

Production of Bio Diesel from Spent Coffee Grounds

Dr.D.N.V.Satyanarayana¹, Smt.M.Sudheera²

^{1,2}Department of Chemical Engineering,
R. V. R. & J. C. College of Engineering(A), Guntur,
Andhra Pradesh, India

Received May 22, 2017

Accepted June 16, 2017

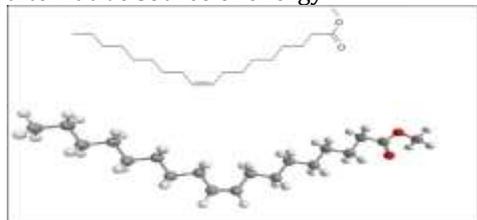
ABSTRACT

Biodiesel production is a topical field of research which has become a steadily growing industry over the past decade. The importance given to biodiesel production can be explained by its environmental benefits and the continual rise of oil prices. Biodiesel is then a promising solution to the environmental degradation of our planet as it produces lower exhaust emissions when compared to conventional fuels. As a matter of fact, it cuts down greenhouse gas emissions by more than 52% compared to petroleum diesel. This alternative fuel can be made from renewable sources such as animal fats, greases and vegetable oils. In this context, the purpose of this work is the valorization of waste coffee grounds as a starting material for biodiesel production. Transesterification is the method used throughout; hence its processes and downstream operations including oil extraction are described. Furthermore, several tests that unveil the quality and perform a characterization of the produced biodiesel have been applied and described as well. The goal of this work is to emphasize on the feasibility of conversion of coffee oil, extracted chemically from waste coffee grounds collected locally, into a biodiesel.

Key words: Transesterification, biofuel, octane number, cetane number, ASTM, pyrolysis

Introduction

Biodiesel, often referred to as B100 in its pure form, is a biodegradable and environmental friendly fuel that serves as an alternative to conventional fossil diesel. This clean renewable fuel can be derived domestically through chemical processes from a variety of oils, fats and greases. Biodiesel is defined by ASTM International as a mixture of long-chain monoalkylic esters from fatty acids obtained from renewable resources that can be readily used in diesel engines. Not only does this latter meet most of the standard properties of petro-diesel, but it also has many characteristics that makes it a very promising alternative source of energy.



Theory:

India is the world's fifth largest primary energy consumer and fourth largest petroleum consumer after States, China and Japan. Despite the recent global economic slowdown, India's economy is expected to grow at 6 to 8 % per year in the near term. With an outlook for moderate to strong

economic growth and a rising population, growing infrastructural and socio-economic development will stimulate an increase in energy consumption across all major sectors of the Indian economy. In the recent past, starting in Indian fiscal year, imports of gasoline and petroleum products has outgrown total domestic consumption by more than 14 %. Indian's base is substantial. The country continues to rely on imports for a considerable amount of its energy use, consequently. Indian's oil import expenditure escalated to over \$135 in 202, up 22% over the previous year. Concurrently, petroleum consumption in India has also grown in tandem to 148 million tons. Thus, in terms of end usage, energy demand across the transport sector is the greatest. Roads, being one of the dominant infrastructures for transport, carry an estimated 85 to 90 % of the country's passenger traffic and 65% of its freight. Traffic on roads is growing at the rate of 7 to 10 % per year; while the vehicle growth is of the order of 8 to 10 % per year. Easy availability, adaptability to individual needs and cost saving are some of the factors which favor road transport. Total registered motor vehicles in India in fiscal year 2005/06 are approximately 90 million and the forecast is that the numbers may exceed 160 million by the end of fiscal 2016. Economic growth, increasing urbanization, a rise

in consumer spending levels and improved road infrastructure have stimulated new vehicle registrations (particularly four-wheelers against to two-wheelers. As vehicle ownership expands, petroleum demand in the transport sector is expected to grow in tandem. Diesel and gasoline account for more than 95 % of the requirement for transportation fuel and the demand is expected to grow 6 to 8 % over the coming years.

Biodiesel Feedstocks:

Biodiesel can be produced from a range of organic and renewable raw materials. These latter include either fresh or waste vegetable oils, oilseed plants, animal fats or algae oil. Different potential raw materials are then available for biodiesel production, however, **edible oils** are currently the most used. The widely used oils are rapeseed oil (mainly in the European Union, >80%), soybean oil (USA, Brazil), sunflower oil (France, Spain) and palm oil (Asia and Central America). The availability of these edible oils explains their popularity in biodiesel production. Since cost also matters in biodiesel production and edible oils account for food materials, the use of **non-edible** vegetable oils has been considered and studied with promising results. In this regard, technologies are also being developed to exploit cellulosic materials such as leaves, biomass derived from waste, etc. Also, 26 species of plants containing oil in their seeds are reported to be sources for biodiesel production. The most significant examples are: castor oil plant, cotton, tobacco, karanja, jatropha, etc. These oils make a good alternative to edible oils if the problem of water requirement related to their use are neglected.

