

## Experimental Studies on Production of Biodiesel from *Oryza sativa* (Rice) Bran Oil

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### Abstract

Increased environmental awareness and depletion of resources are driving industry to develop viable alternative fuels from renewable resources that are environmentally more acceptable. Vegetable oil is a potential alternative fuel. The most detrimental properties of vegetable oils are its high viscosity and low volatility, and these cause several problems during their long duration usage in compression ignition (CI) engines. The most commonly used method to make vegetable oil suitable for use in CI engines is to convert it into biodiesel, i.e. vegetable oil esters using process of transesterification.

Rice bran oil is an underutilized non-edible vegetable oil, which is available in large quantities in rice cultivating countries, and very little research has been done to utilize this oil as a replacement for mineral Diesel. In the present work, the transesterification process for production of rice bran oil methyl ester has been investigated. The optimum conditions for transesterification of rice bran oil with methanol and KOH as catalyst were found to be 60°C reaction temperature, 2h reaction time, 6:1 molar ratio of rice bran oil to methanol and 2% catalyst (w/w). The various properties such as viscosity, density, flash point, fire point etc. are compared with ASTM and DIN standard. The TLC method use for the confirmation of biodiesel and to calculate the yield. Results showed that biodiesel obtained under the optimum conditions has comparable properties to substitute mineral Diesel, hence, rice bran oil methyl ester biodiesel could be recommended as a mineral Diesel fuel substitute for compression ignition (CI) engines in transportation as well as in the agriculture sector.

**Keywords:** Compression Ignition (CI); Biodiesel; Transesterification; Rice Bran Oil

### Introduction

Diesel fuels have an important role in the industrial economy of any country. The high energy demand in the industrialized world and widespread use of fossil fuels is leading to fast depletion of fossil fuel resources as well as environmental degradation. The world petroleum reserves are so unevenly distributed that many regions have to depend on others for their fuel requirements. The degrading air quality due to emissions is the main adverse effect of petroleum based fuels. All these factors necessitate continued search and sustainable development of renewable energy sources that are

environmentally friendly. Biomass sources, particularly vegetable oils, have attracted much attention as an alternative energy source [1]. They are renewable, non-toxic and can be produced locally from agriculture and plant resources. Their utilization is not associated with adverse effects on the environment because they emit less harmful emissions and greenhouse gases [2].

India is the third-largest economy on a purchasing power parity basis and has the world's second-largest population, according to World Bank data. The country's energy demand continues to climb as a result of its dynamic economic growth and modernization.

**Figure 1:** India petroleum and other liquids production and consumption (1990-2015).

Source: EIA, International Energy Statistics and Short-Term Energy Outlook.

The work has been carried out on rice bran oil. RBO is used as raw material for the production of biodiesel. Rice bran oil is a vegetable oil, extracted from bran of the rice seed. Rice bran oil has been using widely in many Asian countries such as China, Japan, Korea, India and Vietnam. Rice bran oil is the oil extracted from the germ and inner husk of rice. Rice bran oil is a non-conventional, in expensive and low-grade vegetable oil. Rice bran oil contains a range of fats, with 47% of its fats monounsaturated, 33% polyunsaturated and 20% saturated. The fatty acid composition of rice bran oil are shown in the table 1.

**Figure 2:** Rice bran seeds.

**Figure 3:** Structure of rice seed  $\gamma$ -oryzanol.

S. No.	Fatty acids	(%)
1	Palmitic C16:0	18.8
2	Stearic C18:0	2.4
3	Oleic C18:1	43.1
4	Linoleic C 18:2	33.2
5	Arachidic C20:0	0.7

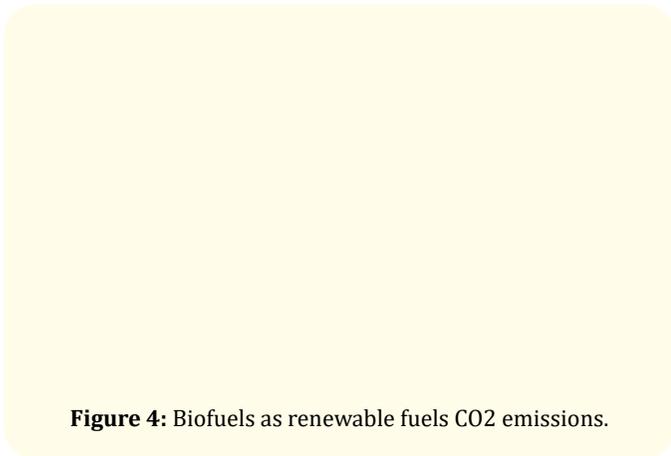
**Table 1:** Fatty acid composition of rice bran oil.

Source: Srivastava and Prasad [2].

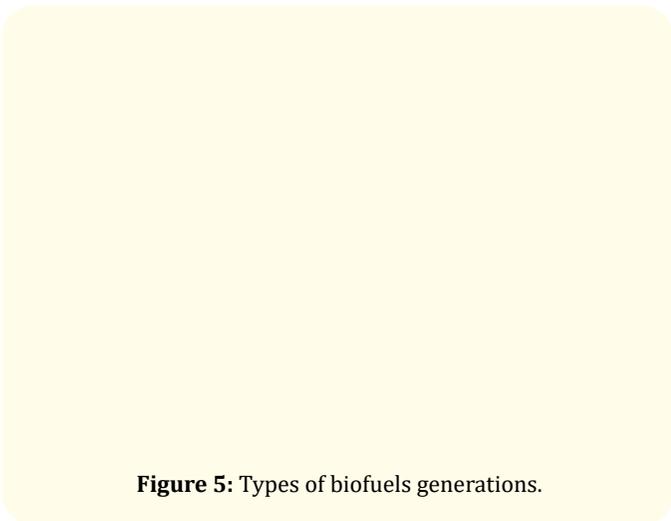
### Biofuel

Biofuels are drawing increasing attention worldwide as substitutes for petroleum-derived transportation fuels to help address cost, energy security and global warming concerns associated with liquid fossil fuels. The term is used here to mean any liquid fuel made from plant material that can be used as a substitute for petroleum-derived fuel.

