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Effect of Homogeneous Catalysts on Production of Biodiesel from Crude Neem Oil Feedstock and Cost Analysis of Biodiesel Production

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Abstract

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 0.45 v/v methanol-oil-ratio, 0.5% v/v H2SO4 acid catalyst, 50˚C and 45 min reaction time. After pretreatment of neem oil, transesterification reaction was carried out with 4.5:1 methanol-to-oil molar ratio, 1% KOH as alkaline catalyst, 75 min reaction time and 50˚C reaction temperature to produce the fatty acid methyl ester. This two step process gave maximum average yield of 70±2%.

1. Introduction

The use of alternative fuels instead of conventional fossil fuels is becoming increasingly significant due to decreasing petroleum reserves and increasing greenhouse gases, all of which lead to global warming, ozone depletion and political and health concerns (Fukuda et al., 2001). Plant oils have been used as alternative fuels for many years, since they are renewable and readily available. However, these oils cannot be used directly as fuel sources in diesel engines due to: (a) high viscosity which leads to poor fuel atomization during the injection process, (b) low volatility and (c) polymerization which results in deposit formation, incompletion combustion and poor emissions (Ma and Hanna, 1999). To overcome these disadvantages, oils can be converted into fatty acid methyl esters (FAME) which are also known as biodiesel. Biodiesel is an alternative fuel that is non-toxic, completely biodegradable and renewable and can be adapted easily without any modification to diesel engines.

Several processes have been developed for biodiesel production, such as pyrolysis, micro emulsification and transesterification. The chemical change of the products from the reactants caused by the thermal energy in the presence of air or nitrogen sparging is called a pyrolytic process. These products are similar to the petroleum-derived fuel. However, during the pyrolysis process, the removal of oxygen leads to reduce the environmental benefits (Ma and Hanna, 1999). The problem of the high viscosity of the substrates has been investigated using microemulsions with solvents (methanol, ethanol and 1-butanol) to meet the international standards of petroleum-derived fuels. However, an increase of lubricating oil viscosity, irregular injector needle sticking, incomplete combustion and heavy carbon deposits were reported in the laboratory screening endurance test. Therefore, transesterification process plays a vital role, in order to overcome these disadvantages.

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The process of displacing alcohol from an ester to form another ester is called transesterification. Transesterification is the most simple and efficient method to produce biodiesel by using acids, alkalis, or enzymes as catalysts. Triglycerides with high free fatty acid and water contents are not essential for a biodiesel conversion process using an acid catalyst. However, the reaction rates are slower than those of the alkali catalytic process (Freedman et al., 1986). The alkali-catalysis transesterification process has been widely used in the biodiesel industry, because it gives a high yield of conversion of fatty acid methyl esters from triglycerides at low temperatures and pressures in a relatively short reaction time of 4-10 hours. However, it has several drawbacks including product separation, soap formation and negative environmental impacts such as greenhouse gas, CO, hydrocarbons, NOx and particles in exhaust emissions (Nielsen et al., 2008).

Neem is a tree in the family ‘maliaceae’ which grows various parts in Bangladesh. It’s scientific name ‘Azadirachtaindica’. The evergreen tree is large, reaching 12 to 18 meters in height with a girth of up to 1.8 to 2.4 meters. The seeds have 40% oil which has high potential for the production of biodiesel. It has a higher molecular weight, viscosity, density, and flash point than diesel fuel. Neem oil is generally light to dark brown, bitter and has a strong odor that is said to combine the odors of peanut and garlic [M.A. Fazal et al., 2011].

Neem comprises mainly of triglycerides and large amounts of triterpenoid compounds. It contains four significant saturated fatty acids, of which two are palmitic acid and two are stearic acid. It also contains polyunsaturated fatty acids such as oleic acid and linoleic acids [Muthu et al., 2010]

2. Materials and Methodology

2.1. Materials

Crude neem oil was purchased from local market. The magnetic stirrer with hot plate was at DTU laboratory.

Chemicals are used in transesterification process like Pottassium hydroxide pellet (88% purity), Methanol (99% purity), Concentrated sulphuric acid and Sodium hydroxide pellet (88% purity).

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 transesterfication.Three 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 processes such as
Oil filtration,
Acid esterification
and alkaline transesterification.

2.3.1. Oil filtration

Neem oil has 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 continue until no bubbles of water vapor anymore. After one hour 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 up to 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 move to the top layer and it's discarded. The lower layer is separated for further processing of transesterified into methyl ester. This process reduces the acid value of crude neem oil to less than 1% of FFA.Viscosity reduction increases with increase in methanol-to-oil ratio.

