Study of Transesterification Reaction Using Batch Reactor

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***Abstract*: Biodiesel (Fatty acid methyl ester) which is derived from triglyceride by Transesterification has attracted considerable attention during the past decade as a renewable, biodegradable and nontoxic fuel. Several processes for biodiesel fuel production have been developed, among which Transesterification using alkali as catalyst gives high level of conversion of triglycerides to their corresponding methyl ester in a short duration. This process has therefore been widely utilized for biodiesel fuel production in a number of countries. In India, non – edible oils like karanja oil and jatropha oil are available in abundance, which can be converted to biodiesel. In the present studies, biodiesel has been prepared from karanja oil. As the acid values of this oil were more than 3, hence it can be converted to biodiesel by Transesterification process. The methyl ester produced by these methods was analyzed to a certain their suitability as diesel fuels. Then the comparison of physiochemical properties was done karanja oil, karanja oil methyl ester and biodiesel. The various properties of methyl esters are found to be comparable with that of diesel fuel. However it requires further studies for considering the product as a suitable biodiesel.**

***Keywords:* Karanja oil, biodiesel and Transesterification.**

I. INTRODUCTION

In the last few years interest & activity has grown around the globe to find a substitute of fossil fuel. According to Indian scenario the demand of petroleum product like diesel is increasing day by day hence there is a need to find a solution. Under Indian condition only non-edible oil can be used as biodiesel which are produced in appreciable quantity and can be grown in large scale on non-cropped marginal lands and waste lands. Non- edible oils like jatropha, karanja and mahua contain 30% or more oil in their seed, fruit or nut. India has more than 300 species of trees. Which is produce oil bearing seeds. Milletia pinnata is a species of tree in the pea family, fabaceae, native in tropical & temperate asia including parts of India, China, Japan, Malaysia, Australia & Pacific islands. Pongamia pinnata is one of the few nitrogen fixing trees (NFTS) to produce seeds containing 30 - 40 % oil. It is often planted as an ornamental and shade tree but now – a – days it is considerd as alternative source for biodiesel[1].

Physical properties of crude karanja oil

Table 1
Physical properties of crude karanja oil

Property	*Unit*	*Value*
Color	*-*	*Yellowish red*
Odor	*-*	*Characteristic odor*
Density	*gm/cc*	*0.924*
Viscosity	*mm^2/sec*	*40.2*
Acid value	*Mg/KOH*	*5.40*
Iodine value	*-*	*87*
Saponification value	*-*	*184*
Calorific value	*Kcal/kg*	*8742*
Specific gravity	*-*	*0.925*
Unsaponification matter	*-*	*29*
Flash point	*ºC*	*225*
Fire point	*ºC*	*230*
Cloud point	*ºC*	*3.5*
Pour point	*ºC*	*-3*
Boiling point	*ºC*	*316*

Cetane number	***-***	***42***
Copper strip corrosion	***-***	***No corrosion observed***
Ash content	***In %***	***0.07***

II. BIODIESEL

Biodiesel is a renewable and clean burning combustible fuel for diesel engines. It is nontoxic, biodegradable, and virtually free from aromatics and sulfur contents. This is because its primary components are domestic renewable resources such as vegetable oil and animal fats consisting of long – chain alkyl (methyl, ethyl, or propyl) esters. A catalyst such as sodium hydroxide is also necessary in order for the biodiesel to be considered a finished product, and is added with the new compounds to produce biodiesel[2].

Biodiesel as fuel has some advantages and disadvantages.

Advantages:-

- it is biodegradable, non – toxic, environmentally friendly, and renewable resource.
- It can be reduce the amount of greenhouse gas emissions and it emits less CO_2, SO_2, CO HC and PM in comparison to conventional diesel.
- Biodiesel is more cost efficient because it is produced locally.
- Biodiesel has a high flash point, which makes it a safer fuel.
- It does not need engine modification up to B_{20}.

Disadvantages:-

- It emits higher NO_x emissions in comparison with conventional diesel.
- Its higher pour and cloud points create problems in cold weather.
- It has a corrosive nature against copper and brass.
- It has a higher viscosity in comparison with diesel fuel.
- It has low volatility.

III. METHDOLOGY

Different methodologies used for production biodiesel are:-

Direct use/ blending

Vegetable oil can be directly used as diesel fuel without any change to engine. The very first engine (by Rudolf diesel) was tested using vegetable oil as fuel. The primary concern with vegetable oil as fuel is its high viscosity (atomization of vegetable oil is difficult), which lead to problems in the long run.

