	>61.0	No reaction	No reaction	95.8

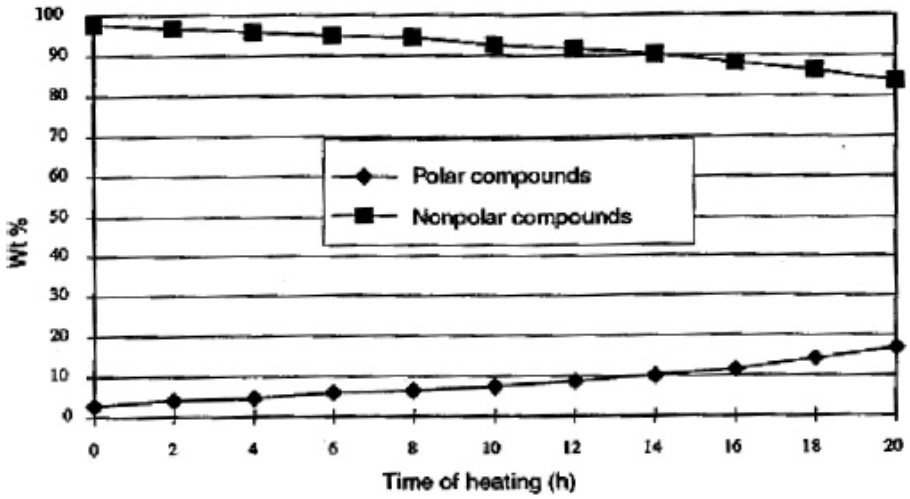


Figure 3.8. Formation of polar compounds during the heating of rapeseed oil

As described previously, waste cooking oil is usually contaminated with many impurities, with FFA and water being the major impurities. To extend the use of the supercritical methanol method for the transesterification of waste cooking oil, the effect of water and FFAs on the yield of methyl esters was studied.50,51 The reactivity of the transesterification of triglycerides and the alkyl esterification of fatty acid was investigated using different supercritical alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-octanol).50 Esterification and transesterification reactions were conducted out under identical conditions, such as a temperature of 300 °C and an oil/fatty acid to alcohol molar ratio of 1:42. The result demonstrated that the alkyl esterification had higher reaction rates, compared to the transesterification. The rate of esterification of saturated and unsaturated fatty acids with various alcohols was also studied. Saturated fatty acids such as palmitic and stearic acids had slightly lower reactivity than that of the unsaturated fatty acids (such as oleic, linoleic, and linolenic acids). Among all the supercritical alcohols, the rate of transesterification was faster when supercritical methanol was used.50 To investigate the effect of water on the yield of methyl esters in the transesterification of triglycerides and the methyl esterification of fatty acids, the reaction was conducted at a temperature of 350°C, a pressure of 43 MPa, and an oil/fatty acids to alcohol molar ratio of 1:42.51 The presence of water did not have a significant effect on the yield, because complete conversions of oil were always achieved, regardless of the water content. However,

the fatty acid esterification reaction was affected by the presence of water. The supercritical methanol method is determined to be more water-tolerant than the conventional method using an alkaline catalyst. The yield of methyl esters obtained from various raw materials that contained different amounts of water and FFA via the supercritical methanol method is shown in Table 7.6. Waste palm oil with water and FFA contents over 61 wt % and 20 wt %, respectively, produced 95.8 wt % of ester using the supercritical methanol method. However, the feed did not produce any ester while using acid and alkaline methods. These results proved that crude vegetable oil as well as their wastes could be readily used for biodiesel production by the supercritical methanol method.

Despite having all the above advantages, the supercritical methanol method has some serious disadvantages. These include the requirement of high temperature (350 °C) and high pressure (45 MPa). In addition, this method requires a large amount of methanol (1:42 molar ratio of oil to alcohol).

Therefore, to apply this method on an industrial scale, further investigations of the production process, such as continuous operation and scaling up, as well as economic evaluations, are needed.

3.1.12.6. Conclusions and future prospects

Waste cooking oil is an economical choice for biodiesel production, because of its availability and low cost. This oil has many undesirable compounds such as polymers, free fatty acid (FFA), and many other chemicals that are formed during frying, which are of major concern during the transesterification reaction. Pretreatment of the waste cooking oil to remove these undesirable chemicals is not practical. Depending on the water and FFA content of the waste cooking oil, a transesterification method should be selected. If the FFA and water contents are <1 wt % and <0.5 wt %, respectively, then an alkaline catalyst is more suitable for the ester production. If the FFA content of oil is high (>1 wt %), then an acid catalyst is a good choice. However, because of the requirement of high catalyst concentration and high molar ratio, and because of corrosion problems, these catalysts are also not

recommended for the transesterification of waste cooking oil. A two-step method (an acidcatalyzed step, followed by an alkaline-catalyzed step) is not feasible, because it requires many steps, which makes the biodiesel process costly. Enzyme-catalyzed transesterification is a very good option to all chemical-catalyzed reactions; however, it must be developed for its commercialization. The catalyst-free supercritical methanol method has great potential for biodiesel production from waste cooking oil; however, the requirements of high temperature (350 °C), high pressure (45MPa), and high molar ratio of oil to alcohol (1:42) makes the use of this process difficult on an industrial scale. It is recommended that the development of a novel solid acid catalyst that consists of large pores, a moderate to high concentration of strong acid sites, and a hydrophobic surface could be a better choice for the transesterification of waste cooking oil with high FFA. The performances of biodiesel obtained from waste cooking oil as transportation fuel or as an additive are better in all aspects, except for increased NO*x* emissions and high Conradson carbon residue (CCR) [79].

3.1.13. Bıodıesel Economy

Economic advantages of biodiesel can be listed as follows: it reduces greenhouse gas emissions, it helps to reduce a country's reliance on crude oil imports and supports agriculture by providing a new labor and market opportunities for domestic crops, it enhances the lubricating property and it is widely accepted by vehicle manufacturers [80]. The major economic factor to consider for input costs of biodiesel production is the feedstock, which is about 80% of the total operating cost.

Other important costs are labor, methanol and catalyst, which must be added to the feedstock. In some countries, filling stations sell biodiesel more cheaply than conventional diesel. The cost of biodiesel fuels varies depending on the base stock, geographic area, variability in crop production from season to season, the price of the crude petroleum and other factors. Biodiesel has over double the price of petroleum diesel. The high price of biodiesel is in large part due to the high price of the feedstock.

However, biodiesel can be made from other feedstocks, including beef tallow, pork lard and yellow grease. Biodiesel is becoming of interest to companies interested in commercial scale production as well as the more usual home brew biodiesel user and the user of straight vegetable oil or waste vegetable oil in diesel engines. Biodiesel is commercially available in most oilseed-producing countries.
Biodiesel is a technologically feasible alternative to petrodiesel, but nowadays biodiesel cost is 1.5–3 times higher than the fossil diesel cost in developed countries. Biodiesel is more expensive than petrodiesel, though it is still commonly produced in relatively small quantities (in comparison to petroleum products and ethanol). The competitiveness of biodiesel to petrodiesel depends on the fuel taxation approaches and levels. Generally, the production costs of biodiesel remain much higher compared to the petrodiesel ones. Therefore, biodiesel is not competitive to petrodiesel under current economic conditions. The competitiveness of biodiesel relies on the prices of biomass feedstock and costs, linked to the conversion technology. Recent increase of biodiesel potential is not only in the number of plants, but also in the size of the facilities. The tremendous growth in the biodiesel industry is expected to have a significant impact on the price of biodiesel feedstocks. This growth in the biodiesel industry will increase competition. An earlier evaluation of the potential feedstocks for biodiesel by Hanna et al. (2005) also identified the expected price pressures on biodiesel feedstocks.

Fiscal incentives for biodiesel such as reductions both in feedstock and processing costs and tax exemptions will be the key instrument to enhance the biodiesel application as an alternative fuel for transport in near future. Biodiesel has demonstrated a number of promising characteristics, including reduction of exhaust emissions (Dunn, 2001). The advantages offered by biodiesel have to be considered at levels, beyond the agricultural, transport and energy sectors only. Economic benefits of a biodiesel industry would include value added to the feedstock, an increased number of rural manufacturing jobs, increased income taxes, investments in plant and equipment. In the recent years, the importance of non-food crops increased significantly.

The opportunity to grow non-food crops under the compulsory set-aside scheme is an option to increase the biodiesel production. The possibility of growing non-food crops under compulsory set-aside scheme is an opportunity for the biodiesel market, but it is not an appropriate instrument to promote non-food production. Blends of up to 20% biodiesel mixed with petrodiesel fuels can be used in nearly all diesel equipments and are compatible with most storage and distribution equipment. Higher blends, even B100, can be used in many engines built with little or no modification. Transportation and storage, however, require special management. Material compatibility and warrantee issues have not been resolved with higher blends. Biodiesel has become more attractive recently because of its environmental benefits. The cost of biodiesel, however, is the main obstacle to commercialization of the product. With cooking oils used as raw material, the viability of a continuous transesterification process and recovery of high-quality glycerol as a biodiesel by-product are primary options to be considered to lower the cost of biodiesel (Maand Hanna, 1999; Zhang et al., 2003).

Most of the biodiesel that is currently made uses soybeanoil, methanol and an alkaline catalyst. Methanol is preferred, because it is less expensive than ethanol (Graboski and McCormick, 1998). Base catalyst is preferred in transesterification, because the reaction is quick and thorough. It also occurs at lower temperature and pressure than other processes, resulting in lower capital and operating costs for the biodiesel plant. The high value of soybean oil as a food product makes production of a cost effective fuel very challenging. However, there are large amounts of low-cost oils and fats, such as restaurant waste and animal fats that could be converted to biodiesel. The problem with processing these low-cost oils and fats is that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst (Canakci and Van Gerpen, 2001).

A review of 12 economic feasibility studies shows that the projected costs for BD from oilseed or animal fats have a range of US$0.30–0.69/l, including meal and glycerin credits and the assumption of reduced capital investment costs by having the crushing and/or esterification facility added onto an existing grain or tallow facility. Rough projections of the cost of BD from vegetable oil and waste grease are,

respectively, US$0.54–0.62/l and US$0.34–0.42/l. With pre-tax diesel priced at US$0.18/l in the US and US$0.20–0.24/l in some European countries, biodiesel is thus currently not economically feasible, and more research and technological development will be needed (Demirbas, 2003; Bender, 1999). The total energy use for biodiesel production in the common method is 17.9 MJ/l biodiesel. Transesterification process alone consumes 4.3MJ/l, while from our calculation, the supercritical methanol method requires as much as 3.3 MJ/l, or energy reduction of 1.0MJ for each liter of biodiesel fuel. In the common catalyzed method, mixing is significant during the reaction.

In our method, since the reactants are already in a single phase, mixing is not necessary. Since our process is much simpler, particularly in purification step which only needs a removal of unreacted methanol, it is further expected that about 20% of cost reduction can be realized from transesterification process. Therefore, the production cost for biodiesel fuel from rapeseed oil falls to be US$0.59/l, compared to US$0.63/l for the common catalyzed method (Saka and Kusdiana, 2001). The brake power of biodiesel was nearly the same as with petrodiesel, while the specific fuel consumption was higher than that of petrodiesel. Carbon deposits inside the engine were normal, with the exception of intake valve deposits. The results showed the transesterification treatment decreased the injector coking to a level significantly lower than that observed with petrodiesel (Demirbas, 2003). Although most researchers agree that vegetable oil ester fuels are suitable for use in CIE, a few contrary results have also been obtained. The results of these studies point out that most vegetable oil esters are suitable as diesel substitutes but that more long-term studies are necessary for commercial utilization to become practical.

