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Biodiesel from neem cake – obtaining a dual recycling product – a theoratical approach

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ABSTRACT

Sustainable production is the need of the hour for a sustainable environment. To obtain a sustainable future is possible only through recycling of the recycled product .In the world where demand cannot meet with the existing requirements it is necessary to go on with the natural resources prevailing. In this case, biodiesel occupies a unique place to satisfy the expectations. Biodiesel from neem cake has an excellent efficiency to provide a good combustion to run vehicles and generators at a sufficient economy. The paper details on producing biodiesel from neem oil through fractional distillation involving both esterification and trans-esterification processes. The fuel recovered by this process is further recycled to extract esters. The unique *technique* that this paper provides is an approach to minimize the wastage and economy of the recyclically recovered fuel while using it in generators. The power thus obtained is made to use in sufficient quantities to initiate the recycling further thus enhancing the process to be a cyclic one. The practical work of the above said is being conducted in the laboratory. The prevention of solidification of fuel is also made possible through a technique which is discussed in the paper. This way the approach further insists on a complete usage of the already recovered green fuel including the unburnt fuel to mix along with the normal diesel used in automobiles. This approach also focuses on minimizing the emission effects from automobiles and generators.

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Introduction

BIODIESEL, the ecofriendly product made from vegetable and animal fats, even some times produced from used waste cooking oils from restaurants and non-edible plant oils. It takes the replacement role for the petroleum - based fuel used for the mobile transport. Biodiesel yields significantly less carbon monoxide, hydrocarbons, particulates, sulphate compared to petroleum diesel. It can yield slightly more nitrogen oxides, but research is addressing this. In this paper the bio diesel is produced from neem oil. Here the neem oil is extracted from the neem cake formed in the initial oil extraction process. The neem oil obtained contains 300 – 2500 ppm of azadirachtin. The composition of neem oil extracted contains the following substances depending upon the method of extraction. Survey suggests that almost 25 liters of neem oil can be extracted from 150 kg of neem cake. The cost of neem cake is Rs.7 per kg .India has the largest neem seed productivity in the Asian sub – continent. The composition of neem oil is given below; the neem oil contains mainly of triglyceride. Bio diesel is produced by the process of trans–esterification process by reacting triglycerides of the oil with alcohol solutions like methanol or ethanol is used in presence of the catalyst sodium hydroxide to give esters of fatty acids and glycerol. The glycerol can be again recycled for the recovery of ethanol or can be used to manufacture soap through soapanification process and the traces of water and residual methanol must be removed through the washing process. The bio diesel thus produced is separated from the glycerol and then can be used as the fuel in generators. The emission is reduced when the bio-diesel is blended with the petroleum based diesel used in automobiles. The unburnt fuel can be again removed and mixed with some other proportions like B50 instead of B20 proportion.

Methodologies and discussion

Using converted vegetable oils and animal fats as an alternative to Petrol-Diesel fuel has been around for decades. The original Diesel engine was designed to run on cheap vegetable oils. The engine was commonly demonstrated running on peanut oil. The process of converting vegetable oils into Biodiesel is called Transesterification. An alcohol and a catalyst are mixed with the oil in order to “crack” the oil into Esters and Glycerol. During this process, the catalyst allows the alcohol to substitute itself for the Glycerin, and the heavier Glycerin falls out of the mixture, leaving alkyl esters. The Glycerol is removed and what remains is the “alkyl esters of fatty acids” commonly known as Biodiesel.

Transesterification process

Animal fats and vegetable oils are basically triglycerides, containing glycerine. The catalyst and alcohol are mixed together to form Methoxide, which is mixed vigorously into the oil for a period of time. This process “breaks” the oils into esters and glycerin. The heavier glycerin, soaps and waxes sink to the bottom while the Biodiesel floats to the top where it is siphoned or decanted off and the Glycerin is purified. We can use either ethanol or methanol in our process. Ethanol is less dangerous but Methanol is much less expensive so most people use Methanol over Ethanol. We can use either sodium hydroxide (caustic soda, NaOH) or potassium hydroxide (KOH) as our catalyst. Sodium hydroxide is much easier to get and it's cheaper.