Pyrolysis

Pyrolysis means conversion of one substance to another by application of heat. Catalysts are used to speed up the process. Products can be obtained from the same material depending on different path of reaction and this makes pyrolytic chemistry difficult. Pyrolysis of vegetable oil gives different lower hydrocarbons that can be used as fuel[3].

Micro – emulsions

Micro emulsion is defined as colloidal dispersion of fluid microstructures (1 – 150nm) in solvent forming two immiscible phases. The common solvents used are methanol and ethanol. Micro – emulsions is the probable solution to high viscosity of vegetable oil. Their atomization is relatively easy because of lower viscosity[3].

Transesterification

Transesterification is a kind of organic reaction where alcohol group in ester is substituted. It can also be reaction of vegetable oil/fat with alcohol to give ester and glycerol. The applicability of Transesterification is not restricted to laboratory. Several relevant industrial processes use this reaction to product different types of compounds. An example is the production PET (polyethylene terephthalate), which involves a step where dimethylterephthlate is transesterified with ethylene glycol in the presence of zinc acetate as catalyst. Furthermore, large number of acrylic acid derivatives are produced by Transesterification of methyl acrylate with different alcohols, in the presence of acid catalysts.

IV. TRANSESTERIFICATION REACTION

Transesterification is the well established chemical reaction of vegetable oils and animal fats with an alcohol to form fatty acid alkyl esters and glycerol. Neat vegetable oils and animal fats cannot be used directly in diesel engines because of their high viscosity and low volatility, and the major objectives of Transesterification are to overcome these problems.

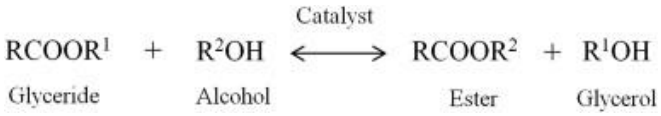

Fig. 1. General equation of Transesterification

A 3:1 M ratio of alcohol to oil is required to complete the reaction; however, since the reaction is reversible, the excess alcohol is practically used to shift the equilibrium to the product side and raise the product yield.

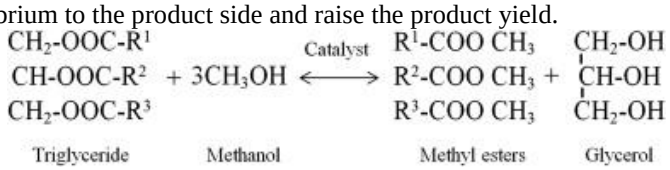

Fig. 2. General equation for transesterification of triglyceride in the presence of methanol

Methanol and ethanol are the most common alcohols used in Transesterification especially methanol due to its physical and chemical advantages and its low cost. In addition a catalyst is normally used to accelerate the reaction and improve the conversion yield. Base, acid, and enzyme are three types of catalyst which are usually used in the Transesterification reaction. This reaction is represented by the general equation. If methanol is used in this process it is called methanolysis. Methanolysis of triglyceride is shown in equation[4].

The Transesterification reaction consists of a sequence of three reversible consecutive reactions. In the first step, triglycerides are converted to diglyceride; in the second , diglycerides are converted to monoglycerides. In the last step, monoglycerides are converted to glycerol. Three esters are obtained from one triglyceride molecule, one ester molecule for each glyceride at each step. The basic mechanism is show in equation[5].

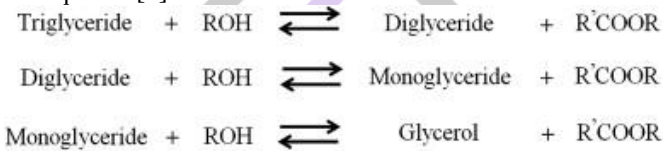

Fig. 3. The three reversible and consecutive reactions in the transesterification of triglyceride.

V. EXPERIMENTAL SETUP AND STEPS

Transesterification was carried out in a batch type reactor. This reactor consists of following components
Magnetic stirrer with heater arrangement.
Two necked round bottomed flask.
Temperature controller.
Stirrer controller.