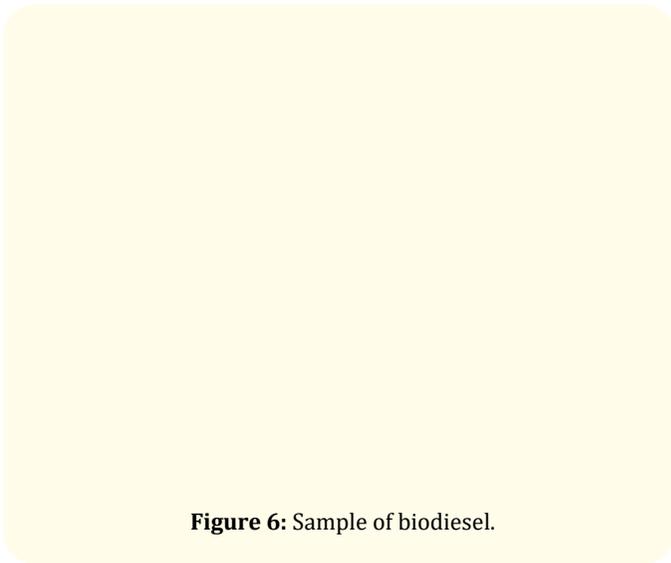
Relatively recent popularized classification for liquid biofuels includes “first generation” and “second generation” fuels. First generation is generally derived from food crops like sugarcane soybean etc. The biochemical methods like fermentation or hydrolysis are employed to convert them to biofuels. Second generation is those fuels which generally produce from non-food crops. (Lignocelluloses biomass such as wood, forestry waste, organic waste etc). Biochemical or thermochemical methods are used to synthesis biofuels.



**Figure 4:** Biofuels as renewable fuels CO2 emissions.



**Figure 5:** Types of biofuels generations.



**Figure 6:** Sample of biodiesel.

### Biodiesel

Bio-diesel refers to a vegetable oil or animal fat based diesel fuel consisting of long chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel is made by chemically reacting vegetable oil, soybean oil, or animal fat with an alcohol produced from different fatty acids [3]. The process used to convert these oils to Biodiesel is called transesterification. Bio-diesel is employed in standard diesel engines and is therefore distinct from the vegetable and waste oils used in fuel converted diesel engines. Bio-diesel can be used alone, or mixed with petro diesel in certain proportions. Biodiesel is often referred to as monoalkyl ester with long chain fatty acids [8]. Blends of 20% biodiesel and lower can be utilized in diesel instrumentation with only minor modifications [6].

### History

Rudolf Diesel invented the diesel engine in the 1890s. From the beginning, this engine could run on a variety of fuels, including vegetable oil. However, because cheap petroleum fuels were easily available, few people were interested in alternatives (Pahl, 2005, pp. 18-22). As early as the 1930s, there was interest in splitting the fatty acids from the glycerin in vegetable oil in order to create a thinner product similar to petroleum diesel. In 1937, G. Chavanne was granted a Belgian patent for an ethyl ester of palm oil (which today we would call biodiesel). In 1938, a passenger bus fueled with palm oil ethyl ester plied the route between Brussels and Louvain (Knothe, 2005, p. 10).

During World War II (1939 to 1945), when petroleum fuel supplies were interrupted, vegetable oil was used as fuel by several countries, including Brazil, Argentina, China, India, and Japan. However, when the war ended and petroleum supplies were again cheap and plentiful, vegetable oil fuel was forgotten.

### Modern interest in biodiesel

In the 1970s, the petroleum oil embargo caused many countries to look to vegetable oil as a possible fuel. Scientists in Austria, the United States, South Africa, and many other countries rediscovered that straight vegetable oil could be used to run diesel engines; however, eventually the poor quality of the fuel spray caused by the thickness (viscosity) of the vegetable oil caused damage to the engines. Scientists then conducted experiments to convert the vegeta-

ble oil into biodiesel. The word “biodiesel” was probably first used in about 1984 (Van Gerpen., *et al.* 2005, p. 4). The first biodiesel manufacturing plant specifically designed to produce fuel was started in 1985 at an agricultural college in Austria. Since 1992, biodiesel has been commercially manufactured across Europe, with Germany being the largest producer.

### Future of biodiesel

Scientists are currently researching ways to produce biodiesel using new feedstock that are less limited by the availability of land. For example, some types of algae can produce oil. Energy crops could also be grown on land that is not suitable for food crops, such as soil that is too acidic or too salty, that has too many minerals or is too shallow, or that is in danger of eroding. In these cases, energy crops might help stabilize and restore this land.

Scientists are also experimenting with producing fuel from non-oilseed feedstock such as inexpensive, non-edible biomass (agricultural residue, waste from the wood products industry, and switch grass and other grasses) that can be converted into a diesel replacement. While it is a fairly simple process to convert vegetable oil or animal fat into biodiesel, the conversion of cellulosic feedstock to fuel is more complicated and more expensive. To produce a hydrocarbon fuel, the biomass is generally first converted into a synthetic gas using high heat. Then the gas can be converted into a liquid diesel fuel.

### Biodiesel as a fuel

Biodiesel meets both the biomass-based diesel and overall advanced biofuel demand of the Renewable Fuel standard. Biodiesel is a liquid fuel usually stated as B100 or neat biodiesel in its pure, unhomogenised form. Like petroleum diesel, biodiesel is used as fuel in compression- ignition engines. How well biodiesel performs in weather condition depends on the blend of biodiesel [4]. The smaller the proportion of biodiesel within the mix, the better it performs in cold temperatures. Biodiesel that is most frequently used as a blend with regular diesel fuel can be used in several diesel vehicles without any engine modification. The most common biodiesel blend is B20, which is 6% to 20% biodiesel blended with petroleum diesel [4]. B5 (5% biodiesel, 95% diesel) is commonly used in fleets [5]. Before using biodiesel, it's necessary to check the engine's warranty to make sure that higher-level blends of alternative fuel do not void or have an effect on it. One advantage of biodiesel is that it can impart satisfactory lubricity to diesel fuels at blend levels as low as 1%.