3.1.13.1. Biodiesel policy

In general, energy policy includes issues of energy production, distribution and consumption. It is the manner a given entity has decided to address these issues. The attributes of energy policy may include international treaties, legislation on commercial energy activities (trading, transport, storage, etc.), incentives to investment, guidelines for energy production, conversion and use (efficiency and emission standards), taxation and other public policy techniques, energy-related research and development, energy economy, general international trade agreements and marketing, energy diversity and risk factors contrary to possible energy crisis. Current energy policies also address environmental issues including environmental friendly technologies to increase energy supplies and encourage cleaner, more efficient energy use, air pollution, greenhouse effect (mainly reducing carbon dioxide emissions), global warming and climate change (Demirbas, 2006c). Many farmers who raise oilseeds use a biodiesel blend in tractors and equipment as a matter of policy, to foster production of biodiesel and raise public awareness. It is sometimes easier to find biodiesel in rural areas than in cities. Additional factors must be taken into account, such as the fuel equivalent of the energy required for processing, the yield of fuel from raw oil, the return on cultivating food and the relative cost of biodiesel versus petrodiesel. Some nations and regions that have pondered transitioning fully to biofuels have found that doing so would require immense tracts of land if traditional crops are used. While well intentioned, policy makers are on the wrong track for promoting biodiesel. Biodiesel policy should reflect that theme by aggressively eliminating the government imposed barriers to its success. Biodiesel policy should be based firmly in the philosophy of freedom. Given the history of petroleum politics, it is imperative that today's policy decisions ensure a free market for biodiesel. Producers of all sizes must be free to compete in this industry, without farm subsidies, regulations and other interventions skewing the playing field. The production and utilization of biodiesel are facilitated firstly through the agricultural policy of subsidizing the cultivation of nonfood crops. Secondly, biodiesel is exempt from the oil tax. European research and testing indicate that used as a diesel fuel

substitute, biodiesel can replace petroleum diesel. Biodiesel, produced mainly from rapeseed or sunflower seed, comprises 80% of Europe's total biofuel production. The European Union accounted for nearly 89% of all biodiesel production worldwide in 2005. Germany produced 1.9 billion liters or more than half the world total. Other countries with significant biodiesel markets in 2005 included France, the United States, Italy and Brazil.

All other countries combined accounted for only 11% of world biodiesel consumption in 2005. In Germany biodiesel is also sold at a lower price than fosil diesel fuel. Biodiesel is treated like any other vehicle fuel in the UK. European Union has set the goal of obtaining 5.75% of transportation fuel needs from biofuels by 2010 in all member states in February 2006. Many countries have adopted various policy initiatives. Specific legislation to promote and regulate the use of biodiesel is in force in Germany, Italy, France, Austria and Sweden.

Table 3.10. Biodiesel Production Capacity of Europan Union in 2003

Country	(1000 metric tons)
Germany	1025
France	500
Italy	420
Austria	50
Denmark	40
United Kingdom	5
Sweden	8
Total	2048

Source: EBB (2004).

Table 3.10 shows the biodiesel production capacity of European Union in 2003. By 2010, the United States is expected to become the world's largest single biodiesel market, accounting for roughly 18% of world biodiesel consumption,

followed by Germany. New and large single markets for biodiesel are expected to emerge in China, India and Brazil.

3.1.13.2. Conclusion

Biodiesel, defined as the monoalkyl esters of fatty acids derived from vegetable oil or animal fat, in application as an extender for combustion in compression ignition engines (CIEs), has demonstrated a number of promising characteristics, including reduction of exhaust emissions. It is well known that transport is almost totally dependent on fossil fuels. Biodiesel is one of these feasible alternatives.

The biodiesel fuels have not been acceptable because they are more expensive than petroleum fuels. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in biodiesel fuels for diesel engines. Alternative fuels for CIEs have become increasingly
important due to increased environmental concerns, and several socioeconomic aspects. In this sense, biodiesel derived from vegetable oils and animal fats represents a promising alternative to conventional diesel fuel (Dorado et al., 2003). The CIE or diesel engine exhaust emissions have the potential to cause a range of health problems. The ozone-forming potential of the speciated HC emissions was nearly 50% less than that measured for petrodiesel. The exhaust emissions of carbon monoxide (CO) from biodiesel were 50% lower than CO emissions from petrodiesel. The exhaust emissions of particulate matter (PM) from biodiesel were 30% lower than overall PM emissions from petrodiesel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on engine family and testing procedures. Biodiesel emissions showed decreased levels of polycyclic aromatic hydrocarbons (PAH) compounds and nitrited PAH compounds which have been identified as Biodiesel standards have been developed in the United States, Europe and elsewhere around the world. Main advantages of biodiesel include domestic origin, reducing the dependency on imported petroleum, biodegradability, high flash point and inherent lubricity in the neat form. Biodiesel is a biodegradable, combustible liquid fuel

derived from new or used vegetable oils or animal fats. Low blends of biodiesel can be used in any normal internal combustion diesel engine with no modifications. Higher blends of biodiesel (over 20%) may require minor modifications.

The properties of biodiesel are close to diesel fuels. The biodiesel was characterized by determining its viscosity, density, cetane number, cloud and pour points, characteristics of distillation, flash and combustion points and higher heating value (HHV) according to ISO norms. Biodiesel reduces carbon dioxide, carbon monoxide, PAHs, nitrated PAHs emissions. The use of biodiesel decreases the solid carbon fraction of PM and reduces the sulfate fraction, while the soluble, or HC, fraction stays the same or increases. Emissions of nitrogen oxides increase with the concentration of biodiesel in the fuel. Some biodiesel produces more nitrogen oxides than others, and some additives have shown promise in modifying the
increases [88].

3.2. Cracking

3.2.1. Introduction

In petroleum geology and chemistry, cracking is the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of catalysts. Cracking is the breakdown of a large alkane into smaller, more useful alkanes and alkenes. Simply put, hydrocarbon cracking is the process of breaking a long-chain of hydrocarbons into short ones. More loosely, outside the field of petroleum chemistry, the term "cracking" is used to describe any type of splitting of molecules under the influence of heat, catalysts and solvents, such as in processes of destructive distillation or pyrolysis. Fluid catalytic cracking produces a high yield of gasoline and LPG, while hydrocracking is a major source of jet fuel, diesel, naphtha, and LPG.

3.2.2. Inıtıatıon

In these reactions a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves breaking a chemical bond between two carbon atoms, rather than the bond between a carbon and a hydrogen atom.

3.2.3. Crackıng Methodologıes

3.2.3.1. Thermal cracking

Thermal cracking was the first category of hydrocarbon cracking to be developed. Thermal cracking is an example of a reaction whose energetics are dominated by entropy (ΔS°) rather than by enthalpy (ΔH°) in the Gibbs Free Energy equation $\Delta G^\circ=\Delta H^\circ-T\Delta S^\circ$. Although the bond dissociation energy D for a carbon-carbon single bond is relatively high (about 375 kJ/mol) and cracking is highly endothermic, the large positive entropy change resulting from the fragmentation of one large molecule into several smaller pieces, together with the extremely high temperature, makes $T\Delta S^\circ$ term larger than the ΔH° term, thereby favoring the cracking reaction.

Modern high-pressure thermal cracking operates at absolute pressures of about 7,000 kPa. An overall process of disproportionation can be observed, where "light", hydrogen-rich products are formed at the expense of heavier molecules which condense and are depleted of hydrogen. The actual reaction is known as homolytic fission and produces alkenes, which are the basis for the economically important production of polymers.

Thermal cracking is currently used to "upgrade" very heavy fractions or to produce light fractions or distillates, burner fuel and/or petroleum coke.

Two extremes of the thermal cracking in terms of product range are represented by the high-temperature process called "steam cracking" or pyrolysis (ca. 750 °C to 900 °C or higher) which produces valuable ethylene and other feedstocks for the petrochemical industry, and the milder-temperature delayed coking (ca. 500 °C) which can produce, under the right conditions, valuable needle coke, a highly crystalline petroleum coke used in the production of electrodes for the steel and aluminium industries. The first thermal cracking method, the Shukhov cracking process, was invented by Russian engineer Vladimir Shukhov, in the Russian empire, Patent No. 12926, November 27, 1891. William Merriam Burton developed one of the earliest thermal cracking processes in 1912 which operated at 700–750 °F (371–399 °C) and an absolute pressure of 90 psi (620 kPa) and was known as the Burton process. Shortly thereafter, in 1921, C.P. Dubbs, an employee of the Universal Oil Products Company, developed a somewhat more advanced thermal cracking process which operated at 750–860 °F (399–460 °C) and was known as the Dubbs process. The Dubbs process was used extensively by many refineries until the early 1940s when catalytic cracking came into use.

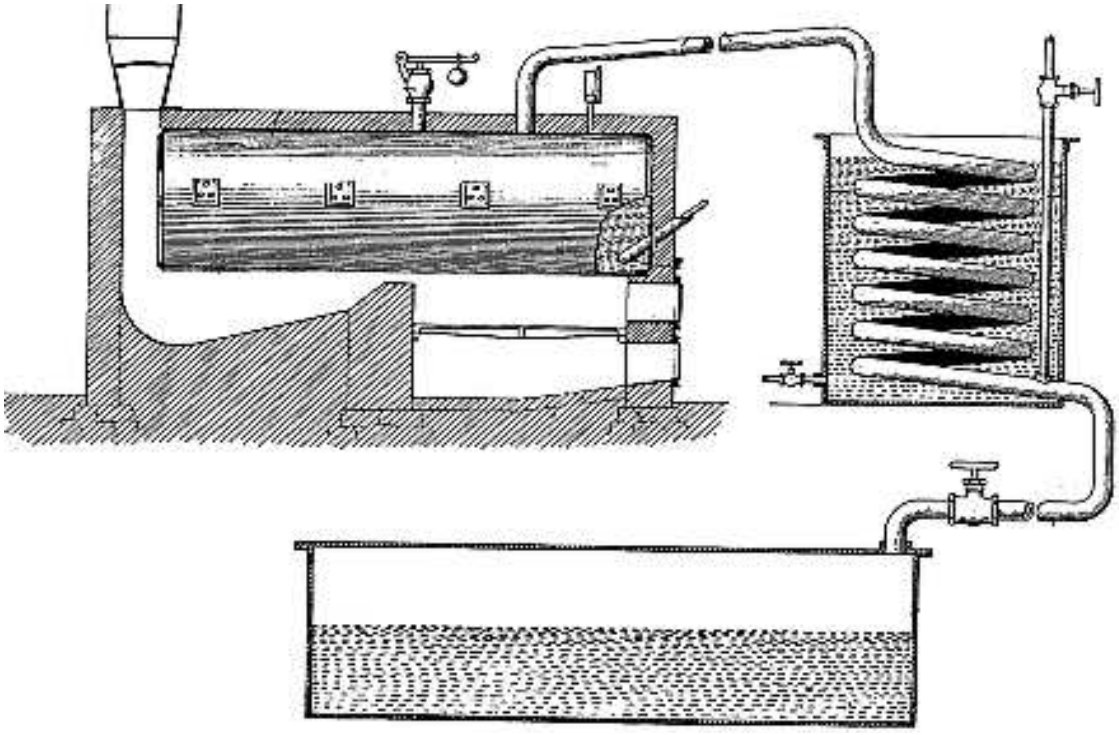


Figure 3.9. Thermal Cracking Process Devices

3.2.3.2. Steam cracking

Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (or commonly olefins), including ethene (or ethylene) and propene (or propylene). Steam cracker units are facilities in which a feedstock such as naphtha, liquefied petroleum gas (LPG), ethane, propane or butane is thermally cracked through the use of steam in a bank of pyrolysis furnaces to produce lighter hydrocarbons. The products obtained depend on the composition of the feed, the hydrocarbon-to-steam ratio, and on the cracking temperature and furnace residence time. In steam cracking, a gaseous or liquid hydrocarbon feed like naphtha, LPG or ethane is diluted with steam and briefly heated in a furnace without the presence of oxygen. Typically, the reaction temperature is very high, at around 850°C, but the reaction is only allowed to take place very briefly. In modern cracking furnaces, the residence time is reduced to milliseconds to improve yield, resulting in gas velocities faster than the speed of sound. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil. The products produced in the reaction depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time. Light hydrocarbon feeds such as ethane, LPGs or light naphtha give product streams rich in the lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphthas as well as other refinery products) feeds give some of these, but also give products rich in aromatic hydrocarbons and hydrocarbons suitable for inclusion in gasoline or fuel oil. A higher cracking temperature (also referred to as severity) favors the production of ethene and benzene, whereas lower severity produces higher amounts of propene, C4-hydrocarbons and liquid products. The process also results in the slow deposition of coke, a form of carbon, on the reactor walls. This degrades the efficiency of the reactor, so reaction conditions are designed to minimize this. Nonetheless, a steam cracking furnace can usually only run for a few months at a time between de-

cokings. Decokes require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils. This converts the hard solid carbon layer to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.

