



PRODUCTION AND OPTIMIZATION OF BIODIESEL FROM WASTE VEGETABLE OIL

A.Ravindar¹, P M Sameera², P. Raja Rao³

^{1,2,3}Division of Biochemical Engineering and BioTechnology

University College of Technology, Osmania University, Hyderabad (India)

S N V Pharma MahaVidyalaya, Taranaka, Secunderabad (India)

ABSTRACT

Biodiesel is an attractive alternative to fossil fuel. Its portability, availability, renewability, higher combustion efficiency, lower sulfur and aromatic content make it an ideal fuel for use in transportation and in industry. Biodiesel can be produced from animal fat and vegetable oils obtained from variety of plants. The present work exploits the biodiesel production from waste vegetable oils (fried oils) and esterification process study was carried out for development of the same. The feed-stocks used are waste cooking oils. Extensive experimentation was carried out at bench scale. Transesterification reaction is carried out at 30, 40, 50, and 60°C with 1.5% of KOH as catalyst. Samples are taken at different reaction times of 0, 30, 60, 90 and 120 min. The organic layers are then analyzed by thin layer chromatography technique and glycerol is analyzed using sodium periodate oxidation method. It is observed that a maximum of 90% of conversion is obtained with waste vegetable oil at 60°C temperature. These laboratory based solutions can then be applied to overcome the technical barriers at commercial level.

Keywords: Waste vegetable oil, Biodiesel production, Transesterification

I. INTRODUCTION

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. Finite fossil fuel reserves, political, economic, health and environmental (ozone depletion, global warming) issues and concerns have promoted biodiesel as an alternative renewable and eco-friendly fuel. Biodiesel has shown its ability to meet the energy demand of the world in the transportation, agriculture, commercial and industrial sectors. The annual world consumption of diesel is approximately 934 million tons. As a green renewable and potentially unlimited, biodiesel has recently come out as the superlative alternative fuel which can be used in compression ignition engines with minor or no modifications. The use of biofuels in place of fossil fuels would slow the progression of global warming by reducing sulfur and carbon oxides and hydrocarbon emissions. Because of economic benefits and more power output, biodiesel is often blended with diesel fuel in ratios of 2, 5 and 20%. Using a mixture containing 20% biodiesel reduces carbon dioxide net emissions by 15.66% while using pure biodiesel makes the net emission of carbon dioxide zero variety of cheap raw materials, and high yields



Methods for production of Biodiesel: Biodiesel production was carried by using different processes, direct use and blending, micro-emulsions, thermal cracking, and transesterification. Four main processes have been investigated for production of biodiesel. They are a) Direct use and blending, b) Pyrolysis, c) Micro-emulsification and d) Transesterification.

Transesterification has been demonstrated as the simplest and most efficient route for biodiesel production in large quantities. So, transesterification has become popular and the production method of choice. Transesterification can be carried out by using a catalyst or enzyme or by using supercritical alcohol without catalyst.

Methodology: In this study, Waste Cooking Oil (WCO) was obtained from local restaurants around the university campus. It was used as the raw material for the biodiesel production. Alkaline catalyst, potassium hydroxide (KOH) was used in the transesterification process to reduce the free fatty acid, FFA, and carrying out the transesterification process. The process variables are Reaction temperature, Ratio of alcohol to oil, Catalyst type and concentration, Mixing intensity and Purity of reactants.

II. MATERIALS AND METHODS

The esterified Waste vegetable oil are being used. Initially the crude quality of these oils are collected from the Hotels and mirchi vendors on the roads. Then these oils are refined and characterized for the free fatty acid content, the saponification value, the iodine value, and the peroxide value according to the AOCS official methods. The FFA content in the reaction mixture was determined by titrimetric analysis.

Transesterification is the process of exchanging the organic group R" of an ester with the organic group of an alcohol. Transesterification is basically sequential reaction. The TGs are first reduced to DGs. The DGs are subsequently reduced to MGs. The MGs are finally reduced to fatty acid ester. The production of biodiesel is based on oil and methanol. It is clear that 1 mol triglyceride reacts with 3 mol methanol to produce 3 mol methyl ester and 1 mol glycerol.

Further investigation indicates that diglyceride and monoglyceride are detected as intermediates during the transesterification reaction catalyzed by KOH and NaOH.