**Figure 7:** Biodiesel vehicle.

**Figure 8:** The Biological cycle.

### Advantages of biodiesel

- **Produced from renewable resources:** Biodiesel is a renewable energy source unlike other petroleum products that will vanish in years to come. Since it is made from animal and vegetable fat, it can be produced on demand and also causes less pollution than petroleum diesel.
- **Can be used in existing diesel engines:** One of the main advantage of using biodiesel is that can be used in existing diesel engines with little or no modifications at all and can replace fossil fuels to become the most preferred primary transport energy source.
- **Less greenhouse gas emissions:** Fossil fuels when burnt release greenhouse gases like carbon dioxide in the at-

mosphere that raises the temperature and causes global warming. To protect the environment from further heating up, many people have adopted the use of biofuels. Experts believe that using biodiesel instead of petroleum diesel can reduce greenhouse gases up to 78%.

- **Cleaner biofuel refineries:** When oil is extracted from underground, it has to be refined to run diesel engines. You can't use it straight away in the crude form. When it is refined, it releases many chemical compounds including benzene and butadiene in the environment which are harmful for animals, plants and human life. Biofuel refineries, which mainly uses vegetable and animal fat into biofuel releases less toxic chemicals, if spilled or released to the environment.
- **Biodegradable and non-toxic:** When Biofuels are burnt, they produce significantly less carbon output and few pollutants. As compared to petroleum diesel Flashpoint for biodiesel is higher than 150°C whereas the same is about 52°C for petroleum diesel, which makes it less combustible. It is therefore safe to handle, store and transport.
- **Better fuel economy:** Vehicles that run on biodiesel achieve 30% fuel economy than petroleum based diesel engines which means it makes fewer trips to gas stations and run more miles per gallon.
- **More health benefits:** Air pollution cause more deaths and diseases than any other form of pollution. Biodiesel produce less toxic pollutants than other petroleum products.

#### Disadvantages of biodiesel

- **Variation in quality of biodiesel:** Biodiesel is made from variety of biofuel crops. When the oil is extracted and converted to fuel using chemical process, the result can vary in ability to produce power. In short, not all biofuel crops are same as amount of vegetable oil may vary.
- **Not suitable for use in low temperatures:** Biodiesel gels in cold weather but the temperature that it will gel depends on the oil or fat that was used to make it. The best way to use biodiesel during the colder months is to blend it with winterized diesel fuel.
- **Food shortage:** Since biofuels are made from animal and vegetable fat, more demand for these products may raise

prices for these products and create food crisis in some countries.

- **Increased use of fertilizers:** As more crops are grown to produce biofuels, more fertilizer is used which can have devastating effect on environment. The excess use of fertilizers can result in soil erosion and can lead to land pollution.
- **Clogging in engine:** Biodiesel cleans dirt from the engine. This proves to be an advantage of biofuels but the problem is that this dirt gets collected in fuel filter and clogs it.
- **Fuel distribution:** Biodiesel is not distributed as widely as petroleum diesel. The infrastructure still requires more boost so that it is adopted as most preferred way to run engines.
- **Slight increase in nitrogen oxide emissions:** Biodiesel has about 10% higher Nitrogen Oxide (NOX) than other petroleum products. Nitrogen Oxide is one the gas that is used in the formation of smog and Ozone. Once it gets dissolved in atmospheric moisture, can cause acid rain.

#### Aim of the Work

The aim of this study is to produce biosynthesis from rice bran oil and characterize the produced oil with its biodiesel and standard diesel.

The aim of the current work is

- I. Use the vegetable oil, RBO to produce Biodiesel.
- II. Calculate the FFA%, acid value and the yield % of the produced Biodiesel.
- III. Measure the following properties of the produced biodiesel and compare with the standard value
  - Specific gravity
  - Flash point
  - Fire point
  - Cloud point
  - Pour point
  - Kinematic viscosity

#### Biodiesel feedstock

##### Raw material for biodiesel production

There are different potential feedstocks for biodiesel production. The use of edible vegetable oils or the first generation feed-

stocks has been of great concern recently; this is because they raise many concerns such as food versus fuel debate that might cause starvation especially in the developing countries and other environmental problems caused by utilizing much of the available arable land. This problem can create serious ecological imbalances as countries around the world began cutting down forests for plantation purposes. Hence, use of these feed-stocks could cause deforestation and damage to the wildlife. Therefore, non-edible vegetable oils or the second generation feedstocks have become more attractive for biodiesel production. These feedstocks are very promising for the sustainable production of biodiesel. Some examples of *Jatropha curcas*, *Madhuca indica* (mahua), *Pongamia pinnata* (karanja), *Hevea brasiliensis* (Rubber seed), *Azadirachta indica* (neem), *Oryza sativa* (Rice bran), *Ricinus communis* (castor).

#### ***Azadirachta indica* (Neem)**

*Azadirachta indica* (Neem) tree belongs to the Meliaceae family. It is a multi purpose and an evergreen tree, 12-18m tall, which can grow in almost all kinds of soil including clay, saline, alkaline, dry, stony, shallow soils and It is native to India, Pakistan, Sri Lanka, Burma, Malaya, Indonesia, Japan, and the tropical regions of Australia. Planting is usually done at a density of 400 plants per hectare. The productivity of Neem oil mainly varies from 2 to 4 t/ha/yr and mature Neem tree produces 30 - 50 kg fruit. The seed of the fruit contains 20-30wt% oil and kernels contain 40 - 50% of an acrid green to brown colored oil.

#### ***Oryza sativa* (Rice bran)**

Rice bran is the cuticle between the paddy husk and the rice grain and is obtained as a by-product in the production of refined white rice from brown rice and is common in countries such as China and India. The bran is highly nutritious due to the presence of lipids, protein, minerals and vitamins. It is extracted from white rice bran by which the composition of rice bran varies with the rice type, climatic conditions and rice processing methods. The oil content in rice bran varies from 12% to 25%. The estimated potential yield of crude rice bran oil is about 8 million metric tons if all rice bran produced in the world were to be harnessed for oil extraction. Rice bran oil is an underutilized non-edible vegetable oil, which is available in large quantities in rice cultivating countries.

#### ***Madhuca indica* (Mahua)**

*Madhuca indica* is mainly found in India. It belongs to the Sapotaceae family and grows quickly to approximately 20 m in height,

possesses evergreen or semi-evergreen foliage, and is adapted to arid environments. The kernel constitutes about 70% of the seed and contains 50% oil. Each tree yields about 20 - 40 kg of seed per year depending up on the maturity and size of the tree and the total oil yield per ha is 2.7 t per year. Its seed contains about 35 - 40% of *Madhuca indica*.