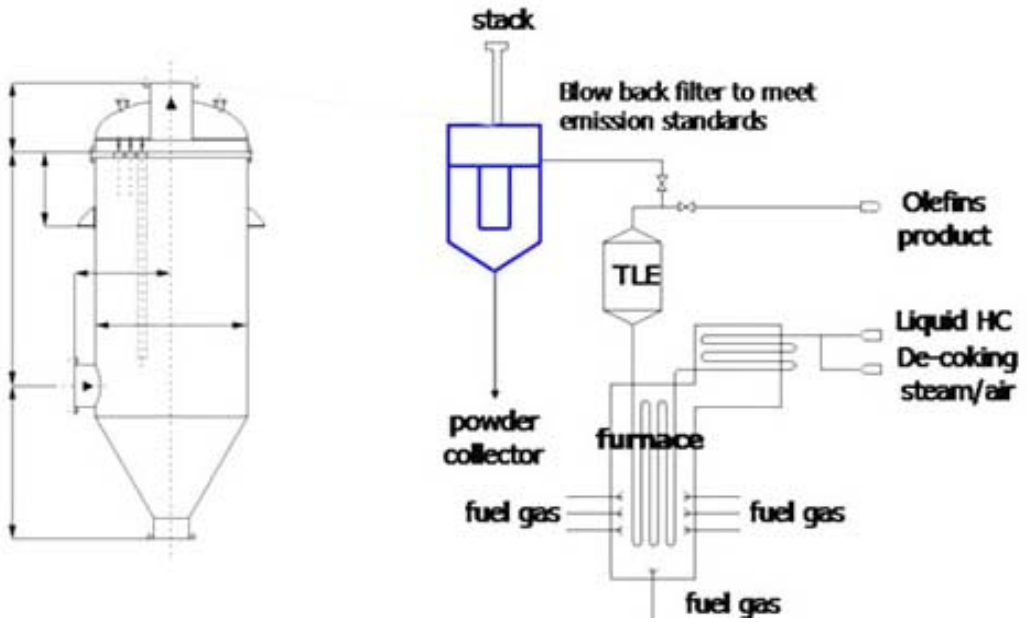


Figure 3.10. Steam Cracking Process Information

3.2.3.3. Catalytic methods

The catalytic cracking process involves the presence of acid catalysts (usually solid acids such as silica-alumina and zeolites) which promote a heterolytic (asymmetric) breakage of bonds yielding pairs of ions of opposite charges, usually a carbocation and the very unstable hydride anion. Carbon-localized free radicals and cations are both highly unstable and undergo processes of chain rearrangement, C-C scission in position beta as in cracking, and intra- and intermolecular hydrogen transfer. In both types of processes, the corresponding reactive intermediates (radicals, ions) are permanently regenerated, and thus they proceed by a self-propagating chain mechanism. The chain of reactions is eventually terminated by radical or ion recombination.

3.2.3.4. Fluid Catalytic cracking

Fluid catalytic cracking is a commonly used process, and a modern oil refinery will typically include a cat cracker, particularly at refineries in the US, due to the high demand for gasoline. The process was first used around 1942 and employs a powdered catalyst. During WWII, in contrast to the Axis Forces which suffered severe shortages of gasoline and artificial rubber, the Allied Forces were supplied with plentiful supplies of the materials. Initial process implementations were based on low activity alumina catalyst and a reactor where the catalyst particles were suspended in a rising flow of feed hydrocarbons in a fluidized bed. Alumina-catalyzed cracking systems are still in use in high school and university laboratories in experiments concerning alkanes and alkenes. The catalyst is usually obtained by crushing pumice stones, which contain mainly aluminium oxide and silica into small, porous pieces. In the laboratory, aluminium oxide (or porous pot) must be heated.

In newer designs, cracking takes place using a very active zeolite-based catalyst in a short-contact time vertical or upward-sloped pipe called the "riser".

Pre-heated feed is sprayed into the base of the riser via feed nozzles where it contacts extremely hot fluidized catalyst at 1,230 to 1,400 °F (666 to 760 °C). The hot catalyst vaporizes the feed and catalyzes the cracking reactions that break down the high-molecular weight oil into lighter components including LPG, gasoline, and diesel. The catalyst-hydrocarbon mixture flows upward through the riser for a few seconds, and then the mixture is separated via cyclones.

The catalyst-free hydrocarbons are routed to a main fractionator for separation into fuel gas, LPG, gasoline, naphtha, light cycle oils used in diesel and jet fuel, and heavy fuel oil.

During the trip up the riser, the cracking catalyst is "spent" by reactions which deposit coke on the catalyst and greatly reduce activity and selectivity.

The "spent" catalyst is disengaged from the cracked hydrocarbon vapors and sent to a stripper where it is contacts steam to remove hydrocarbons remaining in the catalyst pores. The "spent" catalyst then flows into a fluidized-bed regenerator where air (or in some cases air plus oxygen) is used to burn off the coke to restore catalyst

activity and also provide the necessary heat for the next reaction cycle, cracking being an endothermic reaction. The "regenerated" catalyst then flows to the base of the riser, repeating the cycle.

The gasoline produced in the FCC unit has an elevated octane rating but is less chemically stable compared to other gasoline components due to its olefinic profile. Olefins in gasoline are responsible for the formation of polymeric deposits in storage tanks, fuel ducts and injectors. The FCC LPG is an important source of C_3-C_4 olefins and isobutane that are essential feeds for the alkylation process and the production of polymers such as polypropylene.

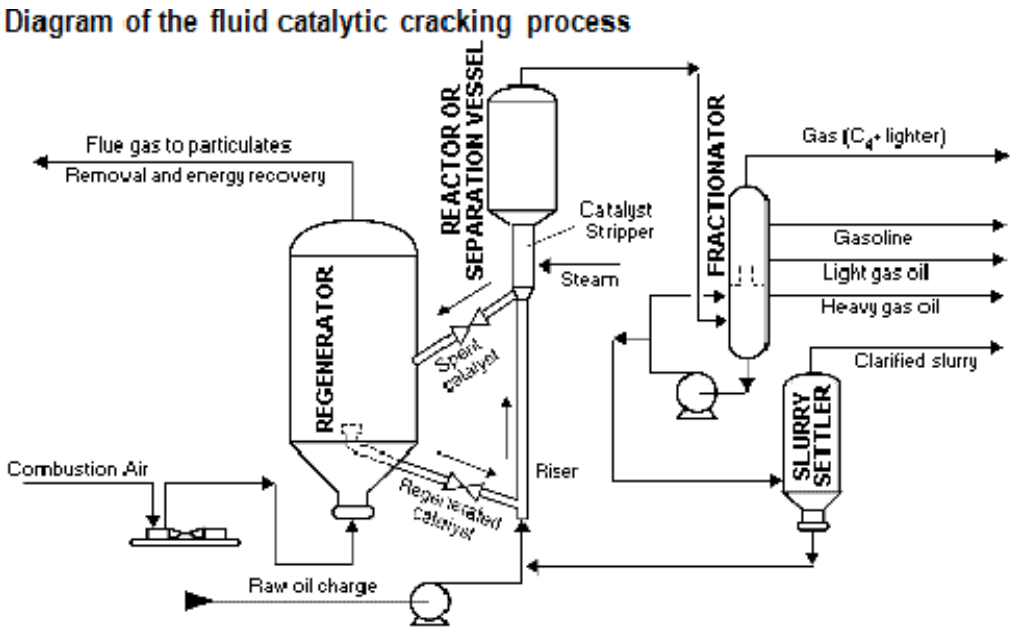


Figure 3.11. Fluid Catalytic Cracking process

3.2.3.5. Hydrocracking

Hydrocracking is a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen gas. Similar to the hydrotreater, the function of hydrogen is the purification of the hydrocarbon stream from sulfur and nitrogen hetero-atoms.

The products of this process are saturated hydrocarbons; depending on the reaction conditions (temperature, pressure, catalyst activity) these products range

from ethane, LPG to heavier hydrocarbons consisting mostly of isoparaffins. Hydrocracking is normally facilitated by a bifunctional catalyst that is capable of rearranging and breaking hydrocarbon chains as well as adding hydrogen to aromatics and olefins to produce naphthenes and alkanes.

The major products from hydrocracking are jet fuel and diesel, but high octane rating gasoline fractions and LPG are also produced. All these products have a very low content of sulfur and other contaminants.

In 1920, a plant for the commercial hydrogenation of brown coal was commissioned at Leuna in Germany . It is very common in Europe and Asia because those regions have high demand for diesel and kerosene. In the US, fluid catalytic cracking is more common because the demand for gasoline is higher.

The hydrocracking process largely depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking. Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (1,000-2,000 psi) and fairly high temperatures (750°-1,500° F), in the presence of hydrogen and special catalysts.

The primary function of hydrogen is, thus: a) If feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds. b) Reduced tar formation c) Reduced Impurities d) Prevent buildup of coke on the catalyst. e) Convert sulfur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia. f) High octane fuel is achieved [87].

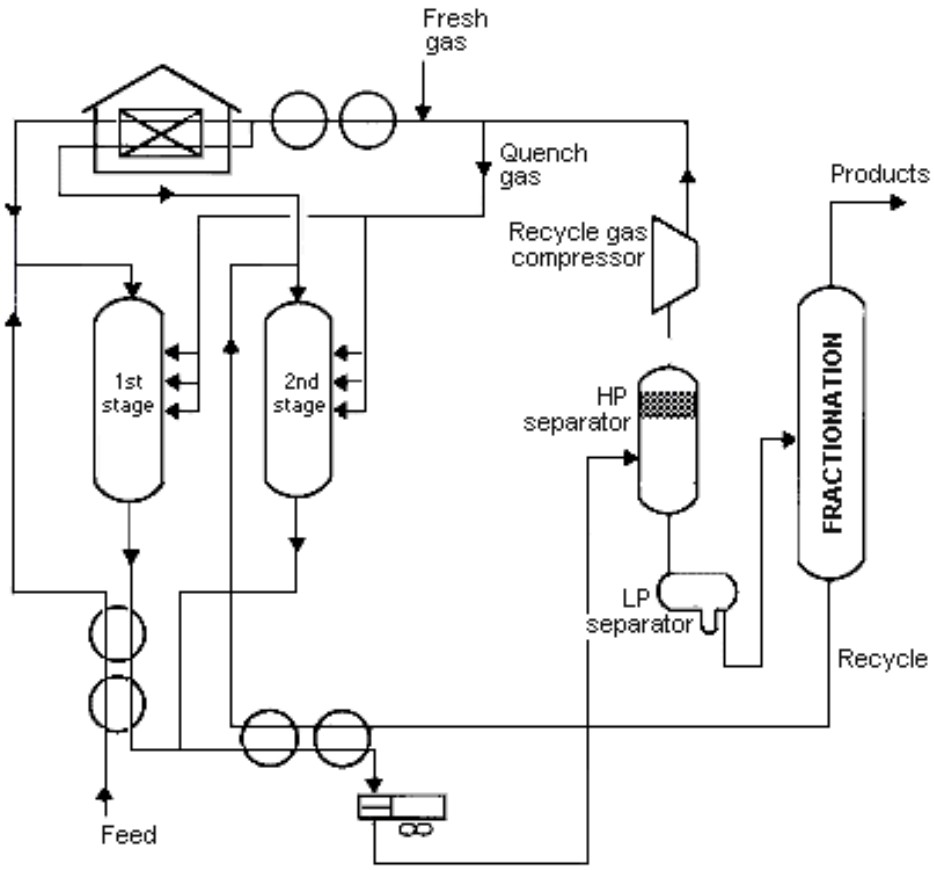


Figure 3.12. Hydrocracking process

3.2.4. Thermal Crackıng Of Used Oıl To Produce Dıstıllate Gasoıl

Thermal cracking, visbreaking, catalytic cracking, fluid catalytic cracking, hydrocracking, and coking are all well known crude oil refinery variations on the basic principle of breaking large hydrocarbon molecules into smaller ones thus increasing the value of crude oil. Lighter liquid fuels are generally more valuable than heavier ones. Gasoline for example, is more valuable than diesel fuel. Thermal cracking is a common refinery process. Refinery thermal cracking was originally used to crack heavy distillates to gasoline at up to 530[degrees]C and more or less 27 bars pressure.

