

Biodiesel production from neem oil using two step transesterification

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ABSTRACT

Currently, most of the biodiesel is produced from the edible/refined type oil using methanol and alkaline catalyst. However, large amount of non-edible type oils and fats are available in our country. In this study, crude neem oil is used as alternative fuel for biodiesel production. The difficulty with alkaline transesterification of these oils have contained large amounts of free fatty acids (FFA). These free fatty acids quickly react with the alkaline catalyst to produce soaps that inhibit the separation of the ester and glycerin. A two-step transesterification process is developed to convert the high FFA oils to its mono-esters. Using 100 ml of oil, the optimum combination of parameters for pretreatment were found to be .45 v/v methanol-oil-ratio, 0.5% v/w H₂SO₄ acid catalyst, 50°C and 45 min reaction time. After pretreatment of neem oil, transesterification reaction was carried out with 0.3:1 methanol-to-oil ratio, 1% KOH as alkaline catalyst, 1hr reaction time and 55°C reaction temperature to produce the fatty acid methyl ester. This two step process gave maximum average yield of 90±2%.

Keywords: Biodiesel, free fatty acid, Neem oil, pretreatment, transesterification.

1. INTRODUCTION

The tremendous increase in number of automobiles in recent years have resulted in greater demand of petroleum products. The depletion of crude oil reserves are estimated for few decades, therefore, effort are on way to research now alternatives to diesel [1]. Due to increasing price of petroleum product and environment concern about emission from the car exhaust, the biodiesel has become an area of high concern [2]. The biodiesel is an alternative feedstock for depletion of fossil fuel. It has derived from renewable resources such as vegetable oil, which could either be fresh or waste vegetable oil are find useful in Europe, America and Asia as a feedstock in production of biodiesel, as a consequently, biodiesel derived from a wide variety of sources can be used as a direct substitute for petro-diesel fuels [3]. They are several non-edible oil seed such as thevetia (thevetia peruviana), karanja (pongomia pinnate), jatropha (jatropha curca), neem (azadirachta india) etc. Among these, azadirachta

indica seed which contain 25%-45% oil on dry matter basis is non edible oil that can be use in biodiesel production [3]. Neem tree is evergreen tree growing in almost every state of India. It is native to Indian subcontinent, South East Asian countries and it grows all over India. It grows in all kinds of soil and in drier areas [1].

The oil contain three bitter compound that can be extracted from it which are nimbin, nimbinin and nimbidin which are mostly responsible for it medicinal value, it can also be use in cosmetics preparation and act as an effective mosquito repellent. Neem oil have high free fatty acid value which is accompanied with moisture content and some other impurities, this two have prime effect on the trans-esterification of glycerides with alcohol using catalyst. However most non-edible oil have high free fatty acid content which it leads to high production cost through trans- esterification, an FFA content more than 2% will form soap and the separation of the product will be very difficult, it produces low yield fatty acids methyl esters [3].

This present investigation is intended to consider aspects related to the feasibility of the production of biodiesel from neem oil. The variables affecting the yield and characteristics of the biodiesel made were studied. The obtained results were analyzed and compared with conventional diesel fuels.

2. MATERIALS AND METHODOLOGY

2.1 Materials

Crude neem oil was purchased from local market . The magnetic stirrer with hot pte was purchased from Taleco Chemicals Pvt. Ltd at Tirunelveli. Chemicals are used in transesterification process like Pottassium hydroxide pellet (88% purity) ,Methanol (99% purity), Concentrated sulphuric acid and Sodium sulphate. All the chemicals are purchased from Himedia and Nice chemicals Pvt Ltd and its analytical reagent grade.

2.2 Equipment

A round bottom conical flask is used as reactor for these experimental purposes. A magnetic stirrer with hot plate arrangement is used for heating the mixture in the flask. The mixture is stirred at the

same speed for all test runs. The temperature range of 40–60°C is maintained during this experiment and its monitored by thermometer. The separating funnel is used to separate the methanol-water mixture after acid pretreatment and the glycerol after transesterification. Four set of trail runs are carried out for each combination of parameter.