Used edible oils are another potential raw material for biodiesel production. They are called to solve the problem of competition with food and cost concern. Besides, using the waste edible oil for biodiesel production can help solve the twin problem of energy shortage and environmental pollution. For example, coffee oil falls within this category.

Another feedstock are **animal fats**. Their advantage is their competitive price. Lastly, with their high oil content (20% to 50%), microalgae have also been recognized to have great potential for biodiesel production. The cultivation of microalgae does not require much land but requires high levels of water, nutrients, minerals and CO₂ for their growth.

History of Biodiesel:

Developed in the 1890s by inventor Rudolph Diesel, the diesel engine has become the engine of choice for power, reliability, and high fuel economy, worldwide. Early experimenters on

vegetable oil fuels included the French government and Dr. Diesel himself, who envisioned that pure vegetable oils could power early diesel engines for agriculture in remote areas of the world, where petroleum was not available at the time. Modern biodiesel fuel, which is made by converting vegetable oils into compounds called fatty acid methyl esters, has its roots in research conducted in the 1930s in Belgium, but today's biodiesel industry was not established in Europe until the late 1980s. The diesel engine was developed out of a desire to improve upon inefficient, cumbersome and sometimes dangerous steam engines of the late 1800s. The diesel engine works on the principal of compression ignition, in which fuel is injected into the engine's cylinder after air has been compressed to a high pressure and temperature. As the fuel enters the cylinder it self-ignites and burns rapidly, forcing the piston back down and converting the chemical energy in the fuel into mechanical energy. Dr. Rudolph Diesel, after whom the engine is named, holds the first patent for the compression ignition engine, issued in 1893. Diesel became known worldwide for his innovative engine which could use a variety of fuels. The concept of bio fuel dates back to 1885 when Dr. Rudolf Diesel built the first diesel engine with the full intention of running it on vegetative source. In 1912 he observed, "the use of vegetable oils for engine fuels may seem insignificant today. But such oils may in the course of time become as important as petroleum and the coal".

In 1970, scientists discovered that the viscosity of vegetable oils could be reduced by a simple chemical process and that it could perform as diesel fuel in modern engine. Since then the technical development has come a long way and the plant oil today has been highly established as biofuel equivalent to diesel.

Recent environmental (e.g. Kyoto Protocol) and economic concerns have prompted resurgence in the use of biodiesel throughout the world. In 1991, the European Community proposed a 90% tax reduction for the use of bio fuels, including biodiesel. Today 21 countries worldwide produce biodiesel. India is one of the largest petroleum consuming and importing countries. India imports about 70 % of its petroleum demands. The current yearly consumption of diesel oil in India is approximately 40 million tones constituting about 40% of the total petro-product consumption. Biodiesel, derived from the oils and fats of plants like sunflower, rape seeds, Canola or Jatropha (Bhagveranda) can be used as a substitute or an additive to diesel. As an alternative fuel biodiesel can provide power similar to conventional diesel

fuel and thus can be used in diesel engines. Biodiesel is a renewable liquid fuel that can be produced locally thus helping reduce the country's dependence on imported crude petroleum diesel.

Early work

The early diesel engines had complex injection systems and were designed to run on many different fuels, from kerosene to coal dust. It was only a matter of time before someone recognized that, because of their high energy content, vegetable oils would make excellent fuel. The first public demonstration of vegetable oil based diesel fuel was at the 1900 World's Fair, when the French government commissioned the Otto Company to build a diesel engine to run on peanut oil. The French government was interested in vegetable oils as a domestic fuel for their African colonies. Rudolph Diesel later did extensive work on vegetable oil fuels and became a leading proponent of such a concept, believing that farmers could benefit from providing their own fuel. However, it would take almost a century before such an idea became a widespread reality. Shortly after Dr. Diesel's death in 1913 petroleum became widely available in a variety of forms, including the class of fuel we know today as "diesel fuel". With petroleum being available and cheap, the diesel engine design was changed to match the properties of petroleum diesel fuel. The result was an engine which was fuel efficient and very powerful. For the next 80 years diesel engines would become the industry standard where power, economy and reliability are required.

Modern Engine: Modern Fuel:

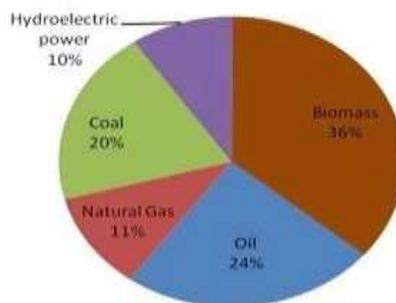
Due to the widespread availability and low cost of petroleum diesel fuel, vegetable oil-based fuels gained little attention, except in times of high oil prices and shortages. World War II and the oil crises of the 1970's saw brief interest in using vegetable oils to fuel diesel engines. Unfortunately, the newer diesel engine designs could not run on traditional vegetable oils, due to the much higher viscosity of vegetable oil compared to petroleum diesel fuel. A way was needed to lower the viscosity of vegetable oils to a point where they could be burned properly in the diesel engine. Many methods have been proposed to perform this task, including pyrolysis, blending with solvents, and even emulsifying the fuel with water or alcohols, none of which have provided a suitable solution. It was a Belgian inventor in 1937 who first proposed using Transesterification to convert vegetable oils into fatty acid alkyl esters and use them as a diesel fuel replacement.