2.3.3. Alkaline Transesterification

After acid pretreatment the esterified oil is taken in flask and heated up to 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 it's 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 3/4th 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, 0.40:1,0.45:1, 0.50:1,0.55:1 methanol-to-oil ratio, among these 0.45:1 gave higher yied. The last two 0.50:1, 0.55:1 have only slight variation. In economic view 0.45:1 proportion is selected for reaction condition. The effect of methanol variation is shown in fig.1. from the figure conversion efficiency is slightly increase up to 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 viscosity reduction increases with increase in methanol-to-oil ratio.

Methanol to Oil Ratio (v/v)	0.35	0.40	0.45	0.50	0.55
Conversion Efficiency (%)	77	84	95	90	87

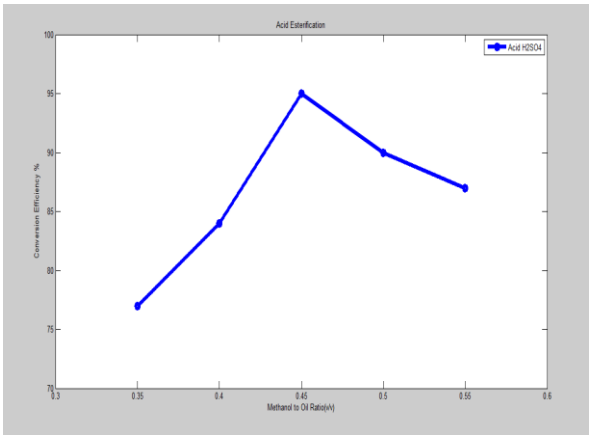

Fig: 1. Effect of Methanol-to-oil ratio on Conversion Efficiency

3.1.2. Effect of acid catalyst amount

Amount of acid catalyst variation is affecting the conversion efficiency. By varying sulphuric acid proportion such as 0.30, 0.40, 0.50, 0.60 and 0.70% v/v. Maximum conversion efficiency 95% is achieved in 0.5 % v/v H2SO4. Effect of acid catalyst variation is shown in fig. 3(i)(b) from the figure more than 0.5% v/v H2SO4, the product color is become black. Lower amount of sulphuric acid addition affects the final product yield.

Acid Catalyst % (v/v)	0.3	0.4	0.5	0.6	0.7
Conversion Efficiency (%)	67	72	95	82	77

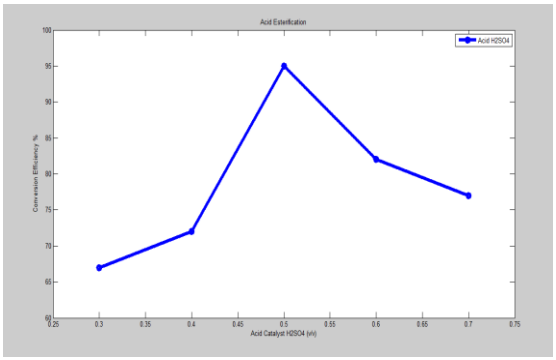

Fig: 2. Effect of acid catalyst amount on Conversion Efficiency

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 methanol-to-oil ratio on conversion efficiency is shown in fig.3(ii) (a) It has been seen that yield is slightly increase up to 4.5:1 methanol-to-oil molar ratio. The maximum methyl ester yield 69% is achieved at 4.5:1methanol to oil molar ratio. With further increase in methanol-to oil molar ratio the conversion efficiency is decreases.

Methanol to Oil Molar Ratio	3	4.5	6	7.5
Conversion Efficiency (%) with 1% NaOH	41	60	51	46
Conversion Efficiency (%) with 1% KOH	50	69	60	55

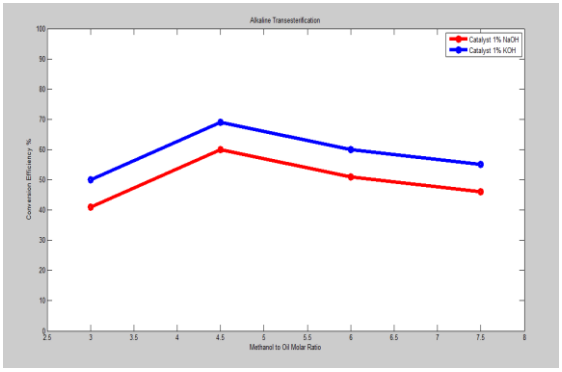

Fig: 3. Effect of methanol on Conversion Efficiency

3.2.2. Effect of Alkaline Catalyst

The amount of catalyst variation is affecting the conversion efficiency. The catalyst proportion is varied from 0.75- 1.50% KOH. The effect of catalyst variation on conversion efficiency is shown in fig.3(ii)(b) From the figure yield is slightly increased up to 1% KOH and after that yield is decreased due to reverse reaction is take place (emulsion formation).The maximum yield is achieved of 70% at 1% KOH.