2.3 Methodology

The aim of this study is to improve the process for producing biodiesel from crude neem oil. There are three process such as oil filtration, acid esterification and alkaline transesterification

2.3.1 Oil filtration

Neem oil have higher moisture content and some other impurities. So, in order to remove the moisture and impurities from the neem oil it should be refined. The purification can be done by boiling oil with about 20% of water. The boiling should

2.2.3 Alkaline transesterification

After acid pretreatment the esterified oil is taken in flask and heated upto 60°C. 1% of KOH is dissolved in 30% (6:1 M) methanol. The dissolved solution is poured into flask. The mixture is heated and stirred for 1hr. On completion of reaction, the mixture is poured into separating funnel over 12 hr. The glycerol and impurities are settled in lower layer and its discarded. The impure biodiesel remain in upper layer. It contains some trace of catalyst, glycerol and methanol. The washing process can be done by the 3/4 th of hot distilled water added with methyl ester and gently stirred. The upper layer is pure biodiesel and lower layer is drawn off.

3. RESULTS AND DISCUSSION

3.1. Acid esterification

3.1.1 Effect of methanol-to-oil ratio

Two important parameter significantly affected the acid value. These are sulphuric acid concentration and methanol quantities. Molar ratio is defined as the ratio of number of moles of alcohol to number of moles of vegetable oil. Theoretically, transesterification reaction requires 3 moles of alcohol for each mole of oil. However, in practically molar ratio should be higher than stoichiometric ratio. By varying methanol proportion such as 0.35:1, 0.40:1, 0.50:1, 0.55:1 methanol-to-oil ratio, among these 0.45:1 gave higher yield. The last two 0.50:1, 0.55:1 have only slight variation. In economic view 0.45:1 M is selected for reaction condition. The effect of methanol variation is shown in fig.1. From the figure conversion efficiency is slightly increase upto 0.45:1 methanol-to-oil ratio. After that conversion efficiency is decreased with increase in methanol-to oil ratio because it leads to increasing the acid value. It has been determined that in

continue until no bubbles of water vapor anymore. After one hours the oil then becomes clear. This refined neem oil is taken as raw material for transesterification process.

2.3.2 Acid esterification

100 ml of refined neem oil is poured into the flask and heated upto 60°C. The 45% v/v methanol is added with the preheated neem oil and stirred for a few minutes. 0.5% of sulphuric acid is added with the mixture. Heating and stirring should continue about 45min at atmospheric pressure. After completion of this reaction, the mixture is poured into a separating funnel for separating the excess alcohol, impurities and sulphuric acid. The excess alcohol, sulphuric acid and impurities moves to the top layer and its discarded. The lower layer is separated for further processing of transesterified into methyl ester. This process reduces the acid value of refined neem oil to less than 1% of FFA.