The overall reaction can be divided into three consecutive reversible reactions (i) a triglyceride molecule firstly reacts with methanol to produce a methyl ester molecule and a diglyceride (ii) the diglyceride produced then reacts with a methanol molecule to produce a monoglyceride and a methyl ester and (iii) the monoglyceride further reacts with one methanol to produce methyl ester and glycerol. Each conversion step yields one FFAE molecule, giving a total of three FFAEs per triglyceride molecule as described by the following equations:

1. Triglyceride (TG) + $R^+OH \rightleftharpoons$ Diglyceride (DG) + R^+COOR_1
2. Diglyceride (DG) + $R^+OH \rightleftharpoons$ Monoglyceride(MG) + R^+COOR_2
3. Monoglyceride(MG) + $R^+OH \rightleftharpoons$ Glycerol(GL) + R^+COOR_3



The use of an alcohol results in the desired FAAEs and a glycerol byproduct which can be utilized in other industries. Feedstock with higher concentration of Free Fatty Acids (FFA's) may pose a problem of soap formation and lead to under reacted material, thus affecting yield. Thus, there is a need to pretreat FFA's before the transesterification using one of the following methods: (a) acid esterification (b) ion exchange resins and (c) extraction with alcohol. Allowable FFA's content in the feedstock is lower than 2.5% wt and the pretreatment step becomes necessary before the transesterification process when the FFA content is higher than 2.5% wt.

Feed stocks for biodiesel production:-The esterified Waste vegetable oil are being used. Initially the crude quality of these oils are collected from the Hotels and mirchi vendors on the roads. Then these oils are refined and characterized for the free fatty acid content, the saponification value, the iodine value, and the peroxide value according to the AOCS official methods. The FFA content in the reaction mixture was determined by titrimetric analysis.



Fig 1: Waste vegetable oil Fig 2 Experimental set up

By considering four temperatures (30°C , 40°C , 50°C , 60°C), three molar concentrations (1:3, 1:6, 1:9). Catalyst (KOH) 12 runs are performed. Table 3.1 shows all the possible experiments in the transesterification optimized. Kinetic runs of transesterification are carried out for two different oils over using potassium hydroxide as the catalyst and Sodium hydroxide as catalyst for 2hrs at atmospheric pressure with different temperatures: 30, 40, 50, 60°C at different molar ratios of methanol to oil. Transesterification reaction is carried out in 1 liter, 4 necked jacketed glass reactor equipped with a condenser, overhead stirrer, which has a provision for temperature measurement and sample withdrawal. The temperature in the reactor was maintained by circulating hot fluid through the jacket. The condenser temperature is maintained by circulating chilled water. The temperature of the condenser is maintain between $8\text{-}10^{\circ}\text{C}$ to minimize the methanol loss. The rpm of the stirrer is maintained at 300rpm.

Kinetics:The study of kinetics of transesterification reaction is carried out by collecting the concentration versus time data at different temperatures (30 , 40 , 50 and 60°C) with different molar ratios. During the reaction the samples are taken at the following reaction times: 0, 30, 60, 90, 120 min. The organic layers are then analysed by thin layer chromatography technique and glycerol is analysed using sodium periodate oxidation method. Both the layers are separated, washed and analyzed.

Product Separation:The separation process is based on the facts that fatty acid alcohol esters and glycerol are sparingly mutually soluble, and that there is a significant difference in density between the methyl ester and glycerol phases. The presence of methanol in one or both phases affects the solubility of ester in glycerol and glycerol in ester (alcohols can act as dispersant). Separating funnel was used to separate the products from



transesterification process by gravity settling. Products separation was carried out by providing a settling time of 1 hour and the total product was separated into two layers, glycerol layer and methyl ester layer (BD layer).

Glycerol layer: Glycerol formed in the reaction, catalyst and unreacted methanol form a layer at the bottom of separating funnel, since catalyst density is high and maximum of catalyst comes into glycerol layer. There is a chance of methyl ester in glycerol layer because of the mutual solubility of methyl ester in methanol and TG, partial glycerides (DG, MG) in minute quantities.