The process of Transesterification converts vegetable oil into three smaller molecules which are much less viscous and easy to burn in a diesel engine. The Transesterification reaction is the basis for the production of modern biodiesel, which is the trade name for fatty acid methyl esters. In the early 1980s concerns over the environment, energy security, and agricultural overproduction once again brought the use of vegetable oils to the fore front, this time with Transesterification as the preferred method of producing such fuel replacements.

Biodiesel Present Status:

During the last decade biofuels have gained their place as an energy source with huge prospects. The most important drivers behind this process are strong government policies in the leading countries, on going technical development and cost reduction and the sharp increase of oil prices on the international markets. Biofuels can greatly reduce the dependence of the world's major economies on fossil fuels and are a key instrument to reduce the emission of greenhouse gases. The Kyoto protocol, which entered into force on February 16, 2005 was an important push for the emerging biofuel industry and related investments, especially in developing countries. An important social and economic motif behind many governments is the desire to develop new markets for farming products as an alternative to traditional food commodities. Ethanol is derived from two sources today. Ethanol is made from crops that are rich in extracted from oil. Ethanol can be blended with gasoline up to 10% for use in normal gasoline engines or higher in adapted engines. The world market leader in ethanol is Brazil, which has fossil oil. Ethanol in Brazil is highly competitive with gasoline. Ethanol from corn is produced in the USA and is a more recent development.

Total Energy Consumption in Vietnam, by Type (2010)



Source: EIA International Energy Statistics

Energy production

Ethanol presently accounts for some 90% of the global biofuel production; the remainder (10%) is oil-based. Oil-based biofuels can be vegetable oil (pure plant oil -PPO) as it is extracted from the crop material or biodiesel which is obtained after Esterification of the oil. Biodiesel can be blended with petroleum based diesel for use in conventional vehicles. Cars that use 100% biodiesel or run on PPO need some technical modifications. The by-far largest producer and consumer of biodiesel in the world is Germany, where crops such as rapeseed are grown by farmers to supply the domestic biofuel market. This market is backed by government policies and financial incentives. Compared to the refining process of crude oil and the production of biofuel can be much more decentralized. Important differences between crude oil and biofuel production are: the much lower energy density (i.e. energy content per kg prime material) of the latter, the linkages with agricultural farming areas and communities, transport costs and the technical characteristics of biofuels versus high grade gasoline. A local producer can extract the oil from the raw vegetal material at one site to increase the energy density and then transport it for further processing (which is likely to be more capital- intensive). The extraction of oil from seeds on a small scale can be done using a simple press or a mill, as it has been done for many centuries all over the world. Many of these technologies are still under development cellulose rich biomass includes wood, grasses and residues, which are much more abundant than food and oil crops. They are also less likely to interfere with food production. Examples are fast growing willow and eucalyptus varieties, switch grass and miscanthus. Organic municipal solid waste provides another type of feedstock for advanced biofuel production. If economically viable and applied on a large scale, these technologies can dramatically increase the volume of the global biofuel markets. Now days, various biofuel resources are being used like Biomass (plant derived), Hydroelectric, wind, Geothermal, Solar etc and these sources are eco-friendly nature to the environment. The contribution of sources is more when compared with other sources.

Biodiesel – A fuel of future

Biodiesel is a safe alternative fuel to replace traditional petroleum diesel. It has high lubricity and is a clean-burning fuel. It can be fuel component for use in existing unmodified diesel engines. This means that no retrofits are necessary when using biodiesel fuel in any diesel powered combustion engine. It is the only alternative fuel that offers such a convenience. Biodiesel acts like petroleum diesel, but produces less air pollution. It comes from renewable sources and is biodegradable and safer for the environment. Producing biodiesel fuels can help create local economic revitalization and local environment benefits. Many groups interested in promoting the use of biodiesel already exist at the local, state and national level. Biodiesel is designed for complete compatibility with petroleum diesel and can be blended in any ratio, from additive levels to 100% biodiesel. In the United States today, biodiesel is typically produced from soybean or rapeseed oil or can be reprocessed from waste cooking oils or animal fats such as waste fish oil and also from waste coffee. Because these are completely a renewable fuel source.

Benefits of Biodiesel:

Biodiesel can be considered a new technology, taking into account that all these years' consumers have had to settle for traditional diesel.