Rising octane requirements decades ago caused refiners to seek other techniques. Cracking reactions start at about 360[degrees] C. Gasoil is a petroleum middle distillate that is also called diesel fuel, heating oil, furnace oil, stove oil, and

other names in various parts of the world. It has a boiling range that is generally considered to start at 200[degrees]C and ends about 360[degrees]C. Hydrocarbons are generally referred to by the number of carbon (C) atoms in the molecule. Thus a molecule with 30 carbon atoms is referred to as a [C.sub.30]. A molecule of [C.sub.30] happens to be in the boiling range of lube oil. The greater the number of carbon atoms in the molecule, the higher the boiling point and vice versa. Viscosity is also a function of the number of carbon atoms in the molecule. A higher carbon number means higher viscosity. Hydrocarbon molecules can be straight chained, ring shaped or other configurations. Straight chained molecules are termed paraffinic. Ring shaped are aromatics. Normal paraffins are the easiest hydrocarbon molecules to crack. Polynuclear aromatics are the most difficult to crack. Such aromatics form in processes and become what is known as "refractory" oils. Interestingly, paraffins also make very good lube oil and the content of the average used motor oil is quite paraffinic. Used oil therefore makes ideal feedstock for a thermal cracking process giving high conversion factors. Another characteristic of straight chained molecules is when they are in the boiling range of gasoil and are used in an engine as diesel fuel, these paraffinic molecules cause the diesel fuel to auto-ignite well.

The measure of this characteristic is referred to as cetane number. The higher the number, the beter the gasoil for use as a diesel fuel. Gasoil cracked from a feedstock of used motor oil has a cetane number in the range of[greater than] 50. Typical refinery produced diesel fuel is in the range of 45.

Gasoil is generally considered to start at [C.sub.11] or [C.sub.12] and extends to about [C.sub.22]. The peak of the boiling range should be in the [C.sub.17] or [C.sub.18] range. If the gasoil is to be used as a heating oil in a moderate climate, local specifications can allow this limit to stretch a bit higher. Lube oil ranges from [C.sub.20] to [C.sub.35]. The heaviest part of the gasoil overlaps the lightest part of the lube oil. Specifications will define limits on viscosity, boiling range, density and other factors. The number of carbon atoms that make up the molecules of a given fuel are a consequence of the tailoring of the fuel to meet those specification requirements. In reality, fuels consist of an array of molecule types and the simple illustration offered is intended for comprehension only. Furthermore, in the ideal

process equipment configuration, this molecule would be cracked once and the gasoil would pass from the cracking section to downstream in the plant. It is evident that if left in the cracking section, the newly created gasoil molecules may be further cracked to shorter hydrocarbon chains, which is undesirable. If a [C.sub.3] molecule was cracked off one of the gasoil molecules, the overall gasoil would be one [C.sub.15] and one [C.sub.12] but we will have produced one [C.sub.3] which is a non condensible off-gas to the process. This is a loss to the gasoil yield of the process. Any given molecule in the feedstock has a certain probability of being cracked at any given point on the length of the molecule. Therefore, the cracking process applied to a given feedstock will yield a range of hydrocarbons of differing boiling points. The discipline of process engineering focuses on creating process conditions that will favour the formation of more of the desired molecules and less of the undesirable ones. A certain distribution of cracked products with differing boiling points will emerge from any thermal cracking process. This is referred to as a yield pattern. This is influenced by several factors. If the [C.sub.30] molecule in the example is not given sufficient time in the thermal cracking section to crack, it will boil over and end up in the gasoil product. This is undesirable since the gasoil will be too heavy as a result. The process conditions that can be varied to accomplish the goal are temperature, pressure, and residence time in the thermal cracker. Pressure raises the boiling point of the hydrocarbon giving it the needed time to have the probability of cracking. Temperature will, to some extent, determine where along the length of the molecule the cracking will occur. Higher temperatures tend to crack pieces off the end of the molecule and the result is lighter cracked products such as gases and naphtha.

3.2.4.1. Stability

When a paraffin is cracked, it cracks to smaller paraffins and olefins. Olefins are unstable and reactive. Reactive compounds bond with each other and the result is colour change as well as gum and tar formation in the gasoil. Part of any used oil thermal cracking plant is a stabilization system.

3.2.4.2. Flash Point

An important parameter that defines the safety of handling of a particular hydrocarbon is flash point. The flash point of a hydrocarbon is the temperature at which the vapours emitting from a heated sample of product will combust or "flash" when exposed to a source of ignition. In Europe, a flash point above 55C is considered a combustible product and relatively safe to handle. A flash point below this value is a flammable liquid.

3.2.4.3. A Commercial Used Oil Thermal Cracker

A new category of used oil processing has emerged in the past few years. Thermal cracking used oil to gasoil is a process that was previously little known to the used oil processing industry. In a thermal cracking process, large hydrocarbon molecules are broken or cracked into smaller ones by the application of heat under the right process conditions. In this fashion, larger molecules of more viscous and less valuable hydrocarbons are converted into less viscous and more valuable liquid fuels.

Coarse Screening: The used oil is first passed through mesh screening and as much as possible of the coarse abrasive solids are removed.

Dehydration (Flash Evaporator): In the next stage of the process, used oil is subjected to sufficient heat to drive off any water and light ends present. These light ends could be gasoline or solvents. Collectively they are referred to as naphtha. The used oil is preheated by cross exchanging it with hot residual product from the cracking section. In this way, heat balance optimum is achieved. Used oil contains emulsified water at concentrations of anywhere from 6% to as high as 15% or more. Plants can be designed for higher water content feeds if desired.

It is simply a matter of proper heat exchange medium being designed to a higher degree of dehydration. The waste water from this stage of the process is separated from the naphtha. The water contains impurities and must be further treated in the plant operator's water treatment facility. An off-gas consisting of any

light non-condensable hydrocarbons such as hydrogen, methane, ethane, propane etc. is routed to plant fuel from this section.

Cracking: The used oil is now passed to the cracking section which consists of a fired process heater and a thermal cracking section. The product is heated and exposed to pressure, temperature, residence time, and other conditions that favour the conversion of the used oil to gasoil boiling range hydrocarbons. The cracking section discharges a hot heavy residual product that concentrates the ash, heavy metals, and other undesirable components. This product exits to storage after preheating the used oil entering the plant as mentioned previously.

Distillation**:** Also emanating from the thermal cracking section is the vaporized hot gas stream. This hot gas stream contains a mix of hydrocarbons that are gasoil boiling range and lighter. Because of the exit temperature of the thermal cracking section, these hydrocarbons are all in a vapour state. The hot gas stream proceeds to the distillation or separation stage where the lighter boiling range naphtha is separated from the gasoil. In certain plant configurations, a heavy boiling fraction is recycled back to the fired process heater. Gasoil in liquid state is routed to the stabilization section from distillation.

Stabilization: Thermally cracked gasoil is unstable. It will discolour rapidly and precipitate gums and tars. The gasoil can be treated with one of several stabilization methods available.

Process: One method involves the [ROBYS.sup.TM] gasoil purification and stabilization method developed by Natural Resources Canada at CANMET's Energy Technology Centre. This is a proprietary process that very effectively deals with gasoil instability. With the [ROBYS.sup.TM] process there is no need for any further treatment. There are no other byproducts to the process. A commodity chemical is recycled for reuse within the system.

Chemical Stabilization Methods: There are several chemical stabilization methods that are utilized. One is the injection of specialty chemical stabilizers for cracked and straight run distillate fuels such as Nalco(R) 5300. Such a method is typically coupled with passing the gasoil through an absorbent clay to improve colour. In this method, the clay must be disposed of. Another method is the use of

highly reactive commodity chemicals such as hydrazine hydrate or dimethylformamide (DMF) [[([CH.sub.3]).sub.2]N-OCH] This is a very powerful solvent that is highly polar.

Hydrazine hydrate and DMF are cancer suspect agents and/or mutagenic (causing DNA mutations) and highly irritant. The DMF stabilization method utilizes reaction vessels, centrifuges to spin out a tarry precipitate and then the gasoil is passed through an absorbent clay. Again, with this method, the spent clay requires disposal.

Hydrotreatment: This is a sophisticated and expensive process that will work very well to stabilize the gasoil and drastically reduce sulphur, nitrogen and other polar compounds. For a stand alone used oil thermal cracking plant it is not feasible due to the very high capital cost and requirement for hydrogen gas. Hydrotreaters are common in oil refineries where economy of scale permits their use. It is conceivable that a used oil thermal cracker adjacent to an oil refinery could sell its raw cracked gasoil to a refiner as co-feed to the hydrotreater.

3.2.4.4. The Products

Off-Gases: These light non-condensable gases are typically all consumed in the fired heater.

Naphtha: This light hydrocarbon liquid has a calorific value and all or part of it can be consumed for process heat generation if the fired heater is properly designed to accommodate a liquid fuel. The naphtha does not have a very high octane value.

Gasoil: This is the main product of the thermal cracking plant and yields of upwards of 80 per cent by weight of dried feed are achievable. The gasoil will have a sulphur content that is dependent on the sulphur level in the used oil feed and the stabilization method used.

Heavy Residual Fuel: The bottoms from the cracking section have a high calorific value and are usable as a residual replacement fuel. This is dependent on local legislation. In the US, the bottoms from such a thermal cracker were sold to a

steel mill. These bottoms are also usable as cutter stock for asphalt. In this way they are termed an asphalt extender.

Residue: If the [ROBYS.sub.TM] process is employed, the residues from the process can be blended with the bottoms residues from the cracking section. [ROBYS.sub.TM] residues have calorific value. The residues are rich in polar compounds and such residue also makes ideal blend stock for asphalt mixes.

3.2.4.5. Summary

Recently, a refinery calibre thermal cracking process was successfully applied in a commercial operating plant by a US company to produce a high yield of ASTM #2 distillate from a feedstock of used oil.

The significant aspect of this technology is its ability to adjust process operating conditions to tailor the desired product gasoil. This is a tremendous advantage in a used oil plant due to the variability of the used oil feedstock.

This thermal cracking technology is emerging as the technology of choice for progressive environmental services companies as they consider technology choices. Conversion of used oil to gasoil is desirable from an environmental point of view since the product displaces the need to consume a virgin gasoil produced from crude oil. Gasoil has a value that is high relative to heavy distillate fuel oils or residual replacement fuels. Gasoil is cleaner burning and the markets for gasoil are very large. From an economic viewpoint, this favours the used oil processing plant since there is not a small group of buyers that would influence or dictate selling price. Also, gasoil is marketable anywhere in the world. Thus the technology has potential application world wide. This could be a significant benefit to the world environment in aiding to solve the used oil problem. Of all the methods of processing used oil to be consumed for its calorific value, the thermal cracking conversion to distillate gasoil technology is the highest form of processing available. This is from an economical and environmental viewpoint.

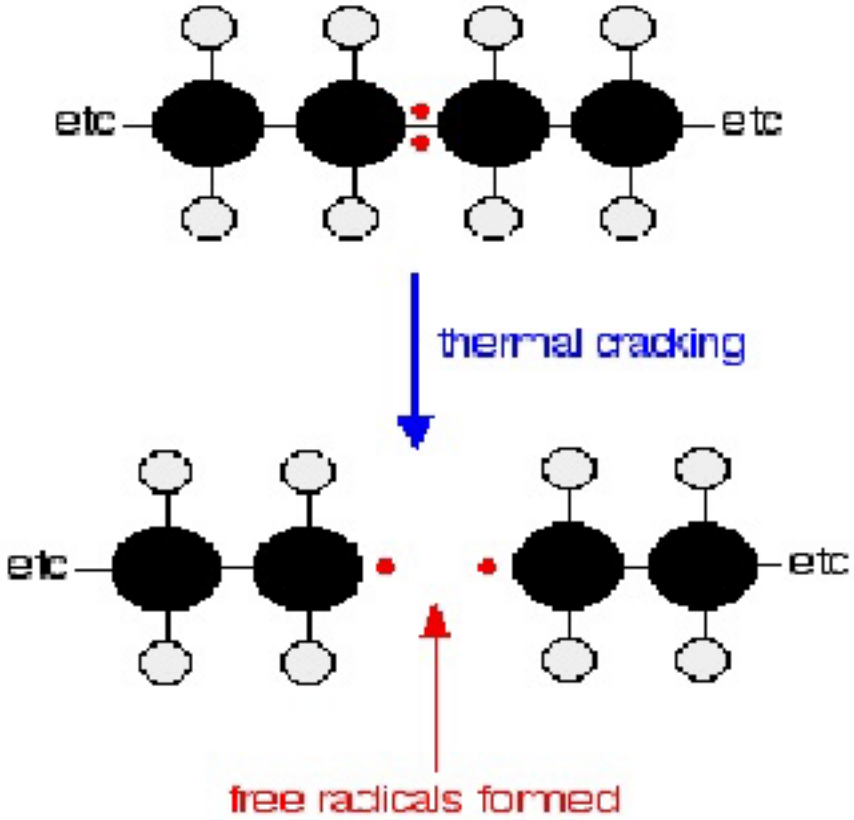


Figure 3.13. Thermal Cracking Method Equation

3.3. Experımental Study

The Purpose of the experiment is comparing sunflower and hazelnut oil's fuel properties by using thermal cracking method and comparing the results by the sunflower and hazelnut oil's fuel properties gained by transesterification methods.