Methyl ester layer : Methyl ester, unreacted TG, DG, and MG come under methyl ester layer which was the top layer in separating funnel during separation. Methanol, catalyst also present in small quantities.

Water washing for biodiesel layer: Biodiesel layer was washed to remove soap formation, FFA, methanol and other contaminants. Water and biodiesel were taken at equal ratios. Slightly shake the funnel to mix water with biodiesel if we shake rigorously then DG and MG present in the biodiesel layer will form emulsion with water. After settling for 30 mins the water effluent layer was separated. Then the pH range was checked for that layer. Washing was repeated until biodiesel comes to neutral in nature. Methanol is sparingly soluble in biodiesel layer, while washing it comes in to water effluents. Now we have pure biodiesel but with little moisture content, to remove moisture drying is carried out. After drying we can get finished product. Water washed BD layer was dried to remove water. Drying was done in a rota vapor unit by applying vacuum for 1h and was stopped by observing that there was no formation of droplets in the condenser. Glycerol layer will have only 50 % glycerol in it, remaining is methanol, FFA and catalyst. For that biodiesel water effluents can be added to recover the glycerol in the biodiesel layer also. Since glycerol is soluble in water, glycerol present in the biodiesel will come in to water effluent.

Products Analysis: Purified glycerol and biodiesel layers were analyzed to obtain the quantities of glycerol and methyl ester formed during the transesterification process. Glycerol was estimated using the AOCS official method (sodium periodate oxidation method), and thin layer chromatography (TLC) was used to analyze biodiesel product.

Glycerol(Sodium periodate oxidation): This method determines glycerol and other polyalcohols containing three or more adjacent hydroxyl groups. The glycerol reacts with the sodium periodate in an acid solution, forming aldehydes and formic acid. The latter is a measure of the glycerol in the sample. The sodium periodate method replaces the acetic method and the dichromate method because it has been found to be more accurate and more specific for the determination of glycerol as well as being simpler and more rapid.

TLC Analysis: A TLC plate is a sheet of glass, metal, or plastic which is coated with a thin layer of a solid adsorbent (usually silica or alumina). A small amount of the mixture to be analyzed is spotted near the bottom of this plate. The TLC plate is then placed in a shallow pool of a solvent in a developing chamber so that only the very bottom of the plate is in the liquid. This liquid, or the eluent, is the mobile phase, and it slowly rises up the TLC plate by capillary action. As the solvent moves past the spot that was applied, equilibrium is established for each component of the mixture between the molecules of that component which are adsorbed on the solid and the molecules which are in solution.

Measuring Rf values : When the solvent front gets close to the top of the plate, the plate is removed from the beaker and the position of the solvent is marked with another line before it has a chance to evaporate. If one could repeat this experiment under exactly the



same conditions, then the R_f values for each component would always be the same. Retention factor is proportional to conversion and in the present work retention factor of methyl ester component was taken as the conversion.

III. RESULTS AND DISCUSSION

Transesterification of Esterified Oil: Esterified waste vegetable oil are used in the present work, and it contains FFA less than 1% initially. And the esterified product was processed in transesterification reaction with KOH catalyst. Methanol was used in the reactions, hence the product formed is methyl ester. Effects of following variables on the conversion of reactants (FFA/TG) to methyl ester during transesterification reactions were studied.

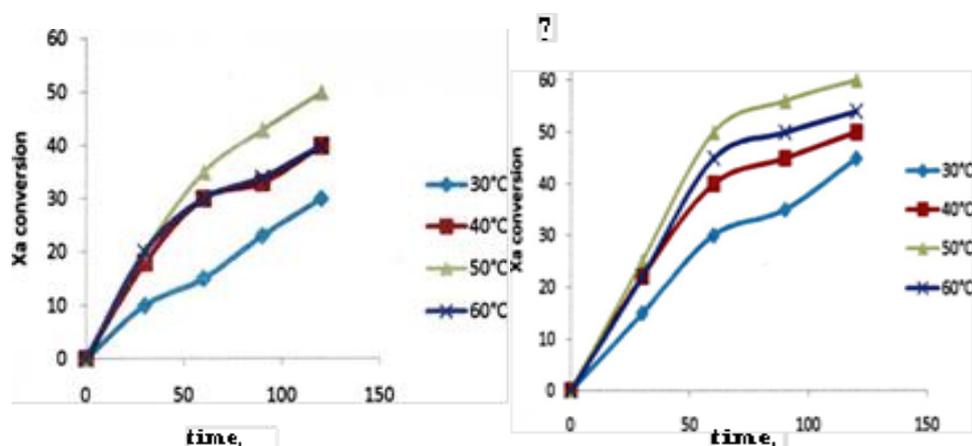


Fig3 : Effect of Temperature with time.