- Biodiesel is not harmful to the environment. A vehicle tends to pollute the environment and emits harmful gasses, if injected with HSD whereas if the engine is using biodiesel, it emits no harmful gasses and rather keeps the environment pollution free.
- Biodiesel may not require an engine modification. Biodiesel can be blended with diesel so as to improve the efficiency of the engine without any hassles.
- Biodiesel is cheap. You can even make biodiesel in your backyard. If your engine can work with biodiesel fuel alone, then you really need not go to the gas station to buy fuel. You can just manufacture some for your Own personal use.
- Any vehicle using Biodiesel has very low idle starting noise. It is noted that biodiesel has a cetane number of over 100.

Biodiesel as a fuel not only helps reducing the pollution, but also reduces health hazards and gives the society A CLEANER AND GREENER TOMORROW.

Advantages of using biodiesel:

- **Easy to use** - Biodiesel can be used in existing engines, vehicles and infrastructure with practically no changes. Biodiesel can be pumped, stored and burned just like petroleum no changes. Biodiesel can be used pure, or in blends with petroleum diesel fuel in any proportion. Power and fuel economy by using biodiesel is practically identical to petroleum diesel fuel, and year round operation can be achieved by blending with diesel fuel.

- **Power and performance** - The degree to which fuel provides proper lubrication is its lubricity. Low lubricity petroleum diesel fuel can cause premature failure of injection system components and decreased performance. Biodiesel provides excellent lubricity to the fuel injection system.
- **Emissions and Greenhouse Gas Reduction** - Biodiesel provides significantly reduced emissions of carbon monoxide, particulate matter, unburned hydrocarbons and sulfates compared to petroleum diesel fuel. Additionally, biodiesel reduces emissions of carcinogenic compounds by as much as 85% compared with diesel. When blended with petroleum diesel fuel, these emission reductions are generally directly proportional to the amount of biodiesel in the blend.
- **Green house Gases** - Carbon dioxide released from biodiesel and the combustion does not contribute any new emissions of CO₂ as it is part of the carbon cycle. Closed carbon cycle will reduce 80% of CO₂. Example: growing oil feedstock consumes 4-6 times more CO₂ than biodiesel exhaust

Sources Of Biodiesel :

Alternative diesel fuels made from natural, renewable sources such as vegetable oil and fats. The most commonly used oils for the production of Biodiesel are:

Coffee oil: coffee oil comes from spent coffee grounds. The grounds can contain as much as 11 to 20 % oil. Currently grounds are disposed of or used as compost. After oil extraction the grounds can still be used to make biodiesel.

Beef Tallow: Crude beef tallow was obtained from a commercially available source. Animal tissue is converted to tallow using rendering; a process by which lipid material is separated from meat tissue and water under heat and pressure.

Coconut oil: Refined, bleached, deodorized (RBD) coconut oil was used for production of biodiesel.

Jatropha oil: Crude jatropha oil was obtained from a commercially available source. Jatropha oil comes from the shrub *Jatropha curcas*, also known as physic nut. The plant is native to Mexico, Central America, Brazil, Bolivia, Peru, Argentina, and Paraguay.

Jojoba oil: Jojoba (*Simmondsia chinensis*) is an evergreen perennial shrub grown in Arizona, Mexico, and neighboring areas. The dehulled seeds of jojoba contain 44% of liquid wax, which is not a triglyceride.

Fish oil: Fish oil was obtained from a commercially available source in Peru.

Corn oil: Crude, dry distiller's grain (DDG) extracted corn oil was obtained from a commercially available source. The extracted corn oil comes from the DDG stream of the ethanol production process.

Babassu oil: Babassu oil was purchased from Jedwards International, Inc. Babassu oil is extracted from the seeds of the babassu palm tree, *Attalea speciosa*. The tree is common in Brazil, Mexico, and Honduras; it grows well in areas typically cultivated for coconut or palm. The kernels contain 60-70% oil.

Crude linseed oil: Crude linseed oil was purchased from Botanic Oil Innovations, Inc. Linseed has been traditionally used as a drying oil. It grows in Argentina, India, and Canada. It is an annual herb and contains 37-42% oil. The crude oil contains 0.25% phosphatides, a small amount of crystalline wax, and a water-soluble resinous matter with antioxidant properties.

Neem oil: Pure, cold pressed neem oil was purchased from The Ahimsa Alternative, Inc. Neem (*Azadirachta indica*) is a large evergreen tree, 12 to 18 m tall, found in India, Pakistan, Sri Lanka, Burma, Malaya, Indonesia, Japan, and the tropical regions of Australia. The kernels contain 40-50% of an acrid green to brown colored oil.

Palm oil: Palm oil was obtained from a commercially available source.

Rice Bran oil: Refined, bleached, deodorized, winterized (RBDW) rice bran oil was purchased from Jedwards International, Inc. Rice bran oil is a non-edible vegetable oil which is greatly available in rice cultivating countries. Rice bran is a co-product of rice milling, containing about 15-23% oil.

Soybean oil: Refined soybean oil was obtained from a commercially available source.