3.3.1. Materıals Whıch Used The Experıment

1. Sunflower oil 5lt (Hazelnut oil)
2. The Thermal Cracking Reactor (Including; boiler, heat exchanger)
3. Transesterification Reactor (Including chemicals which are used in this method)
4. In the experiments, Mitsubishi Canter 4D34-2A (Figure 4.1.), four stroke diesel engine with four cylinders which has a maximum torque 295 Nm at

1800 rpm has been used. Note that the maximum torque value and maximum brake power values that obtained in the test engine could be change depending upon the fuel that used in engine. Specifications of the engine are presented in Table 4.1. The engine torque was measured by the help of a hydraulic dynamometer. Table 4.2. shows technical specifications of the dynamometer.

5. The speed sensor used to detect prime mover speed is the magnetic pickup (MPU). When a magnetic material (usually a gear tooth driven by the prime mover) passes through the magnetic field at the end of the magnetic pickup, a voltage is developed. The frequency of this voltage is translated by the speed into a signal which accurately depicts the speed of the prime mover. S type load cell is used to measure the torque of dynamometer (Stainless steel which has a sensivity of 1/3000. Dynamometer control unit was used for receiving and collecting all the data that was used by the system.
6. TESTO 350 XL gas analyzer is used to measure exhaust emissions. Emission data was collected by the help of a computer program. Measurement accuracy of the gas analyzer is ±10 ppm for CO, 1% for CO_2 and ±1 ppm for NO_x. Measurement capacity of the device is 0-10000 ppm for CO, 0-50% for CO_2 emission and 0-3000 ppm for NO_x.
7. Measuring devices: Instruments used for analysis were Zeltex ZX 440 NIR petroleum analyzer (accuracy, ±0.5) for determining cetane number, ISL CPP 97-2 (accuracy, ±0.5°C) for pour point, Koehler Saybolt viscosity test for viscosity, Kyoto electronics DA-130 for density measurement and Tanaka flash point control unit FC-7 for flash point.

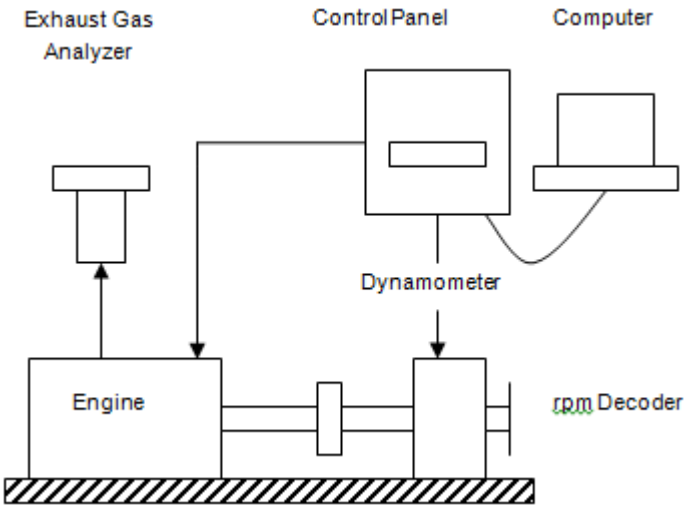


Figure 3.14. Layout of experimental setup

Table 3.11. Technical specifications of the test engine

Brand	Mitsubishi Canter
Model	4D34-2A
Configuration	In line 4
Type	Direct injection diesel with glow plug
Displacement	3907cc
Bore	104mm
Stroke	115mm
Power	89kW @ 3200rpm
Torque	295Nm @ 1800rpm
Oil Cooler	Water cooled
Weight	325kg

Table 3.12. Technical specifications of the dynamometer

Torque range	0-1700 Nm
Speed range	0-7500 rpm
Body weight	45 kgf
Total weight	110 kgf
Body diameter	350 mm
Torque arm length	350mm

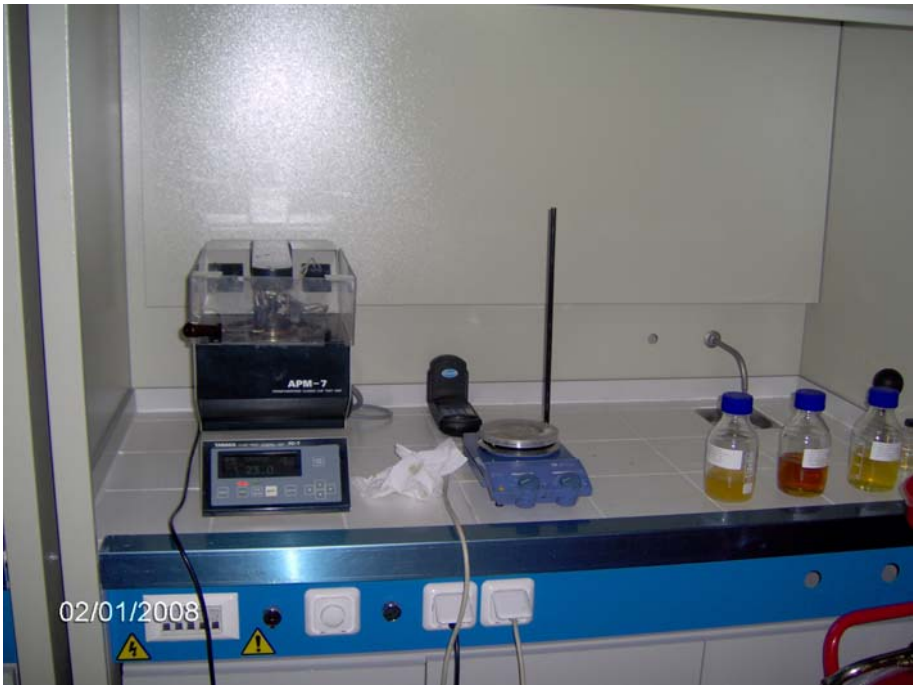


Figure 3.15. Tanaka AVP flashpoint



Figure 3.16. Koehler Saybolt viscosity test for viscosity



Figure 3.17. Zeltex ZX 440 NIR petroleum analyzer (accuracy, ±0.5)

TERMS: ASTM D6751-08 details standards and specifications for biodiesels blended with middle distillate fuels. This specification standard specifies various test methods to be used in the determination of certain properties for biodiesel blends. Some of the tests mentioned include flash point and kinematic viscosity. This is a standard set by the standards organization ASTM International. ASTM International is one of the largest voluntary standards development organizations in the world. It sets technical standards for materials, products, systems, and services. ASTM International standards have an important role in the information infrastructure that guides design, manufacturing and trade internationally. ASTM International, originally known as the American Society for Testing and Materials (ASTM), was formed over a century ago, when a group of engineers and scientists got together to address frequent rail breaks in the burgeoning railroad industry.

Their work led to standardization on the steel used in rail construction, ultimately improving railroad safety for the nation. As the century progressed and new industrial, governmental and environmental developments created new standardization requirements, ASTM responded with consensus standards that have been widely adopted internationally.

EN590 describes the physical properties that all automotive diesel fuel must meet if it is to be sold in the European Union and several other European countries.

Based on 98/70/EG it allows the blending of up to 7% fatty acid methyl ester biodiesel with 'conventional' diesel - a 7:93 mix. EN 14214 is a European Standard that describes the requirements and test methods for FAME - the most common type of biodiesel.

The technical definition of biodiesel is a fuel suitable for use in compression ignition (diesel) engines that is made of fatty acid monoalkyl esters derived from biologically produced oils or fats including vegetable oils, animal fats and microalgal oils. When biodiesel is produced from these types of oil using methanol fatty acid methyl esters (FAME) are produced. Biodiesel fuels can also be produced using other alcohols, for example using ethanol to produce fatty acid ethyl esters, however these types of biodiesel are not covered by EN 14214 which applies only to methyl esters i.e. biodiesel produced using methanol. This European Standard exists in three

official versions - English, French, German. The current version of the standard was published in November 2008 and supersedes EN 14214:2003.

Differences exist between the national versions of the EN 14214 standard. These differences relate to cold weather requirements and are detailed in the national annex of each standard. It is broadly based on the earlier German standard DIN 51606. The ASTM and EN standards both recommend very similar methods for the GC based analyses. Blends are designated as "B" followed by a number indicating the percentage biodiesel. For example: B100 is pure biodiesel. B99 is 99% biodiesel, 1% petrodiesel. B20 is 20% biodiesel and 80% fossil diesel.

Some terms which used in the experimental result's tables:

Sunflower oil's experimental result's by using thermal cracking method: SOC
Sunflower oil's experimental result's by using transesterification method: SOT
Hazelnut oil's experimental result's by using thermal cracking method: HOC
Hazelnut oil's experimental result's by using transesterification method: HOT

3.3.2. Process Thermal Crackıng Method

The Boiler which has can be aproximately 10 lt capacity connected to the heat exchanger with copper pipes. In the experimental setup 20 meters in the 42 gallons(159 lt) barrel and as spirally shape have used. Barrel must be filled cold water for condensation of vaporized oil in the copper pipes. First of all boiler must be clean and dry. After that oil must be added to the boiler between the maximum and minimum limits of the boiler. Boiler must be close and sealed tightly because after the heating started, vaporized oil starts pushing on the boiler walls. Heater may set aproximately 450 ^{o} C. Cracked oil starts to pass in the copper pipes and enter the barrel which filled full of cold water. Gas starts to get cold and condensate and heats the water, by adding fresh cold water, water may cooled and condensation can be quick. The liquid oil exits from the bottom of the barrel in the copper pipes. This liquid oil is now, cracked once and condensated again liquid oil. Finally product are ready to check out the fuel properties of the sunflower oil after this method.



Figure 3.18. The thermal cracking expertiment setup

3.3.3. Process Transesterıfıcatıon Method

Experimental study was conducted in Petroleum Research and Automotive Engineering Laboratories of Department of Mechanical Engineering in Cukurova University. Sunflower and hazelnut oils were supplied from Turkish oil sources and used for biodiesel production. Biodiesels were produced with transesterification using methyl alcohol and sodium hydroxide (NaOH) as a reactant and catalyst. Chemicals used during experiments were purchased from Merck and methanol was purified prior to use. Transesterification was carried out in a spherical glass reactor equipped with reflux condenser, stirrer and thermometer. Molar ratio of alcohol to oil

was 6:1 for all sample oils. In order to obtain sodium methoxide (CH_3ONa), methanol and NaOH were mixed.

In first production, CH_3ONa and Sunflower oil were mixed in reactor, mixture was heated up to 60°C (becuase of low vaporization point of alcohol) and kept at this temperature for 60 min by stirring. At the end of reaction period, crude methyl ester was waited at separating funnel for 8 h. And then, deep phase containing crude glycerin was separated from crude methyl ester. Finally, crude methyl ester was washed by warm water until washed water became clear and dried at 105°C for 1 h. Same steps were used for hazelnut oils.