#### ***Pongamia pinnata* (Karanja)**

*Pongamia pinnata* (L.) Pierre (karanja or honge), an arboreal legume is a medium sized evergreen tree belonging to the family (Leguminosae; Pappilonaceae). Which grows in Indian subcontinent and south-east Asia. A single tree is said to yield 9 - 90 kg seeds, indicating a yield potential of 900-9000 kg seed/ha. It is one of the few nitrogen fixing trees (NFTS) that produce seeds with a significant oil content. *Pongamia pinnata* has been recognized as available source of oil for the burgeoning biofuel industry. The oil is reddish brown and rich in unsaponifiable matter and oleic acid.

#### **Selection of feedstock for biodiesel**

In general, seeds and nuts should be selected considering all the outcomes and shortcomings, it should be stored in cool and dry conditions, and processed quickly to avoid degradation. The seeds should be processed close to the time when the oil will be processed into biodiesel. Before processing the seeds must be cleaned, screened, and, in some cases, hammered or dehulled [6]. The meal or cake in some cases must be heated to deactivate toxic components before use. Biodiesel is not the same as straight vegetable oil or animal fat. A normal diesel engine will eventually be damaged through the use of straight vegetable oil or straight animal fat fuel. Vegetable oils or animal fats must be converted into biodiesel by reacting the oil or fat with an alcohol and a catalyst. This process is referred to as "transesterification1 [7]".

#### **Alcohols used in biodiesel production**

Alcohols that can be used in biodiesel production are those with short chains, including methanol, ethanol, butanol and amyl alcohol. The most widely used alcohols are methanol (CH<sub>3</sub>OH) and ethanol (C<sub>2</sub>H<sub>5</sub>OH) because of their low cost and properties. Methanol is often preferred to ethanol in spite of its high toxicity because its use in biodiesel production requires simpler technology; excess alcohol may be recovered at a low cost and higher reaction speeds are reached.

### Catalyst used in biodiesel production

The catalyst used for the transesterification of triglyceride may be classified as basic, acid or enzymatic. Basic catalyst includes Sodium Hydroxide (NaOH), Potassium hydroxide (KOH), carbonates etc. Acid catalyst includes sulfuric acid, sulfonic acid and hydrochloric acid; their use has been less studied. Heterogeneous catalyst that have been considered for biodiesel production include enzymes, titanium silicates, and compounds from alkaline earth metals, anion exchange resin guanidine in organic polymers [9]. Lipases are the most frequently used enzymes for biodiesel production.

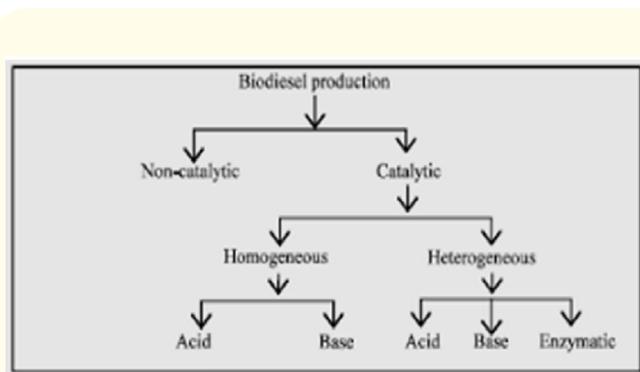


Figure 9

### Production method of biodiesel

#### Biodiesel production technologies

It is well known that viscosity is the main barrier that prevents the use of direct vegetable oils in conventional diesel engines. Therefore, there are many techniques, methods and processes that have been used recently to produce biodiesel from various feedstocks. These methods include Ultra and Supercritical process, pyrolysis, micro emulsification and transesterification.

#### Supercritical process

In the critical state, the oil and methanol are in a single phase, and reaction happens spontaneously and quickly [7]. The process can tolerate water within the feedstock, free fatty acids are converted to methyl esters rather than soap, thus a wide variety of feedstocks may be used and also the catalyst removal step is eliminated.

### Ultrasonic reactor method

In the ultrasonic reactor methodology, the ultrasonic waves cause the reaction mixture to produce and collapse bubbles uniformly. This cavitation at the same time provides the space for blending and heating required to carry out the transesterification process. Thus, using an ultrasonic reactor for biodiesel production drastically reduces the reaction time, reaction temperatures, and energy input.

### Pyrolysis (Thermal cracking)

Pyrolysis is the thermal decomposition of the organic matters in the absence of oxygen and in the presence of a catalyst. The paralyzes material can be vegetable oils, animal fats, natural fatty acid or methyl ester of fatty acids. It has been observed that pyrolysis process is effective, simple and waste less.

### Micro-emulsification

Micro-emulsification is defined as transparent, equilibrium thermodynamically stable colloidal dispersion of microstructure with diameter ranges from 100 to 1000<sup>o</sup>A. Micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, and alcohol such as ethanol, butanol, hexanol and a surfactant and a cetane improver, with or without diesel fuels. Micro-emulsification has been considered as a viable approach to solvent problem of the high viscosity of vegetable oils.

### Transesterification (Alcoholysis)

Animal and vegetable oils are composed of triglycerides, which are esters of three free fatty acids and glycerol. In the transesterification process, the addition of alcohol and alkali de-polymerization occurs, making it a stronger nucleophile. It can be seen that the reaction did not have other inputs than triglycerides and alcohol. Under normal conditions, the reaction will proceed very slowly, so heating is used to accelerate the reaction using a catalyst (acid and/or base). Common catalysts for transesterification include sodium hydroxide, potassium hydroxide and sodium methoxide [6]. The most economical process for processing virgin vegetable oil, which only requires low temperature and pressure and produces more than 98% of the crop. However, biodiesel made from different sources or in other ways may require acidic catalysts, which are much slower [12].

### Factor affecting of biodiesel

There are many factors which affect the production of biodiesel like catalyst, presence of water, free fatty acid in oil samples, reaction time, reaction temperature and agitation speed.