Used cooking oil: Crude used cooking oil was obtained from a commercially available source.

Yellow grease: Crude yellow grease was purchased from Wildlife Sciences. Yellow grease is made up of restaurant greases, which are fats and oils left over from cooking. It can also be from rendering plants producing different quality greases.

Hemp oil: The oil is derived from the plant *Cannabis sativa* and contains significant amounts of -linolenic acid. Hemp is legally grown in Canada as a niche crop and is used mainly in the health food market. Hemp seeds have an oil content of 33 percent. Since the prices of edible vegetable oils are higher than that of biodiesel fuel, waste coffee oil is preferred as potential low priced Biodiesel sources. Use of such oil to produce Biodiesel in India have not started many researches have been undergoing in U.S.A. Under Indian Conditions, only such plants can be considered for biodiesel, which produce non-edible oil in appreciable

quantity and can be grown on large scale on non-cropped marginal lands and waste lands. Animal fats, although mentioned frequently, have not been studied to the same extent, as other oils because of property differences. Animal fats contain higher level of saturated fatty acids and therefore, they are solid at room temperature.

Material and Methods

Any type of oil usually have hydrophobic properties, which mean they are insoluble in water. As mention earlier, triglycerides are made up of 1 mol glycerol and 3 mol fatty acids. Fatty acids vary in terms of carbon chain length and number of unsaturated bonds. Typical fatty acids compositions found in several vegetable oils are summarized in table. Fatty acids that have no double bonds are termed saturated such as palmitic acid. These chains contain maximum number of possible hydrogen atoms per atom carbon. Fatty acids that have double bonds are termed unsaturated such as linoleic acid. Normally oils are obtained in the crude form through solvent extracting or mechanically pressing, containing a lot of impurities such as free fatty acids sterols and water. In fact these free fatty acids and water content will have significant effect on the esterification reaction, especially if a base catalyst is used. They could also interfere with the separation of FAME and glycerol during water washing because of soap formation.

| Fatty Acid % | Coffee oil | Cotton oil | Palm oil | Lard oil | Tallow oil | Coconut oil | Soybean oil |
|------------------|------------|------------|----------|----------|------------|-------------|-------------|
| Palmitic (C16:0) | 37.6 | 20.1 | 42.8 | 23.6 | 23.3 | 9.8 | 0.2 |
| Linoleic (C18:2) | 39.8 | 55.2 | 10.1 | 10.7 | 10.7 | 2.2 | 53.7 |
| Oleic (C18:1) | 12.7 | 19.2 | 40.5 | 44.2 | 42.4 | 6.9 | 22.8 |
| Stearic (C18:0) | 7.6 | 2.6 | 4.5 | 14.2 | 19.4 | 3.0 | 3.7 |

Typical Fatty Acid Composition For Different Common Oil Sources

| Common name | Chemical structure | C : D |
|---------------------------|---|-------|
| Caprylic acid | $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ | 8:0 |
| Lauric acid | $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ | 12:0 |
| Myristic acid | $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ | 14:0 |
| Palmitic acid | $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ | 16:0 |
| Palmitoleic acid | $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 16:1 |
| Stearic acid | $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ | 18:0 |
| Oleic acid | $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 18:1 |
| Elaidic acid | $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 18:1 |
| Linoleic acid | $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 18:2 |
| Linoelaidic acid | $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 18:2 |
| α - Linolenic acid | $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 18:3 |
| Behenic acid | $\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$ | 22:0 |
| Arachidic acid | $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$ | 20:0 |

Chemical formulae for various fatty acids

Where C=No.of carbon atoms, D=No. of bonds

Coffee oil and its composition:

Coffee oil is extracted from the waste coffee beans. The rapidly increasing use of fossil fuels worldwide depletes the finite supply and raises major concern over the associated greenhouse gases emissions and air pollutants. As reported by the United States Environmental Protection Agency, the emission of particulate matter from burning B20 (20 % by volume of biodiesel and 80 % by volume of petroleum diesel mixture) would decrease by approximately 10 % in comparison with emission from burning regular diesel. Also, the emission of carbon monoxide and hydrocarbons would decrease 21.1 % and 11 %, respectively. As a result, the demand for renewable energy in the form of biodiesel as an

alternative has increased dramatically. Approximately 1.1 billion gallons of biodiesel have been introduced into the American fuel market in 2011. Purified biodiesel, which meets the biodiesel standard (ASTM D 6751) can be directly used in the diesel engine. Modification of diesel engine is not essential when running with biodiesel fuel. Furthermore, most major engine companies affirm in their Original Equipment Manufacturers (OEMs) that using blends up to B20 will not void the engine warranties. The major feedstock for the biodiesel industry in the United States includes soybean oil, canola oil, white/yellow grease, and tallow and many more. Moreover, 54.32 % of total biodiesel feedstock