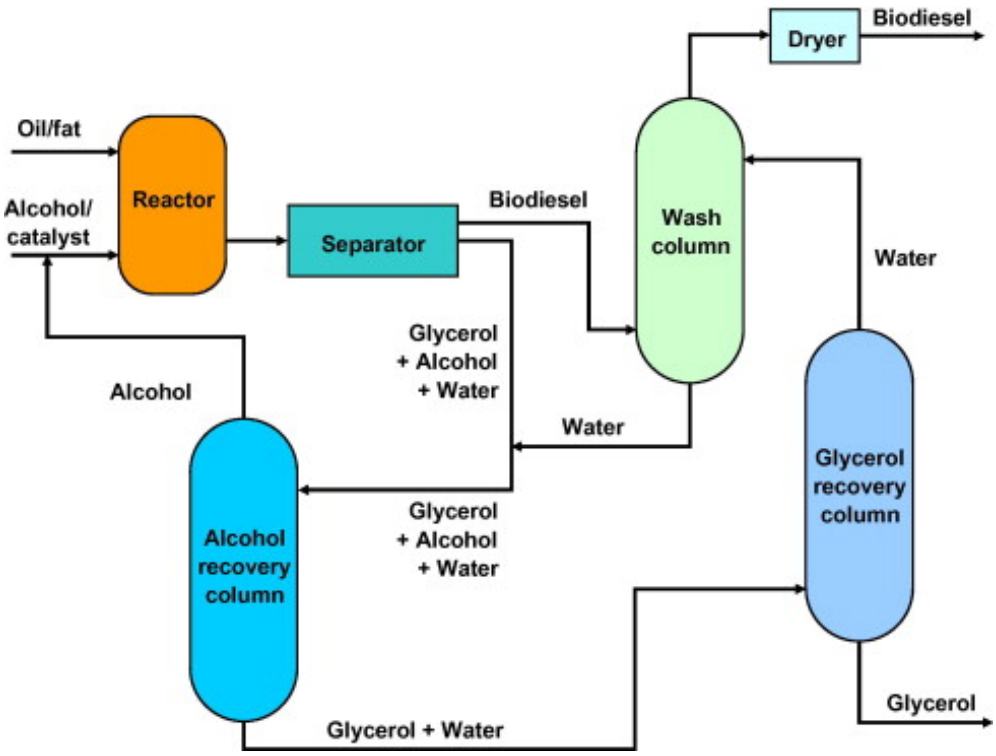


Figure 3.19. Flow diagram of transesterification method

4. RESULTS AND DISCUSSION

4.1. Results Of The Experımental Study

The sunflower oil's fuel properties after applied cracking method are given below in the Table 4.1. Also comparison with the American (ASTM D 6751) and Europe (EN 14214) standarts. As the table; however Density, Cetane Number, Flash Point values are between the standarts values, Kinematic Viscosity some above the upper limit.

Table 4.1. Fuel specifications of sunflower oil by cracking method (SOC)

Properties	SOC	ASTM D 6751	EN 14214	Diesel	EN 590
Density, g/cm^3	0.870	-	860–900	0.841	820-845
Cetane Number	47.1	Min. 47	Min 51	57.7	Min. 51
Flash Point, °C	172	Min.130	Min. 101	68.5	Min. 55
Pour Point, °C	-20	-	-	-16	
Kinematic viscosity, mm^2/s	7.1	1.9–6.0	3.5 - 5.0	3.1	2-4.5

When this process has also tested by using hazelnut oil, aproximately close values can be seen as the sunflower oil experiment fuel property results after cracking method. (Table 4.2.)

Table 4.2. Fuel specifications of hazelnut oil by cracking method (HOC)

Properties	HOC	ASTM D 6751	EN 14214	Diesel	EN 590
Density, g/cm^3	0.890	-	860–900	0.841	820-845
Cetane Number	49.2	Min. 47	Min 51	57.7	Min. 51
Flash Point, °C	168	Min.130	Min. 101	68.5	Min. 55
Pour Point, °C	-28	-	-	-16	
Kinematic viscosity, mm^2/s	7.3	1.9–6.0	3.5 - 5.0	3.1	2-4.5

Sunflower and hazelnut oil's fuel properties after applied transesterification method has also given in the Table 4.3. and in the Table 4.4. and the comparison between the methods cracking and transesterification.

Table 4.3. Fuel specifications of sunflower oil biodiesel

Properties	SOT	ASTM D 6751	EN 14214	Diesel	EN 590
Density, g/cm^3	0.860	-	860–900	0.841	820-845
Cetane Number	48.1	Min. 47	Min 51	57.7	Min. 51
Flash Point, °C	183	Min.130	Min. 101	68.5	Min. 55
Pour Point, °C	1	-	-	-16	
Kinematic viscosity, mm^2/s	4.6	1.9–6.0	3.5 - 5.0	3.1	2-4.5

Table 4.4. Fuel specifications of hazelnut oil biodiesel

Properties	HOT	ASTM D 6751	EN 14214	Diesel	EN 590
Density, g/cm^3	0.881	-	860–900	0.841	820-845
Cetane Number	50.1	Min. 47	Min 51	57.7	Min. 51
Flash Point, °C	170	Min.130	Min. 101	68.5	Min. 55
Pour Point, °C	-12	-	-	-16	
Kinematic viscosity, mm^2/s	4.7	1.9–6.0	3.5 - 5.0	3.1	2-4.5

Table 4.5. Comparing the fuel specifications of oils

Properties	SOT	SOC	HOT	HOC	ASTM D 6751	EN 14214	Diesel	EN 590
Density, g/cm^3	0.860	0.870	0.881	0.890	-	860–900	0.841	820-845
Cetane Number	48.1	47.1	50.1	49.2	Min. 47	Min 51	57.7	Min. 51
Flash Point, °C	183	172	170	168	Min.130	Min. 101	68.5	Min. 55
Pour Point, °C	1	-20	-12	-28	-	-	-16	
Kinematic viscosity, mm^2/s	4.6	7.1	4.7	7.3	1.9–6.0	3.5 - 5.0	3.1	2-4.5

The results show; Hazelnut oil has greater Density than Sunflower oil and cracking method for both oils makes the density greater than the transesterification method. Cetane Number also some greater for Hazelnut oil then Sunflower oil and cracking method makes it lower than the transesterification method. Hazelnut oil has lower Flash Point and the cracking method gives the lower value then the transesterification method. Pour Point is in the lower values in the cracking method. Kinematic Viscosity value is absolutely higher value in the method cracking also some out of upper limit

4.2. Fuel Specifications Of Blends

To minimize diesel fuel usage, either blending with diesel or using additives for biodiesel fuels may be initial ways to enhance characteristics of biodiesels. Different biodiesels are blended within different ratios to compensate specifications, which are out of standards. At first, a blend without diesel fuel was prepared for fuel specification examination. Cetane number of Blend No.1 is in the EN 14214 biodiesel standards.

Analysis of Blend No.1, No.2 and No.3 gives that all fuel properties of blends have reasonable values for engine run. However, main subject is to use lowest rate of diesel fuel; Blend No.2 is outside of this objective with its 80% of diesel fuel. When Blends No. 3 is examined, all fuel specifications are seen avaliable within ASTM and EN standarts.

Table 4.6. Blend variations

Blends / Fuels	Blend No.1 Contents (%)	Blend No.2 Contents (%)	Blend No.3 Contents (%)
Sunflower cracking	50	10	33.3
Hazelnut cracking	50	10	33.3
Diesel	-	80	33.3

Table 4.7. Fuel specifications of blends

Properties	Blend No.1	Blend No.2	Blend No.3	Diesel	ASTM D 6751	EN 14214
Density, g/cm^3	0.881	0.852	0.864	0.841	-	860–900
Cetane Number	48.3	54.8	53.1	57.7	Min. 47	Min 51
Flash Point, °C	170.1	81.4	136	68.5	Min.130	Min. 101
Pour Point, °C	-22	-18	-19.5	-16	-	-
Kinematic viscosity, mm^2/s	7.2	4.6	5.2	3.1	1.9–6.0	3.5 - 5.0

4.2.1. Fuel Properties

In this study, 2 types of oil (Hazelnut and Sunflower) were used. 2 types of method (Thermal Cracking and Transesterification) were applied the oils. Cetane number, pour point, flash point and viscosity of sunflower and hazelnut oil were determined. Then, fuel properties were compared with each other and standarts.

4.2.2. Cetane Number

Generally cetane number is an indicator of the ignition quality of a diesel fuel. If the cetane number is too high, combustion can occur before the fuel and air are properly mixed, which results incomplete combustion and smoke. If a cetane number is too low, incomplete combustion occurs. As shown in results cetane number for 2 methods and for 2 type of oils were measured in min. level as ASTM D6751, EN 14214 standarts.

4.2.3. Density

Densities of the products are also in acceptable area for EN 14214 standarts. Also it can be seen that processes were decreased densities even at minimum values.

4.2.4. Viscosity

Viscosity, which is a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another, affects the atomization of a fuel upon injection into the combustion chamber and thereby, ultimately, the formation of engine deposits. The general rule is; the higher the viscosity, the greater the tendency of the fuel to cause such problem. As shown in results table, viscosity for both products are in acceptable values in transesterification method for all three standarts in table, however for both products, thermal cracking method results are beyond the standarts. It shows us affect of thermal cracking method gives the high viscosity value.

4.2.5. Flash Point

The flash point is the temperature at which the fuel will give off enough vapor to produce a flammable mixture. This is important information for the safe transportation, storage of the fuel. Flash points of products are for both methods below the min. acceptable value in standarts for both 2 methods.

4.2.6. Pour Point

The temperature at which crystal formation is extensive enough to prevent free pouring of fluid is determined by measurement of its pour point. If pour point of a fuel is not low enough, some concerns with storing, transferring and using biodiesel in cold weather can occur.

4.3. Engine Performances

4.3.1. Brake Power Outputs

Figure 4.1. shows the variation of brake power according to different engine speed values with different ratio of blended fuels. There were similar differences in the measured engine power output diesel, Blend No. 3, Blend No. 2 and Blend No. 1 at low engine speeds. The characteristics of power curve were not changed, according to the type of fuel.

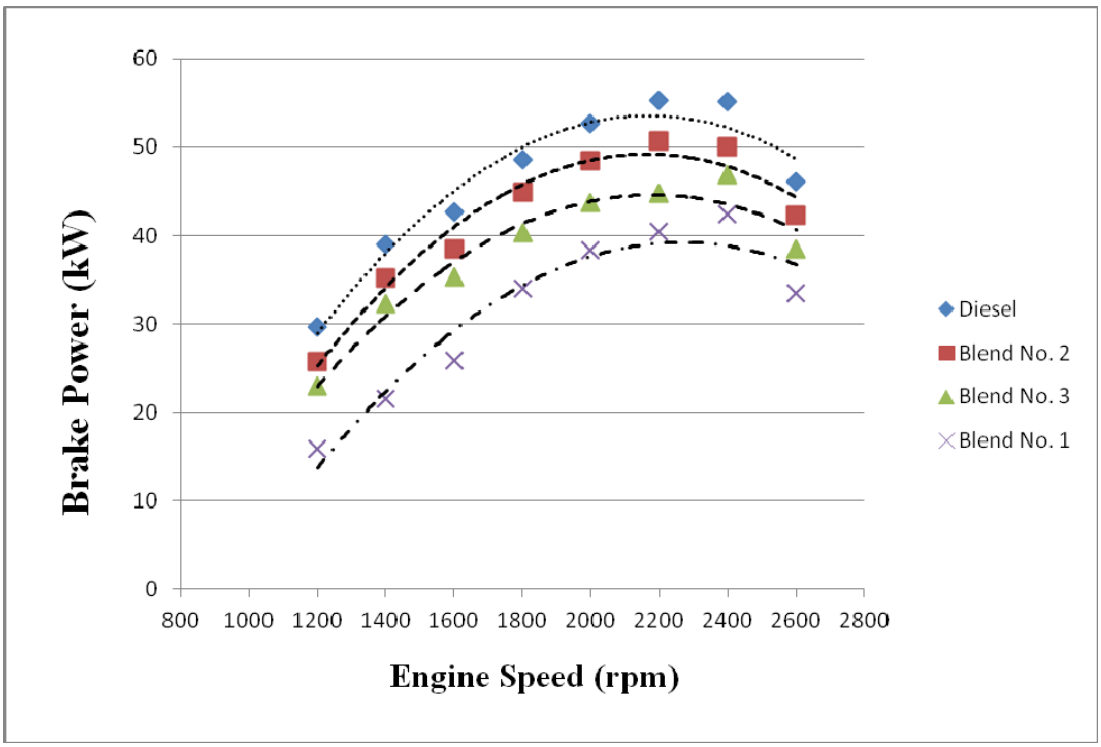


Figure 4.1. Brake power output versus engine speed for diesel and blends

4.3.2. Torque Outputs

The torque outputs of blended fuels is shown in Figure 4.2. The value of the torque outputs increase at low engine speeds, decrease at high engine speeds.