Two necked round bottomed glass beaker is used to collect sample of mixture (oil + Methanol + catalyst). Magnetic stirrer and heater provide the stirring and heating effect simultaneously. Temperature controller is used to control the desired heating effect. Stirrer controller is used to control the stirring effect.

A round bottom flask of 500 ml is used for the present analysis. The karanja oil in the flask was heated on a hot plate having magnetic stirrer arrangement. The mixture was stirred at the same speed for all test runs. Initially 100 ml karanja oil is heated to 57^{o}C. Then the methanol 13% w/w of oil sample and 0.5 % H_2SO_4 are mixed. The mixture is transferred to a reactor. The temperature maintained for the whole esterification process is about 57^{o}C. And heat up to 1 hours and switch off the apparatus and wait until the mixture gets cooled. The resultant mixture is taken into the separating funnel containing acidic oil and impurities with glycerol. After 1 hours impurities settles down at the bottom of acidic oil. Impurities with small amount of glycerol are separated by opening the value of the separating funnel.

Fig.:- Experiment Setup

Initially obtained acidic oil from first step esterification reaction is heated to 57^{o}C. Then the methanol and NaOH are mixed. The mixture is transferred to a reactor. The temperature maintained for the whole second step Transesterification process is about 60^{o}C. The mixture was stirred at the same speed for all test runs. And heat up to different time interval and switch off the

apparatus and wait until the mixture gets cooled. The resultant mixture is taken into the separating funnel containing biodiesel and glycerol. After 30 to 40 minutes glycerol settles down at the bottom of biodiesel. The glycerol is separated by opening the value of the separating funnel.

VI. PROCESS VARIABLES

The most important variables that influence the Transesterification reaction are

Reaction temperature

The literature has revealed that the rate of reaction is strongly influenced by the reaction temperature. However, the reaction is conducted to the boiling point of methanol (60 - 70ºC) at atmospheric pressure for a given time. Such mild reaction conditions require the removal of free fatty acids from the oil by refining or preesterification. Therefore, degummed and deacidified oil is used as feedstock. Pre-treatment is not required if the reaction is carried out under high pressure and high temperature, where simultaneous esterification take place with maximum yield obtained at temperatures ranging from 60 to 80ºC at a molar ratio of 6:1[6].

Ratio of Alcohol to oil

Another important variable is the molar ratio of alcohol to vegetable oil. As indicated earlier, the Transesterification reaction requires 3 mol of alcohol per mole of triglyceride to give 3 mol of fatty esters and 1 mol of glycerol. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products from the reaction mixture. The second option is usually preferred for the reaction to proceed to completion. The reaction rate was found to be highest when 100 % excess methanol was used. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98 %(w/w)[6].

Catalysts

Alkali metal alkoxides are found to be more effective Transesterification catalysts compared to acidic catalysts. Sodium alkoxides are the most efficient catalysts, although KOH and NaOH can also be used. Transesterification occurs in the presence of both alkaline and acidic catalysts. As they are less corrosive to industrial equipment, alkaline catalysts are preferred in industrial processes. A concentration in the range of 0.5 – 1%(w/v) has been found to yield 94 – 99% conversion to vegetable oil esters, and further increase in catalyst concentration does not affect the conversion but adds to extra cost, as the catalyst to be removed from the reaction mixture after completion of the reaction.

Mixing intensity

It has been observed that during the Transesterification reaction, the reactants initially form a two – phase liquid system. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on the kinetics of the Transesterification process forms the basis for process scale - up and design.

Purity of reactants

Impurities in the oil affect the conversion level considerably. It is reported that about 65 – 84 % conversion into esters using crude vegetable oils has been obtained as compared to 94 – 97% yields refined oil under the same reaction conditions, the free fatty acids in the crude oils have been found to interfere with catalyst. This problem can be solved if the reaction is carried out under high temperature and pressure conditions[7].

VII. CONCLUSION

In the present work the properties of karanja oil were found out and compared with diesel. From the comparison it is concluded that the karanja oil is suitable for biodiesel production. The production of biodiesel from karanja oil has been carried out using step transesterification. The maximum yield of biodiesel was obtained from the Transesterification of 9:1 molar ratio of methanol/oil in the presence of H_2SO_4 in the first step process after that acidic oil with 9 mole of methanol in the presence of NaOH as catalyst in the second step process at 60^{o}C reaction temperature and 2 hr reaction time to each transesterification process.

VIII. ACKNOWLEDGMENT

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