consumed in December 2013 came from soybean oil. With the growing demand for soybeans in both food and fuels, the price of soybeans has increased as well. This price pressure is relevant because the feedstock cost for producing biodiesel is approximately 70 % - 95 % of the total cost leading to a high sales price for biodiesel. The price of biodiesel hit a historic high of \$4.81 per gallon in 2008 (Figure1). Because of the economic downturn, Renewable Fuel Standard (RFS) 2 uncertainty, and the lapse of the biodiesel tax credit, the price of biodiesel reached a new record. In order to make the biodiesel price more competitive with diesel price, studies to assess the feasibility of using inexpensive waste materials as feedstock for biodiesel production need to be undertaken. According to a recent research result from Dr. Kondamudi, 10 %-15 % by weight of oil was found within the spent coffee grounds (SCGs). Also, SCGs have a minimum cost of acquisition, and hence, if used as an alternative feedstock for biodiesel production, would reduce the high price of feedstock in the biodiesel industry. Since the SCGs oil proportion is similar to the soybean oil percentage (about 20 % by weight), SCGs have sufficient oil content to be used as a feedstock to produce biodiesel. On the other hand, the world's coffee production in 2011/2012 was 8.64 million tons based on the data from the U.S. Department of Agriculture (USDA) and it was the second largest traded commodity worldwide. During 2011/2012, the coffee consumption within the U.S. alone was 1.38 million tons. Mover, the green coffee production was booming by 17 % between 2000 and 2012.

Fatty acid composition of the biodiesel were found to be linoleic acid (39.8%), palmitic acid (37.6%), oleic (12.7%), and stearic acid (7.6%). In addition, preliminary investigation on the solid waste remaining after oil extraction was conducted for possible use as a feedstock for the production of bioethanol.

Process catalysts:

Transesterification reaction can occur in the absence of catalysts, however, it requires high temperature, pressure and long reaction times. If all these requirements are met, the process cost is relatively high. This method produces relatively high purity esters and soap free glycerol, but because it is un-economical, it is typically not considered for industrial production of biodiesel. Three types of catalysts are generally used for biodiesel production: alkaline catalysts, acidic catalysts, enzymes.

Alkaline catalysts:

Alkaline catalysis is the most commonly used process for biodiesel production. Its main

advantage is that a high ester yield is obtained in short reaction times under mild reaction conditions (Canacki and Van Garpen 1999). However, alkaline catalysts are highly sensitive to free fatty acids in coffee oil. Therefore, only low free fatty acid content oils produce high ester yields after transesterification. Examples of alkali catalysts are sodium hydroxide, potassium hydroxide, alkali metals (such as sodium), alkali metal carbonates (such as sodium carbonate and potassium carbonate).

Acid catalysts:

Acid-catalyzed transesterification requires a relatively high temperature (-100 °C) Pressure (-5 bars) and large amount of alcohol. It is also slower in comparison to alkaline catalysis. The only advantage of this type of catalytic conversion is that it can effectively esterify free fatty acids in coffee oil and is therefore used to transesterify high free acid containing feedstock such as waste oils.

Enzyme catalysts:

Enzymes or lipases extracted from microorganisms can also be used as catalysts for the transesterification reaction.

Methanol:

In our experiment methanol is selected to be used in the biodiesel production due to its lower cost, better performance, less time and energy consumption during the reaction. Methanol is easy and quickly dissolvable due to its low molecular weight which is 32 gm/mol when compared to ethanol which has a weight of 46 gm/mol. The reaction time is less when compared to ethanol because it is manufactured from natural gas. The recovery of ethanol is difficult and becomes more difficult as it forms high viscosity azeotropes with water and it requires additional mechanical agitators. The performance of the ethyl ester is less compared to methyl esters.

Transesterification reactions:

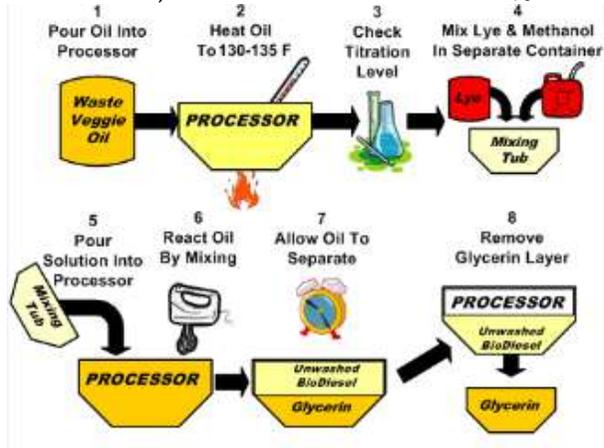
1. Alkali catalyzed
2. Acid catalyzed or Enzyme catalyzed

As for the enzyme catalyzed system, it requires a much longer reaction time than the other two systems. To date it has only been carried out on the laboratory scale and therefore will not be further discussed herein. At present, the high cost of biodiesel is the major obstacle to its commercialization. Biodiesel usual costs compared to petroleum based diesel. It is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil. For example, in the United States, soybean oil was sold on average for \$0.36/l. Therefore, it is not

surprising that biodiesel produced from pure vegetable oil costs much more than the petroleum based diesel. Exploring ways to reduce the high cost of biodiesel is of much interest in recent biodiesel research, especially for those methods concentrating on minimizing the raw material cost. The use of waste coffee oil instead of expensive oils to produce biodiesel is an effective way to reduce the raw material cost because it is estimated to be half the price of vegetable oil. In addition using coffee oil could also help to solve the problem of waste disposal. Most current biodiesel research concentrates on the alkali catalyzed technology carried out on a bench scale and no detailed technological information is available on overall continuous industrial processes in which both reactor and downstream separation units are continuously operated.