viscosity reduction increases with increase in methanol-to-oil ratio

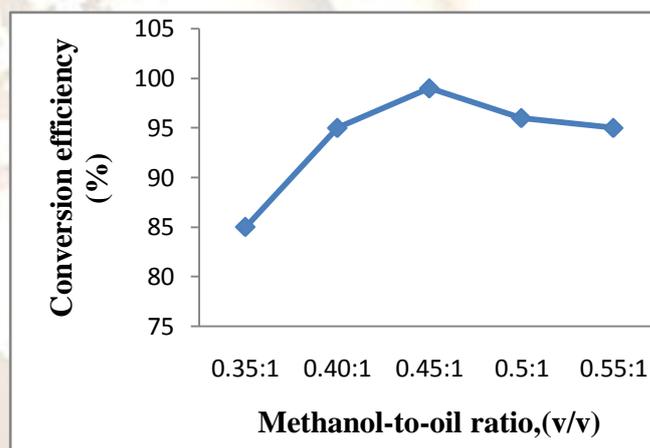


Fig.1. Effect of methanol on conversion efficiency

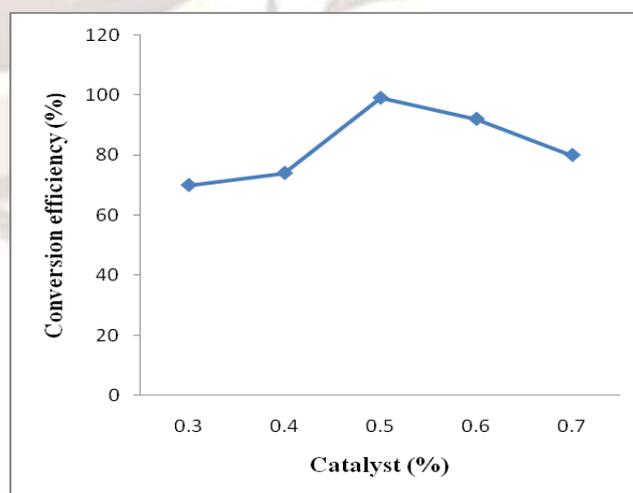


Fig.2 Effect of acid catalyst amount on conversion efficiency

3.1.2 Effect of acid catalyst amount

Amount of acid catalyst variation is affect the conversion efficiency. By varying sulphuric acid propotion such as .25,.5,.75 and 1% v/v. Maximum conversion efficiency is achieved in 0.5 % v/v H_2SO_4 . Effect of acid catalyst variation is shown in fig. 2. From the figure more than 0.5% v/v H_2SO_4 , the product color is become black. Lower amount of sulphuric acid addition affects the final product yield.

3.1.3 Effect of reaction temperature

The conversion efficiency is very low at room temperature even after 2 hr reaction .If increase in temperature the conversion takes place at higher rate. The optimum temperature is achieved at 50°C. At high reaction temperature, the methanol is lost because melting point of methanol is 65°C. Above 50°C product color become black.

3.2. Alkaline transesterification

3.2.1 Effect of methanol-to-oil ratio

Molar ratio is very important factor for transesterificatin reaction. Theoretically, transesterification reaction requires 3 moles of alcohol for each mole of oil. However, in practically molar ratio should be higher than stoichiometric ratio. The higher molar ratio is required for complete the reaction at higher rate. In lower molar ratio, it takes longer duration for complete the reaction. The effect of methano-to-oil ratio on conversion efficiency is shown in fig. 3. It has been seen that yield is slightly increase upto 0.3:1 methanol-to-oil ratio. The maximum methyl ester yield is achieved at 0.30:1M. With further increase in methanol-to oil ratio the conversion efficiency is decreases.

3.2.2 Effect of alkaline catalyst

The amount of catalyst variation is affect the conversion efficiency. The catalyst propotion is varied from 0.5- 2% KOH . The effect of catalyst variation on conversion efficiency is shown in fig.4 . From the figure yield is slightly increased upto 1% KOH and after that yield is decreased due to reverse reaction is take place (emulsion formation). The maximum yield is achieved of 88% at 1% KOH.