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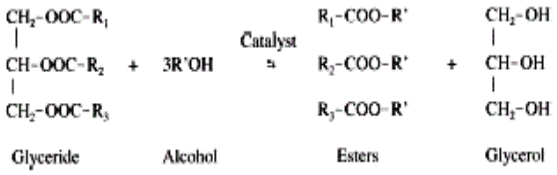

Batch reactor process

Making Biodiesel from virgin oil is the easiest but is also the most expensive. The following will describe the basic process for making a batch of Biodiesel from fresh vegetable oil. A Biodiesel Discovery Kit is available from that includes a couple graduated beakers, funnel, scale for accurately weighing the catalyst and full color instruction manual.

- Methoxide is prepared in a suitable container. This typically consists of 25% Methanol by volume of oil and 4.0 grams sodium hydroxide per liter of oil mixed together well.
- Oil is poured into reaction vessel
- Warm to approx. 50C (120F)
- Methoxide solution prepared is poured on top of the oil
- Agitate the mixture vigorously for about 30 seconds
- Stop stirring and let the mixture settle and separate overnight
- Lighter colored biodiesel on top of a layer of darker glycerine.
- Continue on to *Washing*.

To dry the oil, pour the oil into a suitable vessel and heat the oil to approximately 130F and hold it there for 15 – 20 minutes then remove the heat. The water will drop out and settle to the bottom. Pour the warm, dry oil into the reaction vessel for the rest of the reaction. A procedure called *Titration* is used to determine how much catalyst to use. This means determining the pH -- the acid-alkaline level -- of the oil. An electronic pH meter is best, but not entirely necessary. Use chemical indicator solution such as Phenolphthalein or a "high range" aquarium pH indicator

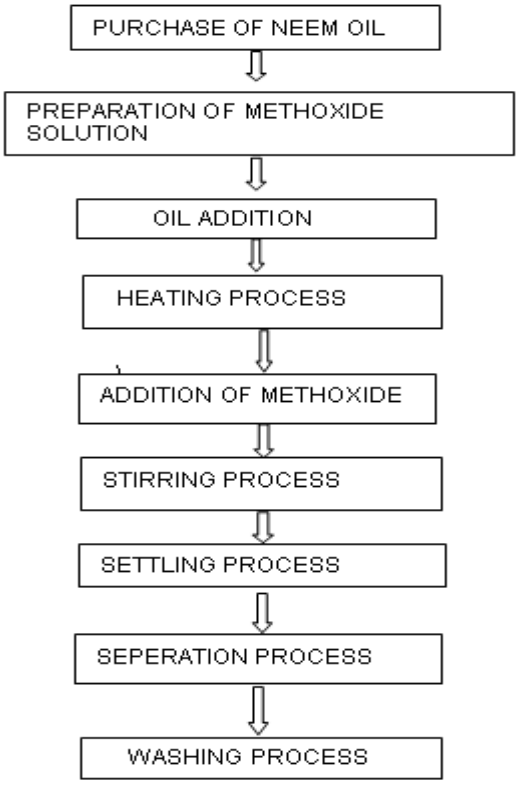

Fig.1: process flow chart

Titration process for determining catalyst

- 1gram of Sodium Hydroxide (catalyst) is dissolved in 1 litre of distilled water .This is the reagent solution.
- In a smaller container, 1 ml of oil is dissolved in 10 ml of alcohol. This is the test solution.
- Appropriate number of drops of indicator solution to the test solution

The following items are needed to perform an accurate titration.

- Two 50ml flasks
- One 5ml graduated pipette
- A 1ml dropper
- A 10ml dropper
- A mixture of NaOH and water in 0.1% concentration
- pH solution and color chart

The NaOH-H_2O mixture can be prepared by adding 1 gram of NaOH to 1000ml distilled water. The mixture will be more accurate if it is first made as a 1% solution (10grams NaOH to 1000ml water). Next, add 100mL of the 1% solution to 900ml of distilled water. This will make a 0.1% NaOH solution.