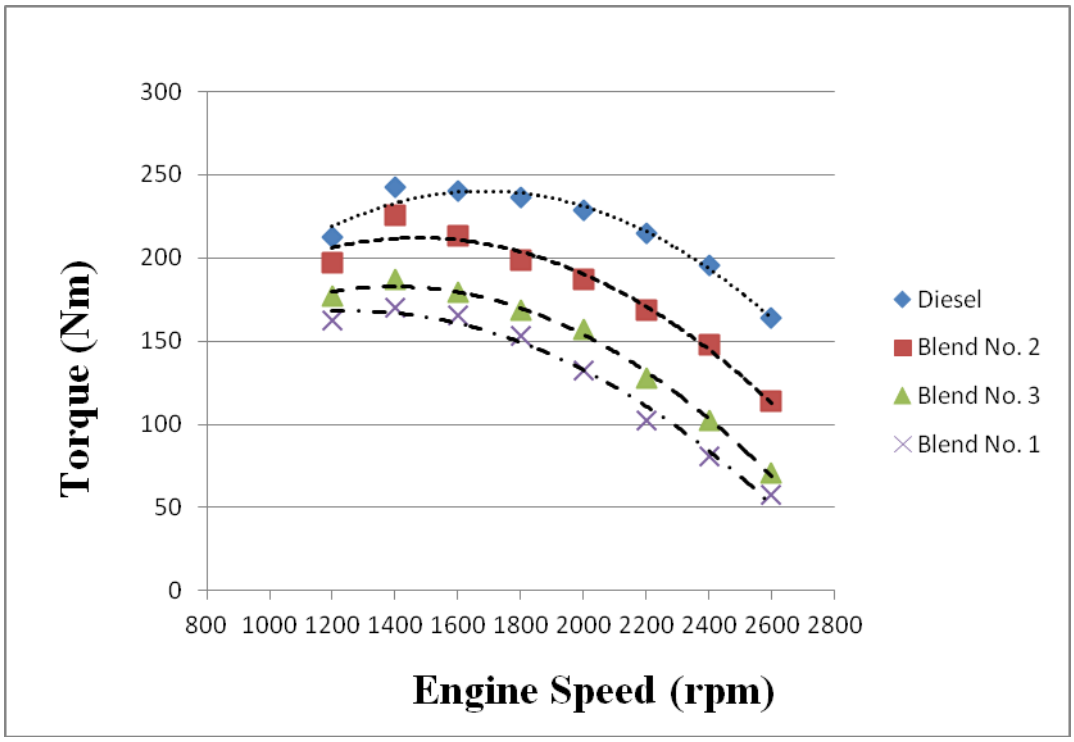


Figure 4.2. Torque output versus engine speed for diesel and blends

4.4. Exhaust Emissions

4.4.1. CO Emissions

Generally, CI engine operates with lean mixtures and hence the CO emission would be low. CO emission is toxic and must be controlled. It is an intermediate product in the combustion of a hydrocarbon fuel, so its emission results from incomplete combustion. Emission of CO is therefore greatly dependent on the air fuel ratio relative to the stoichiometric proportions. Rich combustion invariably produces CO, and emissions increase nearly linearly with the deviation from the stoichiometry. The variation of carbon monoxide with engine speed is shown in Figure 4.3. The reductions in CO emission could be due to the better combustion.

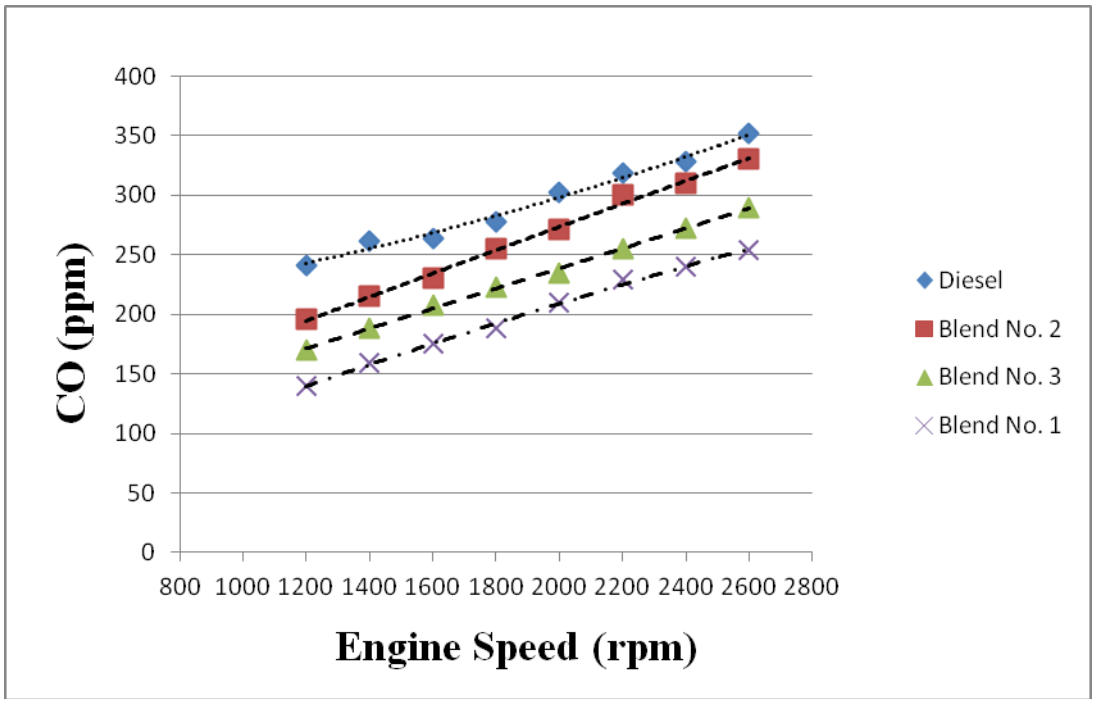


Figure 4.3. CO emission values of blends and Diesel

4.4.2. CO_2 Emissions

Figure 4.4. shows the variation of measured CO_2 emission values of test fuels for different engine speeds. From the graph we can get the result as blends of the oil to diesel decreases CO_2 emissions.

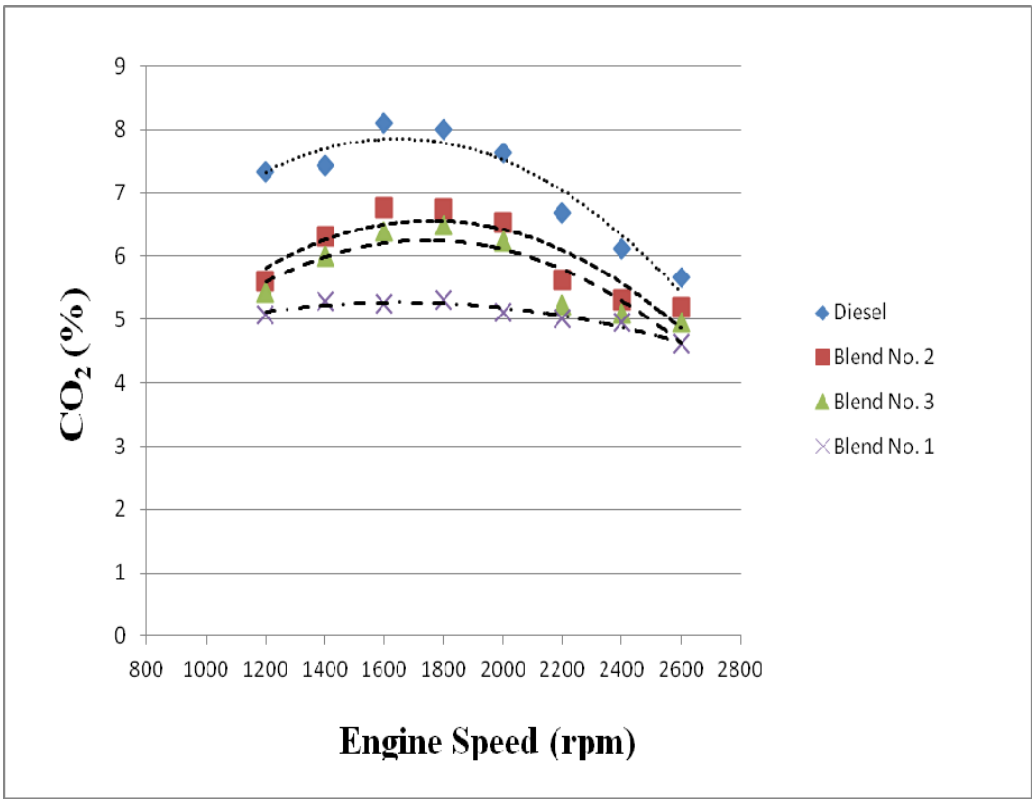


Figure 4.4. CO_2 emission values of diesel and blends

4.4.3. NO_x Emissions

The oxides of nitrogen in the emissions contain nitric oxid (NO) and nitrogen dioxide (NO_2). The formation of nitrogen oxides (NO_x) is highly dependent on in-cylinder temperature, oxygen concentration and residence time for the reactions to take place. The nitrogen oxides (NO_x) emissions of tests fuels in shown in Figure 4.5.

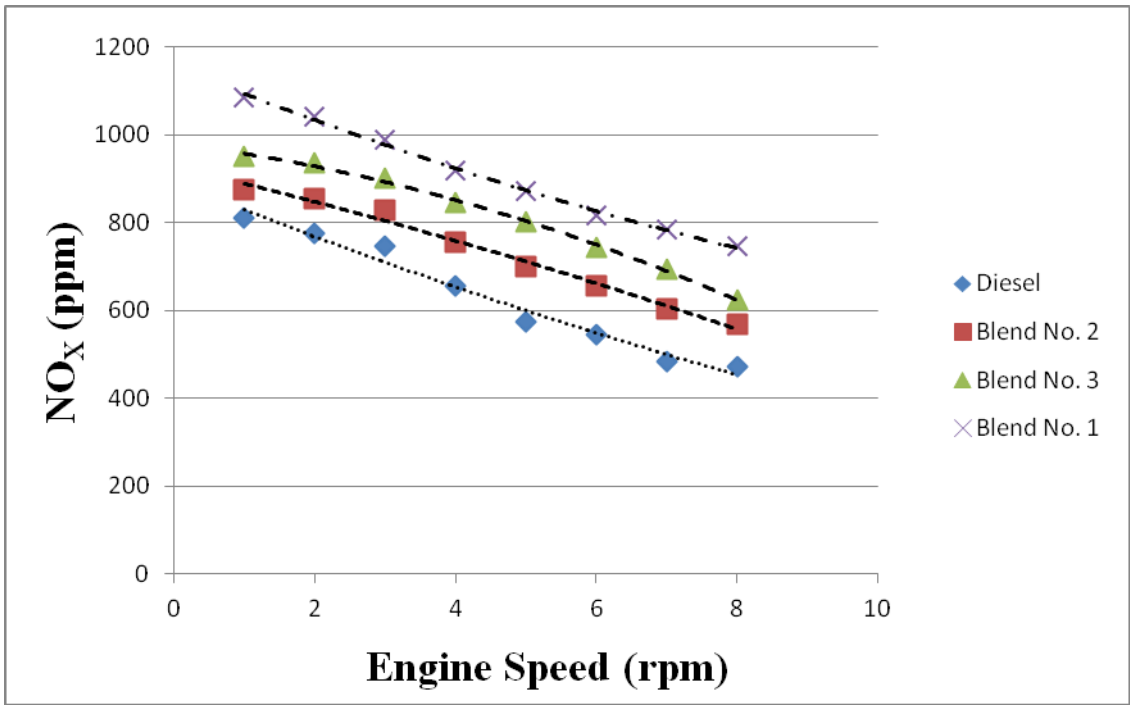


Figure 4.5. NOx emission values of diesel and blends

5. CONCLUSION

In this study between the oils, there are no any major differences as fuel properties. Also for methods results can be said close, only the pour point value from thermal cracking methods seems lower than the transesterification method and viscostiy values are higher for thermal cracking methods. As production difficulty both of methods needs care and devices which can be carefully installed and operated. When transesterification method needs additional products as alcohol and catalist, thermal cracking method's only product is raw material oil. As using time when transesterification method has many steps, thermal cracking method only takes time for cracking and condensating of product. However in thermal cracking method, very high temperature is needed what may be dangerous for not full safely facilities as transesterification method. Hazelnut oil is not an available product may also expensive as sunflower oil also results shows hazelnut oil results are not so different than sunflower oil.