### Effect of water and FFA contents

The water and free fatty acid (FFA) contents are critical factors for transesterification reaction. Base-catalyzed transesterification reaction requires water free and low acid value ( $< 1$ ) raw materials for biodiesel production. If the oil samples have high FFA content (more than 1%) then the reaction requires more alkali catalyst to neutralize the FFA. Presence of water gives greater negative effect than that of FFAs because water can cause soap formation which cause increase in viscosity.

### Reaction time

The increase in fatty acid esters conversion when there is an increase in reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol and oil. After that the reaction proceeds very fast. However, the maximum ester conversion was achieved within, 90 minutes. Further increase in reaction time does not increase the yield product.

### Reaction temperature

Higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils.

### Catalyst concentration

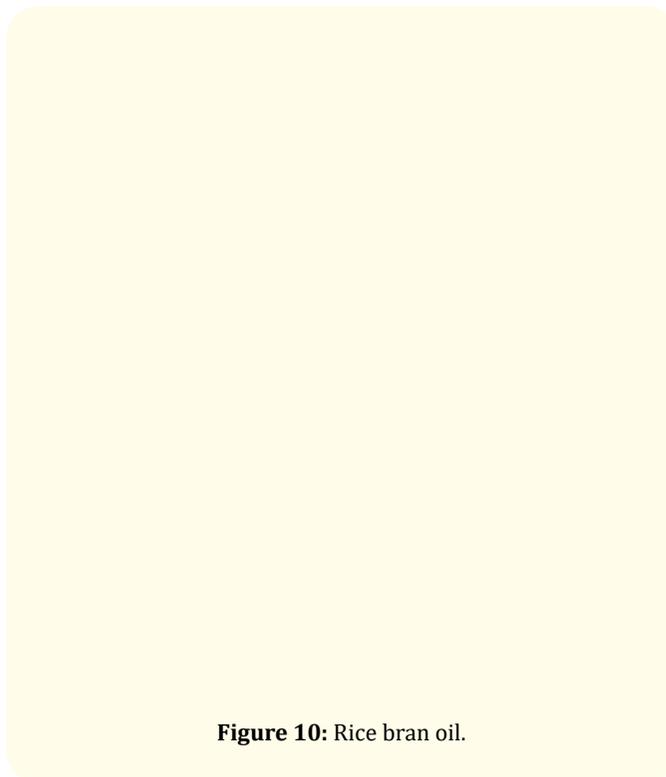
When the concentration of catalyst is increase with oil samples, the conversion of triglycerides into biodiesel is also increases.

## Experimental Analysis

### Material required

#### Rice bran oil

We use rice bran oil as the raw material for the production of biodiesel RBO has some properties, which makes replacement of diesel fuel. Cenatne number of RBO oil is generally in the higher range of diesel fuel. Heat content of vegetable oils are nearly 90% that of diesel fuel. Long chain saturated, unbranched hydrocarbon are especially suitable for conventional diesel fuel. The long, unbranched hydrocarbon chains in the fatty acids meet this requirement. RBO from properly stored seed is yellow in color with unpleasant taste.



**Figure 10:** Rice bran oil.

### KOH

It is the catalyst for transesterification and works by cracking the vegetable oil molecules, splitting the triglyceride from the hydrocarbons and shortening the carbon chain.

### Methanol

A little amount of the methanol is necessary in order to get the highest yield. If 90% yield is obtaining this means 90% fatty acid has been eliminated from the oil. Generally, 15% to 20% methanol based upon the total weight of batch of oil is necessary.

### Water

Mineral Water is used for washing methyl ester to remove the unreacted catalyst.

### Method used

#### Pre-treatment process

In this process firstly Rice bran oil is filtered in order to remove suspended material. The oil is than heated to temperature more 110°C in order to remove moisture for about ten minutes.

### Titration

In order to determine the accurate amount of catalyst titration is carried out, because both insufficient as well as excess amount of catalyst results in decrease in the yield of Biodiesel. For titration solution of 1 ml Rice bran oil and 10 ml isopropyl alcohol is titrated against 0.1% KOH solution. The number of millilitres of 0.1% KOH solution needed is equal to the number of extra grams of pure potassium hydroxide catalyst needed to produce the proper reaction to make biodiesel from RBO. RBO possess lower FFA content, so it directly treated to transesterification.

### Transesterification

100 gm of RBO is taken in a 200 ml beaker. 2 wt% of KOH catalyst and 6:1 molar ratio of Methanol and Oil is taken in 100 ml beaker. Now the temperature of oil is raised to 60°C. When this temperature is reached solution of alcohol and KOH in known quantity is added. Stirrer is switched on. The reaction is allowed to proceed for 120 minutes with continuous stirring.

**Figure 11:** Transesterification.

**Figure 12:** Transesterification reaction.

**Figure 13:** The mechanism of transesterification reaction.

allowed to settle for overnight. Two layers were separated. As glycerol was heavier it settled at the bottom of separating funnel. Biodiesel (Methyl ester) was at top. Glycerol was separated from biodiesel from the bottom of the funnel.

**Figure 14:** Separation.

### Transesterification kinetics and mechanism

Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediated in the process.

### Settling and separation of glycerol and biodiesel

After the prescribed time when the reaction was completed the product mixture was transferred to a separating funnel and

### Washing of methyl ester

After the removal of glycerol methyl ester is washed in order to remove excess catalyst and soap. This is done by first warming water up to 70°C. For washing 20 ml of water is taken. Water is mixed with methyl ester and left for settling for few minutes. Two layers are formed. Water settles at the bottom. It is removed from the bottom of the separating funnel carrying with it unreacted catalyst. Washing is done until clear water is observed. For washing litmus paper test was performed. Litmus paper was dipped in water removed. If its colour changes means it's acidic. When colour change is not observed in litmus paper it means water is neutral and no more washing is required. Minimum three washings are required. Sometimes more than three washings are required if more amount of catalyst is unreacted resulting in formation of soap.

**Figure 15:** Washing.

### Heating

After washing methyl ester is heated in order to remove unreacted alcohol and water that is left at the time of washing. For this methyl ester produced is heated for about ten minutes at a temperature greater than 100°C.