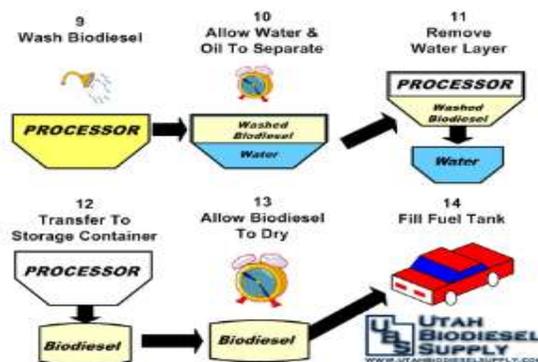
Homogeneous Alkali catalyzed transesterification reaction:

The transesterification of triglycerides with low molecular weight alcohols catalyzed by homogeneous alkali catalyst is the most common process in the biodiesel industry because of the low cost of the catalyst and the good conversions that can be achieved in short reaction time and at moderate temperatures. Catalysts such as alkaline metal hydroxides, alkoxides and carbonates are most often used. Commercially, NaOH and KOH are preferred because of their availability and low cost. The alkoxides are more expensive than the hydroxides and are more difficult to handle because they are hygroscopic. However, as the hydroxide ion is present only as an impurity in alkoxides they do not produce soap through triglyceride saponification. However, the general limitation for the use of homogeneous alkaline catalysts is the total FFA content associated with the feedstock, which must not exceed 0.5 Wt%.



Otherwise, soap formation seriously hinders the production of fuel grade biodiesel. Some researchers investigated the effect of alkaline catalysts on the transesterification of beef tallow. NaOH was found to perform significantly better than NaOMe. Furthermore, a slightly higher concentration of NaOMe with respect to NaOH (0.5 vs 0.3% w/w) was needed to obtain the maximum conversion of the oil into the corresponding esters.

A research studied the reaction of methanol with canola oil at different concentrations of alkaline catalyst (NaOH, KOH, NaOMe and KOMe), reaction temperatures and methanol to oil molar ratios. The results showed that there were significant differences in the product yields among the four catalyst formulations. Potassium based catalysts gave better yields than the sodium based catalysts and methoxide catalysts gave higher yields than the corresponding hydroxide catalysts



Experimental Procedure

The stepwise procedure for the production of biodiesel by alkali catalyzed batch reaction is as follows:

1. Extraction of oil from waste coffee.
2. Finding the acid value of free fatty acids.
3. Transesterification reaction by using the batch process
4. Separation of the diesel and glycerin.
5. Bio-diesel test.

Extraction of oil from waste coffee :

Waste coffee is kept in oven for 2hrs to remove if any moisture content is present. 70 gm of coffee waste is taken and oil is extracted by using hexane as solvent.

Extraction is carried out for four hrs.

Same procedure is followed for same amount of coffee waste with 1:1 ratio of isopropyl alcohol and hexane as solvent. Extraction time is also same.

The results obtained for above two cases are :

| S.No | Solvent | Time of Extraction | Amount of oil obtained/50 gm of feed |
|------|----------------------------|--------------------|--------------------------------------|
| 1 | Hexane | 2 | 2 |
| 2 | Hexane | 4 | 4 |
| 3 | Hexane + Isopropyl alcohol | 2 | 4 |
| 4 | Hexane + Isopropyl alcohol | 4 | 4 |

Transesterification Reaction in batch process:

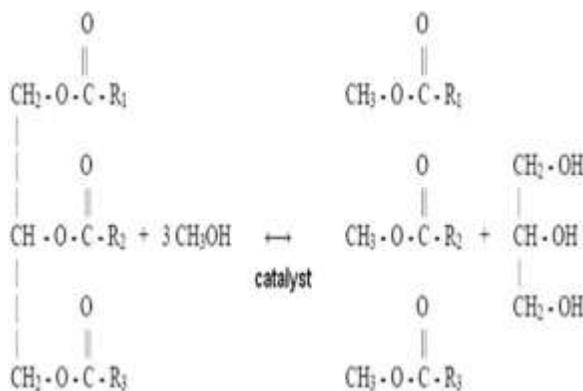
In laboratory scale, production of biodiesel by continuous process tends to be difficult. Batch scale is well suited for lab scale production of biodiesel.