Finally, results of this study shows us, sunflower and hazelnut oils, gained by transesterification and thermal cracking method can be used as an alternative fuel in diesel engines without any major modificatoins. Also products give the best performance and best environmental conditions in correct diesel blends...

5.1 Recomandations For Future Works

In the next studies, researches may experiment other types of oils, discuss the results with the blends of diesel, change the mixing ratios or additional catalysts and also test the engine performances and emission characteristics.

REFERENCES

F. BEHAR * AND M. VANDENBROUCKE GEOCHEMISTRY DEPARTMENT, IFP, 1-4 AVENUE DE BOIS PRÉAU, 92506 RUEIL-MALMAISON CEDEX, FRANCE ENERGY FUELS, 1996,

A.B.M.S. HOSSAIN and A.N. BOYCE 2009 Bio-energy Laboratory, Programm of Biotechnology, Institute of Biological Sciences, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia

A.M. ALSOBAAI, R. ZAKARIA, B.H. HAMEED 2007 Characterization and hydrocracking of gas oil on sulfided NiW/MCM-48 catalysts Chem. Eng. J., 132 (1–3), pp. 173–181

ADINARAYANA ET AL., K. ADINARAYANA, P. ELLAIAH, B. SRINIVASULU, D.R. BHAVANI, G. ADINARAYANA 2003 Response surface methodological approach to optimize the nutritional parameters for neomycin production by streptomyces marinensis under solid-state fermentation Proc. Biochem., 38 , pp. 1565–1572

BIODIESEL PRODUCTION: A REVIEW FANGRUI MAA, MILFORD A. HANNAB, 1998* a Department of Food Science and Technology, University of Nebraska, Lincoln, NE, USA b Industrial Agricultural Products Center, University of Nebraska, 211 L.W. Chase Hall, Lincoln, NE 68583-0730, USA Received 24 March 1998; revised 16 December 1998; accepted 2 February 1999

BIODIESEL STATEMENT". VOLKSWAGEN.CO.UK. 2011

BIODIESEL". HALIFAX.CA. 2009

BIODIESEL_BROCHURE5.PDF (APPLICATION/PDF OBJECT)". 2010.

BOZ, N.; KARA, M.CHEM. ENG. COMMUN. 2009, 196(1), 80-92.

CALVIN, M., 1985. Fuel oils from higher plants. Ann. Proc. Phytochem. Soc. Eur. 26, 147±160.

CANOIRA, L., GALEAN, J.G., ALCANTARA, R., LAPUERTA, M., CONTRERAS, R.Y. 2010. Fatty acid methyl esters (FAMEs) from castor oil: Production process assessment and synergistic effects in its properties. Renewable Energy, vol. 35, p. 208-217.

CAVALCANTE, K.S.B., PENHA, M.N.C., MENDONÇA, K.K.M., LOUZEIRO, H.C., VASCONCELOS, A.C.S., MACİEL, A.P., SOUZA, A.G., SİLVA, F.C. 2010. Optimization of transesterification of castor oil with ethanol using a central composite rotatable design (CCRD). Fuel, vol. 89, p. 1172-1176.

COCHRAN AND COX, W.G. COCHRAN, G.M. COX EXPERIMENTAL DESIGNS (SECOND ED.)JOHN WILLY AND SONS, SINGAPORE 1957

COMAR, V., TILLEY, D., FELIX, E., TURDERA, M., NETO, M.C. 2004. Comparative emergy evaluation of castorbean (Ricinus Communis) production systems in Brazil and the U.S. Proceedings of IV Biennial International Workshop “Advances in Energy Studies, p. 227-237.

CRUZE CLEAN TURBO DIESEL DELIVERS EFFICIENT PERFORMANCE". 2013

DISNEYLAND TRAINS RUNNING ON BIODIESEL - UPI.COM". 2009

EUROPEAN STANDARD EN 14103; FAT AND DERIVATIVES. FATTY ACID METHYL ESTERS (FAME) 2003, European Committeefor Standardization, Brussels.

EWS RAILWAY - NEWS ROOM". 2009

FANGRUI, M., MILFORD, A.H. 1999. Biodiesel Production: A review. Bioresource Technology, vol. 70, p. 1-15.

FERNÃNDEZ-ÃLVAREZ, P.; VILA, J.; GARRIDO, J. M.; GRIFOLL, M.; FEIJOO, G.; LEMA, J. M. 2007 Evaluation of biodiesel as bioremediation agent for the treatment of the shore affected by the heavy oil spill of the Prestige. J. Hazard. Mater. , 147, 914-922

FIRST UK BİODIESEL TRAIN LAUNCHED".2007

FRENCH MCCAY, D.; ROWE, J. J.; WHITTIER, N.; SANKARANARAYANAN, S.; SCHMIDT ETKIN, 2004 D. Estimation of potential impacts and natural resource damages of oil. J. Hazard. Mater. 107, 11-25

GENERIC BIODIESEL MATERIAL SAFETY DATA SHEET (MSDS)" 2010 Gerpen, J.V.; Shank, B.; Pruszko, R.; Clements, D.; Knothe, G.Biodiesel production technology2002-2004,National Renewable Energy Laboratory Report, Golden, Colorado.

GOODRUM, J.W., GELLER, D.P. 2005. Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity. Bioresource Technology, vol. 96, p. 851-855.

HALIFAX CITY BUSES TO RUN ON BIODIESEL AGAIN | BIODIESEL AND ETHANOL INVESTING". BIODIESELINVESTING.COM. 2006

HALIFAX TRANSIT". HALIFAX.CA. 2004

HEDAYAT AND PESOTAN, 2007 A.S. Hedayat, H. Pesotan Tools for constructing optimal two-level factorial designs for a linear model containing main effects and one two-factor interaction J. Stat. Plan. Infer., 137 (2007), pp. 1452–1463

HRIBERNIK, A., KEGL, B. (2007). The influenceof biodiesel on the combustion and emissioncharacteristics of a diesel engine. Strojniški vestnik – Journal of Mechanical Engineering, vol. 53, no. 10, p. 683-695.

HYDROCRACKING, 1920.

IMPORTANCE OF BIODIESEL AS TRANSPORTATION FUEL AYHAN DEMİRBAS 2007 Sila Science, P. K. 216, TR-61035 Trabzon, Turkey Received 1 February 2007; accepted 1 April 2007 Available online 18 May 2007

INTERNATIONAL JOURNAL OF BIOSCIENCE, BIOCHEMISTRY AND BIOINFORMATICS, 2012

JAMES H. GARY AND GLENN E. HANDWERK 2001. Petroleum Refining: Technology and Economics (4th ed.). CRC Press. ISBN 0-8247-0482-7. James. G. Speight (2006). The Chemistry and Technology of Petroleum (4th ed.). CRC Press. ISBN 0-8493-9067-2.

JOHN F. GEYER and S. NEMAT-NASSER 2004 The Technological Institute, Northwestern University, Evanston, IL 60201, U.S.A.

KEMP, WILLIAM. BIODIESEL: BASICS AND BEYOND. CANADA: AZTEXT PRESS, 2006.

KNOTHE, G. "HISTORICAL PERSPECTIVES ON VEGETABLE OIL-BASED DIESEL FUELS" 2001

KOTRBA, RON "'NAME THAT BİODİESEL TRAİN' CONTEST". BİODİESEL MAGAZİNE. 2014.

KRAWCZYK, T., 1996. Biodiesel ± Alternative fuel makes inroads but hurdles remain. INFORM 7, 801±829.

KUMAR, S. AND SINGH, R.K., 2011. Recovery of hydrocarbon liquid from waste high density polyethylene by thermal pyrolysis, Brazilian Journal of Chemical Engineering, VOL. 28, No. 4, 659 – 667.

MANSOURPOOR M, SHARIATI A 2012 Optimization of Biodiesel Production from Sunflower Oil Using Response Surface Methodology. J Chem Eng Process Technol 3:141 doi: 10.4172/2157-7048.1000141

MASSACHUSETTS OIL HEAT COUNCIL 2008 MA Oilheat Council Endorses BioHeat Mandate[dead link]

MCCORMICK, R.L. 2006 Biodiesel Handling and Use Guide Third Edition" Retrieved 2006-12-18.

MCDONALD'S BOLSTERS "GREEN" CREDENTIALS WITH RECYCLED BIODIESEL OIL". NEWS.MONGABAY.COM. 2007

D.C. MONTGOMERY DESIGN AND ANALYSIS OF EXPERIMENTS JOHN WILLY AND SONS, NEW YORK, USA 2001

MONYEM, A.; H. VAN GERPEN, J. 2001, The effect of biodiesel oxidation on engine performance and emissions. Biomass Bioenergy 20, 317-325

NAGEL, N., LEMKE, P., 1990. Production of methyl fuel from miceoalgea. Appl. Biochem. Biotechnol. 24, 355±361.

NATİONAL BIODIESEL BOARD 2005. "Energy Content" (PDF). Jefferson City, USA. p. 1. Retrieved 2013-09-24.

NATIONAL BIODIESEL BOARD ELECTRICAL GENERATION. 2013

NATIONAL BIODIESEL BOARD, 2007. Chrysler Supports Biodiesel Industry; Encourages Farmers, Refiners, Retailers and Customers to Drive New Diesels Running on Renewable Fuel.". Nbb.grassroots.com. 2007-09-24. Retrieved 2010-03-15.

ROBERTSON, ANDREW. 2007 "Biodiesel Heating Oil: Sustainable Heating for the future". Institute of Plumbing and Heating Engineering.

SADIGHI, S., AHMAD, A., SHIRVANI, M. 2011 Comparison of lumping approaches to predict the product yield in a dual bed VGO hydrocracker. , International Journal of Chemical Reactor Engineering, 9, art. no. A4.

SAE TECHNICAL PAPER SERIES NO. 831356. SAE INTERNATIONAL OFF HIGHWAY MEETING, MILWAUKEE, WISCONSIN, USA, 1983

SHAY, E.G., 1993. Diesel fuel from vegetable oils: status and opportunities. Biomass and Bioenergy 4, 227±242.

SONNTAG, N.O.V., 1979. Structure and composition of fats and oils. Bailey's industrial oil and fat products, vol. 1, 4th edition, ed. Swern, D. John Wiley and Sons, New York, p. 1.

THE MASSACHUSETTS BIOHEAT FUEL PILOT PROGRAM". 2007. Retrieved 2012-12-31. Prepared for the Massachusetts Executive Office of Energy and Environmental Affairs

TYSON, S. K.;BIODIESEL 2001 Handling and Use Guidelines, National Renewable Energy Laboratory, NREL Report,Golden, Colorado.

VESTAL, SHAWN 2008 "Biodiesel will drive Eastern Wa. train during summerlong test". Seattle Times. Retrieved 2009-03-01.

ZHANG, Y., DUBE, M.A., MCLEAN, D.D., KATES, M. 2003. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresource Technology, vol. 90, p. 1-16.

http://biodiesel.infopop.cc/eve/forums/a/tpc/f/739605551/m/4247014963

http://en.wikipedia.org/wiki/Biodiesel

http://en.wikipedia.org/wiki/Cracking_%28chemistry%29

http://en.wikipedia.org/wiki/Cracking_%28chemistry%29#History_and_patents

http://greenliving.lovetoknow.com/Advantages_and_Disadvantages_of_Biofuels

http://www.daysoftheyear.com/days/biodiesel-day/

http://www.greenflightinternational.com/First%20B100%20Jet%20Flight%20Press%20Release.pdf

http://www.odec.ca/projects/2007/ardi7m2/history_biodiesels.html

http://www.setlaboratories.com/therm/tabid/107/Default.aspx
www.eia.gov
www.mottcorp.com
www.setlaboratories.com

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