**Figure 16:** Biodiesel after heating.

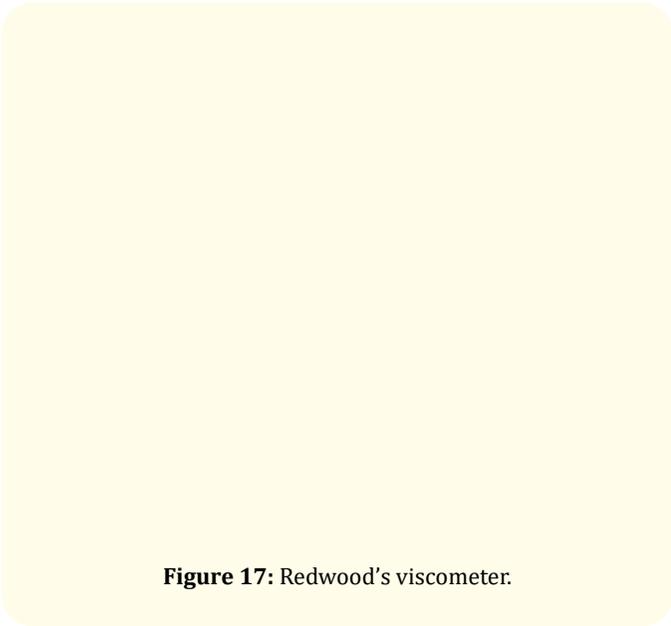
### Analysis of prepared biodiesel

#### Viscosity

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of "thickness"; for example, honey has a much higher viscosity than water. Viscosity is a property of the fluid which opposes the relative motion between the two surfaces of the fluid in a fluid that are moving at different velocities.

Redwood's viscometer is commonly used to determine the viscosity of oils.

The Redwood viscometer consists of vertical cylindrical oil cup with an orifice in the centre of its base. The orifice can be closed by a ball. A hook pointing upward serves as a guide mark for filling the oil. The cylindrical cup is surrounded by the water bath. The water bath maintains the temperature of the oil to be tested at constant temperature. The oil is heated by heating the water bath by means of an immersed electric heater in the water bath. The provision is made for stirring the water, to maintain the uniform temperature in the water bath and to place the thermometer in record the temperature of oil and water bath. The cylinder is 47.625 mm in diameter and 88.90 mm deep. The orifice is 1.70 mm in diameter and 12 mm in length, this viscometer is used to determine the kinematic viscosity of the oil.



**Figure 17:** Redwood's viscometer.

#### Formulae used:

Kinematic Viscosity ( $\gamma$ ) =  $A t - B/t$

$\gamma$  expressed in stokes or centi stokes A and B are constants

A = 0.264 and B = 190, when t = 40 - 85 seconds  
A = 0.247 and B = 65, when t = 85 - 2000 seconds

t is the time taken in seconds for the collecting 50 ml of oil called Redwood second.

#### Procedure

- The cylindrical oil cup and ensure the orifice tube is cleaned properly to free from dirt.
- The orifice is closed with ball valve.
- A 50 ml flask placed below the opening of the Orifice.
- The oil in the cylindrical oil cup is filled up to the mark in the cup.
- Water bath is filled with water.
- The thermometers to measure the oil and water bath temperatures are inserted at their respective places.
- Water bath is heated and stirred in order to maintain the uniform temperature.
- Ball valve is lifted at a particular temperature and the oil is collected in the 50 ml flask and the time taken in seconds for

collecting 50 ml of oil is noted. A stop watch is used to measure the time. This time is called Redwood seconds.

#### Specific gravity

Specific gravity is the ratio of the density of a substance to the density of a reference substance; equivalently, it is the ratio of the mass of a substance to the mass of a reference substance for the same given volume. Apparent specific gravity is the ratio of the weight of a volume of the substance to the weight of an equal volume of the reference substance.

The specific gravity of Biodiesel varies with its fatty acid composition and its glycerin content, both free and bound. The same basics principals apply. A denser biodiesel has higher energy content and will give better mileage and increased power. Since the fatty acid content dictates the specific gravity, a denser vegetable oil will process into a denser biodiesel. Vegetable oils will typically have a specific gravity of from 0.903 to about 0.921 depending on its fatty acid composition and temperature. The densities recorded in literature are at different temperatures. Biodiesel will have a range of about 0.86 to 0.90. So, if you want to find out if your oil is biodiesel or vegetable oil, you can measure its specific gravity with a hydrometer and anything above 0.90 is probably vegetable oil, and anything below 0.90 is probably biodiesel.

Generally, hydrometer is used to determine the specific gravity Usable biodiesel has a density of 0.86 - 0.90 g/ml (grams per millilitre - pure water is roughly 1g per ml). Therefore, a hydrometer which covers that full range is required to check the quality of biodiesel produced. A brewer's hydrometer is unsuitable as the general density range for brewers measuring liquid as sugar turns to alcohol is 0.990 - 1.070 g/ml. The hydrometer used in the commercial production of biodiesel is a BS718 M50SP with a range of 0.850- 0.900 g/ml. It is 270 mm long with 0.001 g/ml divisions, and +/- 0.0006 g/ml at 15 degrees Celsius. For domestic (non-professional) production of biodiesel a cheaper option would be a BS718 M100 with a range of 0.800 - 0.900 g/ml, 0.002 g/ml divisions, and 0.002 g/ml accuracy at 20 degrees Celsius. This hydrometer is 250 mm long is shown in the figure 18.

#### The hydrometer test procedure

- The test jar three quarters full is filled with Bio diesel then hydrometer is slowly inserted.

**Figure 18:** Hydrometer.

- Presence of air bubbles clinging to the glass is removed by spinning to dislodge, which could cause a test error.
- At eye level, the specific gravity figures on the glass stem where the surface of the liquid cuts across it.
- Since many home brew testers only give accurate readings when the temperature of the test liquid is at 60 F (16°C).

### Flash point and fire point

All flammable liquids have a vapour pressure that increases with its temperature. The concentration of evaporated liquid in the air increases with increase in vapour pressure. Different flammable liquids require different concentrations in the air to sustain combustion. Flash point of a flammable liquid is defined as the lowest temperature at which it can form an ignitable mixture in air. However, the vapour stops to burn if the source of ignition is removed. Fire point, which is a slightly higher temperature, is the temperature at which vapours of the flammable liquid continue to burn after being ignited even after the source of ignition is removed. Both the flash point and fire point have no relation to the temperature of the source of ignition.