Experimental setup and pretreatment:

A 1000ml glass cylindrical reactor equipped with magnetic stirrer, thermometer, reflux condenser and a sample port was used. The reactor was kept in a constant heating mantle with a temperature controller, which was capable of maintaining the temperature within ± 0.3°C. Agitation was provided with magnetic stirrer, which was set at a constant speed throughout the experiments. Initially, the reactor was filled with 40 g of coffee oil and heated to required temperature.



1. Biodiesel is processed from coffee oil by batch process using Base catalyzed (NaOH) transesterification reaction.
2. The experimental set up is shown in above figure. In this work biodiesel was produced from waste coffee oil and this can be collected from local coffee shops.
3. If any water molecules and dust is present and if used this oil may damage total biodiesel process. So, coffee oil must be heated at 110°C to remove the water molecules. Generally, the FFA value of coffee oil is higher than the required value and the amount of catalyst has an impact of conversion of esters during the transesterification process and also this biodiesel production is strongly influenced by the FFA content of coffee oil. Owing to its high FFA the transesterification of coffee oil to biodiesel catalyzed directly by Heterogeneous catalysts had very low conversion. Even using longer reaction time, so acid value is reduced before converting into biodiesel.



4. First a three necked flask with a water cooled condenser was filled with 40 ml of coffee oil.
5. The catalyst (1 wt % of oil) was dispersed in methanol (3:1 ratio of M:O) then stirring system was connected to it (about 600 rpm). Then heated to 60°C for three hours. After thorough mixing it was kept overnight; two layers were formed.
6. In that the upper layer consists of biodiesel whereas the lower layer consists of glycerin and this layer consist of excess methanol, unreacted catalyst and soap. This unreacted methanol was separated with the help of separating system and finally remaining glycerin layer was separated and then distilled to get 98% purified glycerin. The separated biodiesel was purified with hot water to get p^H neutral. These purified methyl ester compositions were analyzed by using Gas Chromatograph.

Seperation of biodiesel from Glycerin:

1. The reaction mixture was allowed to stand for 10-12 hours in separating funnel. At this stage two major products obtained that are glycerol and biodiesel.
2. The glycerin phase is much denser than biodiesel phase and is settled down while biodiesel floated up; while phase separation occurred by gravity setting into clear golden liquid biodiesel on the top with the light brown glycerol at the bottom of the separating funnel.
3. On next day the glycerol at the bottom was carefully decanted into a bottle, washed and dried.

Biodiesel tests :

1. Gas chromatography
2. Flash and Fire point
3. Cloud and Pour point test
4. Viscosity
5. Calorific value test

Conclusions:

Biodiesel is a viable and promising solution to the environmental pollution which results from conventional fuels' combustion and to the increasing world energy demand. The use of SCG as one of the various feedstocks for biodiesel production can be considered as a solution to these problems. Biodiesel production and commercialization have been already successfully introduced in many countries where USA, Brazil and Germany are the leaders.

Throughout this work I proved the feasibility of biodiesel production by using SCG as a starting material. I was able to identify the optimized conditions for oil extraction from SCG.

References

1. N.Kondamudi, S.K.Mohapatra and M.Misra, "Spent coffee grounds as a versatile source of green energy", Journal of Agricultural and Food Chemistry. 2008.
2. S.Lebedevas, A.Vaicekauskas, G.Lebedeva, V.Makareviciene, P. Janulis and K. Kazancev, " Use of waste fats of animal and vegetable origin for the production of biodiesel Fuel: quality, motor properties, and emissions of harmful components", Energy Fuels, 2006.
3. A.Tefera, Ethiopia Coffee Annual Report, global agricultural information network, 2012.
4. Van Gerpen, P., Clements D., Knothe G., Shanks B., and Pruszek R., Biodiesel Technology Workshop, Chapter 28, Iowa State University, March 2004.
5. "Feedstocks: A Focus on Camelina", Biodiesel Magazine. September 2008.
6. A.C. Ahmia, et al, Raw material for biodiesel production. Valorization of used edible oil, Revue des Energies Renouvelables, Vol. 17, No. 2, 2014.
7. D. Bajpai, Biodiesel: Source, Production, Composition, Properties and Its Benefits, Journal of Oleo Science, Vol. 55, No. 10, 2006, 487-502.
8. Amish P.Vyas. Effects of Molar Ratio, Alkali Catalyst Concentration and Temperature on Transesterification of Jatropha Oil with Methanol under Ultrasonic Irradiation, Chemical Engineering Department, Nirma University, 2011.
9. Caetano, "Valorization of Coffee Grounds for Biodiesel Production".
10. Ramos M., J., Fernandez C., M., Casas A., Rodriguez L., Perez A. (2009). Influence of fatty acid composition of raw materials on biodiesel properties.
11. Dennis Y., C., Leung X., W., Leung M., K., H. A review on biodiesel production using catalyzed transesterifictaion. Applied energy.(2010).