Effect of temperature : In order to evaluate the kinetic parameters of the process, the reaction temperature is varied i.e. (30, 40, 50, 60°C) and experiments were conducted for 1 hr (with KOH as catalyst) at a stirrer speed of 300rpm and optimizing other parameter such as **Catalyst-** KOH (1.5 wt%), **Oil:** Alcohol to oil molar ratio – 1:3, 1:6, 1:9 **Reaction time-** 60 min, 120 min

Transesterification reaction can be written as $TG + 3\text{methanol} \leftrightarrow 3\text{methyl ester} + \text{glycerol}$

Esterified product of waste vegetable oil (0.998% FFA) was processed in transesterification reaction and the conversion of transesterification reaction was measured from TLC. The value of retention factor of methyl ester was taken as conversion since retention factor is directly proportional to conversion. From this data it is observed that 50% of total conversion is achieved within 20 minutes. And conversion increased with increase in reaction time up to 40 minutes after that the increase in conversion is very low. A maximum conversion of 89% is obtained at 60°C temperature, 1.5 wt% catalyst, and 1:6 molar ratio of oil is to methanol. From the data it is observed that a maximum of 90% of conversion is obtained with waste vegetable oil (non edible oil) at 60°C temperature.

Effect of temperature with catalyst: Experiments were conducted with different temperatures (30°C, 40°C, 50°C and 60°C) at 1:3 oil to methanol molar ratio, catalyst concentration of 1.5% for 2 hrs and with a mixing intensity of 300rpm. The effect of temperature on conversion of FFA is recorded as a function of time and the 1:3 oil to methanol molar ratio, KOH catalyst for waste oil data was shown in figure.

Effect of oil to methanol molar ratios: Molar ratio of oil to methanol is one of the important factors effecting the formation of methyl ester. The stoichiometry of the reaction shows that one mole of FFA requires one mole of methanol to form one mole of methyl ester.

Product Purification

Biodiesel layer was washed to remove soap formation, FFA, methanol and other contaminants. Water and biodiesel have taken at equal ratios, slightly shaken the funnel to mix water with biodiesel. If shaken rigorously then DG and MG present in the biodiesel layer will form emulsion with water. After settling for 30 mins the water effluent layer was separated. Then the pH range was checked for that layer. Washing was repeated until biodiesel comes to neutral in nature. Methanol is sparingly soluble in biodiesel layer, while washing it comes in to water effluents.



Fig4: Observations (WVO to Bio Diesel)

IV. CONCLUSIONS

Biodiesel has been processed using esterified waste vegetable oil. The study was therefore conducted using waste vegetable oil. The detailed parametric study of the base catalysed transesterification reactions were carried out experimentally to study the effect of temperature and molar ratio of oil to methanol. Transesterification reaction is carried out at 30, 40, 50, and 60°C with 1.5% of KOH catalyst. Also the reactions were carried out at different molar ratios of 1:3, 1:6 and 1:9. The results indicated that there is a strong effect of temperature and oil to methanol molar ratios on the reaction rate.

Maximum conversion of 89% was obtained at 60°C with base catalyst and a maximum conversion of 60% was obtained with enzyme catalyst at 50°C. It is also found that 1:3 is optimum molar ratio for enzyme catalysed reaction and 1:6 for base catalysed reactions. Investigations were made in the present study to establish the kinetics of transesterification reaction. The kinetic curves of the transesterification process indicated that under the conditions employed, the rate of reaction was the highest during the initial stage of the reaction. The reaction rate increased with the increase of temperature. The experimental results indicated increasing the temperature increased the equilibrium conversions. The activation energies for the three reversible reactions involved in the reaction were calculated from the Arrhenius equation and were in the range of 8-20000 J/mol for waste oil transesterification reaction through base catalyst.

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