Flash point is the minimum temperature when there is sufficient concentration of vapours of the flammable liquid in air to sustain burning when there is a source of ignition. Flash point and fire point are two important characteristics of liquid fuels that decide their transportation as they define fire hazards of these flammable liquids. It is unanimously agreed that liquids with a flash point less than 60.5 degrees centigrade or 37.8 degrees centigrade are flammable, while liquids having flash points higher than these limits are called combustible liquids.

Fire point is the temperature at which the vapours of the flammable liquid present in air continue to burn after removal of source of ignition. If fire propagates for at least 5 seconds, it is said to be the fire point of the liquid. Though the vapours of the liquid are ignited at a lower temperature called flash point, they are not

sufficient in quantity to sustain burning. In general, fire points can be taken as 10 degrees higher than flash points of flammable liquids. Cleve land open cup apparatus (Figure 19) is widely used to determine the flash point and fire point of liquids.

**Figure 19:** Cleveland open cup apparatus.

### Procedure

Thermometer should be pendent or held in vertical position by any suitable device. The bottom of bulb should be ¼ in from the bottom of the cup. The cup should be filled with the material to be tested in such a manner that the top of meniscus is exactly at the filling line at room temperature. There should be no oil above the filling line or outside of the apparatus.

The test flame should be approximately 5/32 in diameter. The test flame should be applied as the temperature read on thermometer reaches each 5F, the flam should pass through the centre of cup and time passing should be 1 second. When oil reaches a temperature 50F below probable flash point the heating should be decreased. The flash point should be taken as the temperature read on the thermometer when flash occur at any point on the surface of the oil. After determining the flash point the heating should be continued at low rates. The application of test flame should be at

specified intervals. Until the oil burn and continue to burn for at least 5 seconds.

### Cloud point and pour point

Cloud point and pour point are important physical properties of any liquid fuel. Cloud point, as the name suggests is the temperature at which a cloud of wax crystals first appear in a liquid fuel when it is cooled under special testing conditions. The cloud point of any petroleum product is an indicator of how well the fuel will perform under cold weather conditions. Pour point is just the opposite of cloud point as it refers to the lowest temperature at which movement of oil is observed and the fuel can be pumped easily. As such there is only a slight difference in these two temperatures on the temperature scale but the difference between cloud point and pour point is significant in the use of any fuel. Let us find out more about these two physical characteristics of any liquid fuel.

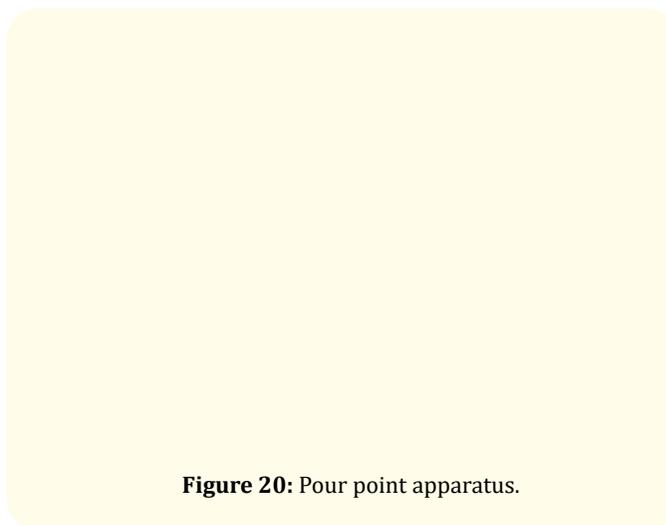
In the industry, cloud point is taken as the temperature below which wax in fuel tends to form a cloudy appearance. This is a condition which is detrimental for any engine as solidified wax makes the fuel thick and it clogs the fuel filters and injectors. This wax also gets applied on the pipeline and has a tendency to form an emulsion with water.

This is a property that holds great significance in cold weathers. Cloud point is also referred to as Wax Appearance Temperature (WAT).

On the other hand, pour point is the lowest temperature at which the fuel continues to flow. Pour point of a fuel is an indication of the temperature at which fuel can still be pumped. Alternatively, pour point can also be described as the lowest temperature at which a fuel performs satisfactorily and beyond this temperature, the fuel stops flowing and starts to freeze. Both cloud point and pour point can be determined using the same pour point apparatus (Figure 20).

### Procedure

- Test jar was filled to the level mark, closed tightly by the cork carrying the thermometer and placed into a pour point apparatus as shown in figure 20.
- Test jar was removed from the jacket quickly without disturbing the specimen. Inspection for cloud point was done and jacket replaced. Operation was done without exceeding time duration of three (3) seconds.



**Figure 20:** Pour point apparatus.

### Cloud point

Cloud point is the temperature of a liquid specimen when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions, observation was done and cloud point was reported to the nearest 1°C. At this point, cloud is observed at the bottom of the test jar, which is confirmed by continued cooling.

### Pour point

The test jar was inspected at an interval of at three (3) minutes by holding in a horizontal position for a few seconds before returning it to cool.

The pour point was reached when the oil surface stayed in the vertical position for a period of 5 seconds without sagging. At this point the thermometer was inserted to cool for 10 seconds and the temperature of the oil was taken.

### TLC analysis of Biodiesel with respect to RBO

TLC (Thin layer chromatography) is commonly used for qualitative analysis. It is fast and effective and also can be used to verify the conversion of the oil during reaction. Some solvent system and detecting reagents commonly used for evaluation of starting material conversion during the reaction are shown below. Solvent systems and detecting reagents parameters by (%v/v/v) for TLC:

- (a) Hexane:ethyl acetate:acetic acid (90:10:1)
- (b) Isohexane:diethyl ether (80:20:1) UV light

- (c) Chloroform:petroleum ether (1:3)
- (d) Petroleum ether:diethyl ether:acetic acid (85:15:1)
- (e) Hexane:ethyl acetate:acetic acid (90:10:1) sulphuric acid:methanol



Figure 21

The results analyzed by TLC for RBO were shown in figure the light brown colour points show the presence of ester. The changes in product compositions with reaction during the transesterification of the oils and the distribution of various components in the reaction system can be clearly seen. In above figure point we see the ester present at the some level for reference (R) and for RBO which is the biodiesel confirmation point. So we can the biodiesel form is close enough to the proportion of standard biodiesel.