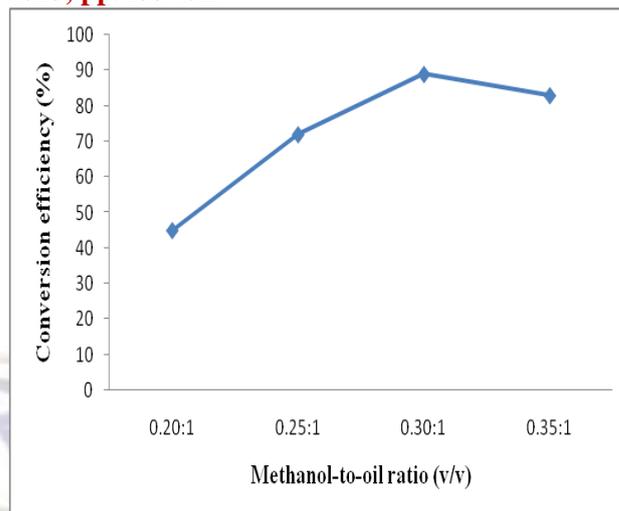


Fig.3. Effect of methanol on conversion efficiency

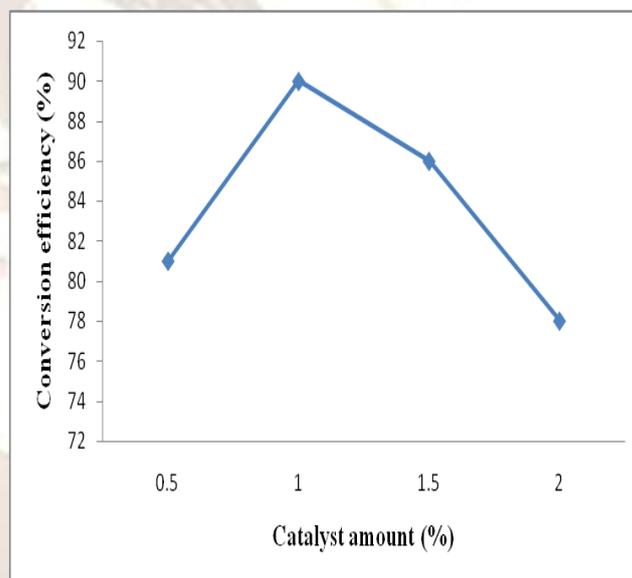


Fig.4. Effect of alkaline catalyst amount on conversion efficiency

4.3. Effect of reaction temperature

The reaction temperature has important role in alkaline-catalyst transesterification .At room temperature no significant yield is notified for even 2hr reaction. The yield is increased with increase in reaction temperature. The effect of temperature variation on conversion efficiency is shown in fig.5. By varying temperature in four different level such as 45,50,55 and 60°C among these 55°C gave maximum methyl ester yield. If greater than 60°C, chance for loss the methanol. The maximum ester efficiency is achieved at 55°C.

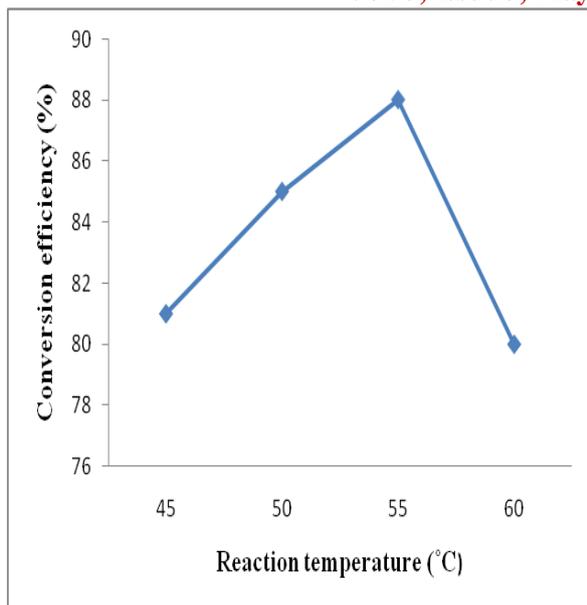


Fig.5. Effect of reaction temperature on conversion efficiency

4.4 Effect of reaction time

The conversion rate is increased with increase in reaction time. In this experiment, reaction time varying from 0.5-2 hr. The effect of reaction time variation on the conversion efficiency is shown fig. 6. From the figure yield was slightly increased upto 1hr reaction and after that yield is decreased. The maximum efficiency is achieved of 90% for 1 hr reaction. From these experiment the optimum yield is obtained at 1 hr reaction.

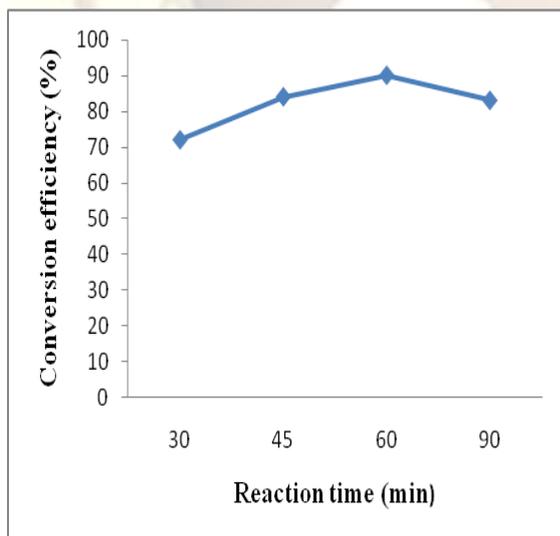


Fig.6. Effect of reaction time on conversion efficiency

5. Conclusion

The high FFA (6%) content neem oil has been investigated for the biodiesel production .It has been found that the feedstock with high FFA its

couldnot be transesterified with alkaline catalyst because the alkaline catalyst react with FFA to form soap. So in this study, two step process was developed to convert FFA to its methyl ester. The first step is acid treatment it reduces the FFA content of oil to less than 1% using acid catalyzed (0.5 % v/v H₂SO₄) reaction with methanol (0.45 v/v) at 50°C temperature and 45 min reaction time. After acid treatment alkaline transesterification reaction was carried out at 1% KOH ,30% methanol, 55°C and 60 min. The maximum yield is 90±2%. The effect of molar ratio, catalyst, reaction temperature and reaction time are analyzed in each step process. Excess addition of sulphuric acid darkens the product it leads to more production cost.

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