The process for titration is as follows:

- Place 10ml of Methanol in a 50ml flask
- Add 1ml of vegetable oil (mix the oil thoroughly prior to drawing 1ml)
- Mix the oil with the Methanol using the squirting action of the dropper
- Add the pH indicator solution (usually 3 drops)
- Place 15ml 0.1% NaOH (known as titrant) solution in a 50ml flask
- Draw exactly 5ml of the NaOH solution into the graduated pipette
- Add the 0.1% NaOH to the methanol/oil mixture one drop at a time. Mix the solution using a swirling action between the drops. Using the eyedropper to mix the solution may help if the oil forms drops in the bottom of the flask.
- Continue to add 0.1% NaOH until a pH of 9 (blue-green color) is reached. This may require more than 5ml. Refill the pipette and continue. Note the amount in ml that was required.

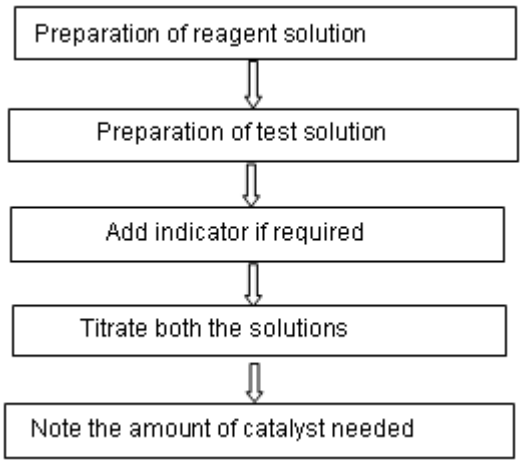

Fig.2: titration process flow chart

Draining of glycerol

After the transesterification reaction, the glycerol to settle to the bottom of the container. This happens because Glycerol is heavier then biodiesel. The settling will begin immediately, but the mixture should be left a minimum of eight hours (preferably 12) to make sure all of the Glycerol has settled out. The Glycerol volume should be approximately 20% of the original oil volume. Figure3 show the difference in viscosity and color between the

two liquids. The object is to remove only the Glycerol and stop when the biodiesel is reached. Glycerol looks very dark compared to the yellow biodiesel. The viscosity difference is large enough between the two liquids that the difference in flow from the drain can be seen.

Fig.3: separation of two liquids

Washing of biofuels

The washing of raw biodiesel fuel is the important process. The purpose is to wash out the remnants of the catalyst and other impurities. There are three main methods:

- Water wash only (a misting of water over the fuel, draining water off the bottom)
- Air bubble wash (slow bubbling of air through the fuel)
- Air/water bubble wash (with water in the bottom of the tank, bubbling air through water and then the fuel)

The quality of fuel prescribes the best method. The method used is a combination of water washing and air bubble washing. Water is misted above the fuel at a rate of 5 gallons/hour. (The rate really depends on the diameter of the tank. The water should not break the surface of the biodiesel). The amount of wash water should equal the amount of oil, and can be drained throughout the washing process.

After the water is drained, the air washing process can start. At this point, the biodiesel is usually a pale yellow color. Air should be bubbled through the biodiesel mixture for approximately 8 hours. The bubbling should be just enough to agitate the biodiesel surface. A final drain of accumulated contaminants is done immediately after the air bubble wash is finished. The fuel is now ready for use.

Results and discussion--purification process

The esters of fatty acid thus obtained from transesterification process will have some residual free fatty acids, which must be removed to meet the biodiesel standards. When the product was neutralized with NaOH–MeOH solution there were no residual free fatty acids, lower glycerides and high bio diesel content product. Hundred percent bio-diesel was obtained using 5.48 ml of 1M NaOH–MeOH solution. However, this method produced high levels of waste methanol and soap. When the fatty acids were neutralized with NaOH–H_2O solution, the method required larger amount of NaOH than the first method. However, with salt addition removal of soap from water was easily obtained. It was also found that increasing levels of NaOH could increase the amount of esters of fatty acids and decrease the amount of glycerides. To meet the quality standard of biodiesel to get 100% fatty acid esters, 3M NaOH–H_2O solution was needed.