### Acid value

A value indicating the amount of free acid present in a substance, equal to the another number of milligrams of potassium

hydroxide needed to neutralize the free fatty acids present in one gram of fat or oil also called acid number. Figure shows acid value different oils and biodiesel. This can be calculated by the following formula

$$\text{Acid Value} = \frac{(v-b) \times \text{Normality of KOH} \times 56.1}{\text{Weight of the oil (gm)}}$$

Where, v is the titration volume in ml and b is the blank.

### Free fatty acid (FFA)

FFA% is the weight ration of FFA found in an oil sample. The weight of an oil sample divided into the weight of the FFA in that sample. To calculate FFA% from an acid value the formula is

$$\text{FFA Value} = \text{Acid value} \times 0.568$$

### Yield

The result is Biodiesel produced from vegetable oil can compete with RBO used.

$$\text{Yield \%} = \frac{(\text{Weight of biodiesel produced}) \times 100}{(\text{Weight of Oil})}$$

## Result and Discussion

### Properties of biodiesel produced and comparison with standard biodiesel and diesel

S. No.	Properties	Produced Biodiesel value	Biodiesel standard	Diesel standard
1.	Specific gravity at 15°C	0.880		.81 to 0.96
2.	Flash point °C	185		60 to 80
3.	Fire point °C	192		100 to 205
4.	Cloud point °C	6		-15 to 5
5.	Pour point °C	-2		-35 to -15
6.	Kinematic viscosity (mm <sup>2</sup> /s) at 40°C	5.30		1.3 to 4.1
7.	Yield	96.18%		

Table 2: Properties of Biodiesel produced and comparison with standard biodiesel and diesel.

### Specific gravity

The Specific gravity of produced biodiesel is 0.880 indicates its high density. A denser biodiesel has higher energy content and will

give better mileage and in increased power. Biodiesel will have a range of about .81 to 0.96. So, this property facilitates the characterization of biodiesel by measuring its specific gravity with a hydrometer and anything above 0.90 is probably vegetable oil, and anything below 0.90 is probably biodiesel.

### Flash point and fire point

The flash point of the produced biodiesel is 185°C and Fire point is 192 which is very high. This makes it a much safer fuel in storage and use than diesel. It is about three times higher than that of diesel thus making it a safe fuel from the point of view of safety and fire risk. It will consequently, ignite at a much higher temperature which will result in shorter delay period, better engine performance and reduced exhaust emissions.

### Cloud point and pour point

#### Cloud point

These test is of importance because the presence of wax can affect fuel flow, volatility, uniformity of property and usability in cold region. The cloud point of the oil is 6°C. And the pour point is -2°C. The pour point is much lower than that of diesel fuel thus limiting their used in cold regions without the use of antifreeze additives. Biodiesel with high proportion of saturated fatty acids tends to have high pour point because many saturated fatty acids are solid at room temperature.

Biodiesel does meet this specification and the viscosity can be corrected by blending it with a fuel that has a lower or higher viscosity

### Yield of the produced biodiesel

$$\text{Yield \%} = \frac{(\text{Weight of biodiesel produced}) \times 100}{(\text{Weight of Oil})}$$

Weight of the RBO used = 100 gm

Weight of the biodiesel produced = 82

Yield % = 100

$$\begin{aligned} \text{Yield \%} &= \frac{85.6 \times 100}{100} \\ &= 85.6 \end{aligned}$$

### Acid value

The acid value and FFA value are surprisingly low compared to other results [Bello and Otu, 2011] and would not require pre-

treatment with acid. The acid value for the oil was 0.06 mgKOH/g which is very much lower than the 23 mgKOH/g by (Muhammad., *et al.* 2012). High acid value can increase fuel density, change fuel colour, and result in the formation of acidic solution which can lead to increased corrosion and deterioration of fuel properties.

$$\text{Acid Value} = \frac{(v-b) \times \text{Normality of KOH} \times 56.1}{\text{Weight of the oil (gm)}}$$

AThe titration volume, v = 0.3 ml with blank,

b = 0.1 ml

Normality of KOH = 0.1N

Weight of oil used = 1gm

$$= \frac{(0.3 - 0.1) \times 0.1 \times 56.1}{1}$$

= 1.12

### Free fatty acid

The free fatty acid was 0.12% which is surprisingly very low compared to 3% threshold suggested by (Ramadhas., *et al.* 2009) that would not lead to soap formation that can inhibit biodiesel yield during transesterification. RBO does not require pretreatment before transesterification because of the low FFA content. This is a great advantage as under industrial condition, pretreatment constitute a significant part of the cost of production.

FFA can be calculated as

$$\text{FFA Value} = \text{Acid value} \times 0.568$$

= 1.12 x 0.568

= 0.637

### Conclusion

RBO has a low free fatty acid (FFA) content and can be transesterified without pretreatment with an acid and this will reduce the cost of production when produced on industrial scale. The based transesterification process convert the RBO into Biodiesel at the optimum condition of methanol to RBO molar ratio of 9:1, 2 hour reaction time, and 2wt% KOH catalyst, which gives 97.8% of biodiesel determined by TLC method. The properties of produced biodiesel such as viscosity, specific gravity, cloud point, pour point, flash point, fire point etc. are compared with ASTM and DIN standards.

The viscosity of rice bran oil reduces substantially after transesterification and becomes comparable to that of Diesel. Flash point, fire point and pour points were higher which makes it a safer fuel to handle. The cloud point is higher than the diesel which creates some problems. The various properties were found to be comparable with that of the standard biodiesel and diesel fuel. The present work shows that the produced biodiesel from the RBO by this method can be successfully used.

### Suggestion for Further Study

1. During separation of glycerol and biodiesel, care should be taken that there is no glycerol in the biodiesel layer. Because excessive glycerol cause damage to engine while using the biodiesel to run the vehicles.
2. We can use microwave heating spite of convectional heating
3. We can change different operating conditions such as temperature, catalyst amount and can see the effect on the production of biodiesel and its yield.
4. The use of inedible vegetable oils as an alternative fuel for diesel engine is accelerated by the need of edible oil as food and the reduction of biodiesel production cost.
5. Apart from that, various aspects must be examined and overcome before biodiesel can be established and continue to mature in the market.

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