Characteristics of the bio-disel obtained

The bio-diesel obtained will be having the following parameters like calorific value, specific gravity, viscosity, cetane number, flash point, pour point, cloud point are relatively equal to the petroleum based diesel. Hence the product is ready to use in any application involving combustion process

Table 1: properties of biodiesel

.Properties	Diesel	Neem oil
Calorific value (KJ/Kg)	43200	41905
Specific gravity	0.80	0.829
Viscosity (at 40[degrees])	3.9	6.8
Cetane number	49	50
Flash point [degree]C	56	87
Fire point [degree]C	64	93
Pour point [degree]C	-20	-16
Cloud point[degree]C	-8	-6

Applications

When the biodiesel produced is used in the home generators they provide an efficient result and also reduces the emission of air pollutants. Thus the pollution effect decreases along with increasing the life of the generators. The generators get spoiled mostly due to the residues of unburnt fuel or the ash content that make the combustion process late. By using biodiesel of neem oil along with the normal petroleum diesel as a blend this problem can be rectified. This method also favours the collection of the residual fuel and mixing it with the petroleum based diesel or with the additional biodiesel according to the composition of the residues obtained. Further the power generated using biodiesel is used in small proportion to initiate the process of producing the biodiesel from the neem oil again to maintain a cyclic production of biodiesel. Thus there is no need of utilizing the electric power for production process of bio diesel.

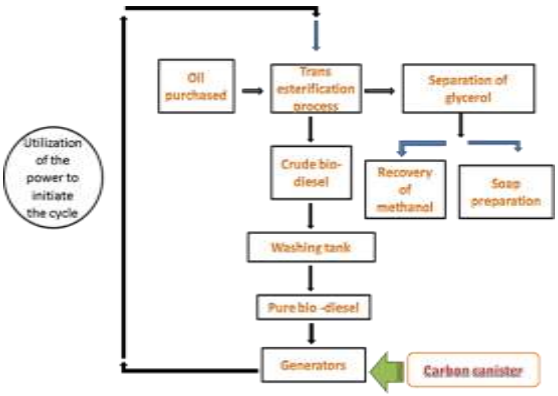

Fig.4: application of bio diesel

Approaches to avoid solidification of biodiesel while storing

Similar to the petroleum diesel, the biodiesel clouds when the weather gets cold, filled with the little crystals of wax clogs the fuel filter. When the biodiesel gets colder it gels / it sets to solid and won't flow or pour. A solution to this problem is depending on the oil used, the bio diesel made from the fresh oil has low pour point than the biodiesel produced from the used oil. Usually the biodiesel from neem oil has the pour point of -16 deg C and a cloud point of -6 deg C. when the temperature gets colder than this, the best way to add the petro-diesel of 30% to the biodiesel we use.

Another important step is to add additives to biodiesel. Additives like antigel or pour point depressant. EVA (ethylene vinyl acetate copolymers)-a compound used as a depressant for the petro-diesel can also be used. In addition a compound called "wintron"-a product of biofuel systems limited can be used.

Another important step is to use winterized biodiesel. Sometimes the biodiesel will start solidifying at 4-5 deg C, because of the presence of any saturated fats in the oil which will crystallize at higher temperatures than unsaturated oils, and separate out, clogging the filter.

To winterize the bio diesel produced,

- Heat the oil first.
- Cool it near to the freezing point
- Saturated fats will solidify and sink at the bottom.
- Use the clear oil on the top to make winter bio diesel.

Conclusions

Bio-diesel from neem oil produced can be used for various purposes depending on the properties obtained. The technique used for the optimization of the process through power management and also with the process of winterizing is done through placing CARBON CANISTERS in the fuel tank. This carbon canister will maintain the temperature of pour point to a certain extent of time. This carbon canister also reduces the evaporative loss in the fuel tank. Biodiesel is the only way to bring sustainability in the future.

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