Alkaline Catalyst %(wt/wt)	0.75	1	1.25	1.5
Conversion Efficiency(%) by NaOH	52	62	55	50
Conversion Efficiency(%) by KOH	62	70	65	60

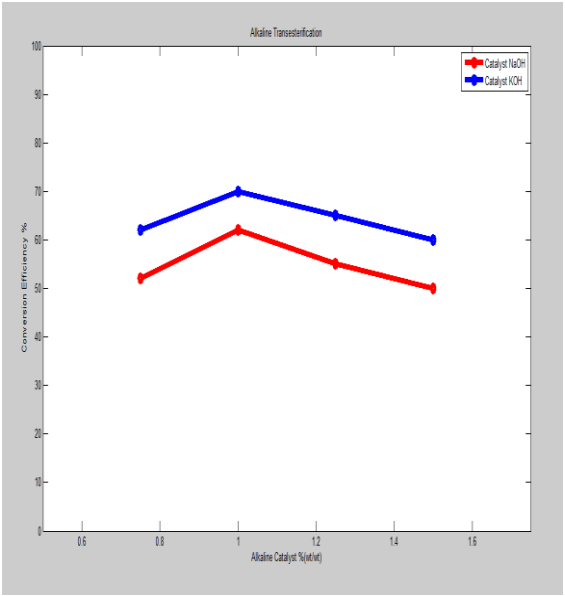

Fig: 4. Effect of Alkaline Catalyst Amount on Conversion Efficiency

3.2.3. 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.3(ii)(c). By varying temperature in four different levels such as 45, 50, 55 and 60˚C among these 50˚C gave maximum methyl ester yield. If greater than 50˚C, chance for loss the methanol. The maximum ester efficiency 72% is achieved at 50˚C.

Reaction Temperature(°C)	45	50	55	60
Conversion Efficiency (%) with 1% NaOH	54	66	64	58
Conversion Efficiency (%) with 1% KOH	64	72	69	62

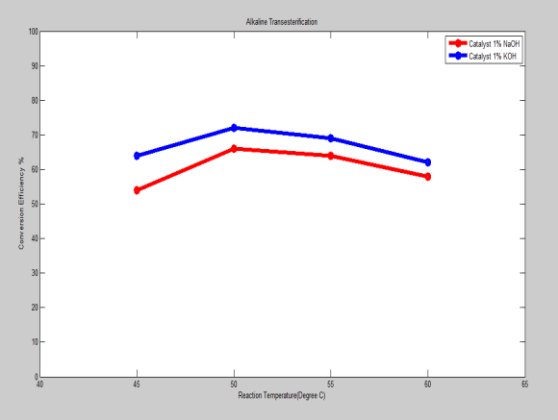

Fig: 5. Effect of Reaction Temperature on Conversion Efficiency

3.2.4. Effect of Reaction Time

The conversion rate is increased with increase in reaction time. In this experiment, reaction time varying from 55-85 min. The effect of reaction time variation on the conversion efficiency is shown fig.3(ii)(d) from the figure yield was slightly increased up to 75min reaction time and after that yield is decreased. The maximum efficiency is achieved of 68% for 75min reaction time. From these experiments the optimum yield is obtained at 75min reaction.

Reaction Time(min)	55	65	75	85
Conversion Efficiency (%) with NaOH	48	52	58	49
Conversion Efficiency (%) with KOH	58	62	68	59

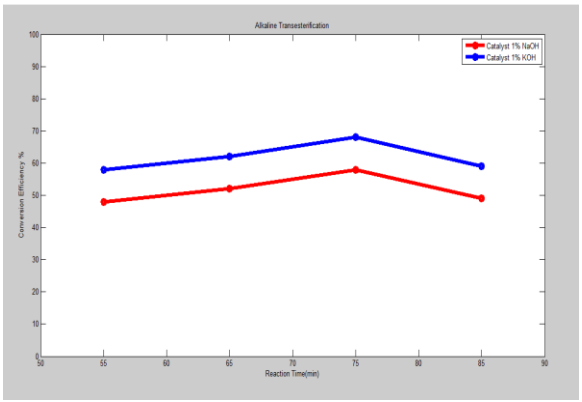

Fig: 6. Effect of Reaction Time on Conversion Efficiency

4. Conclusion

The high FFA (20%) content neem oil has been investigated for the biodiesel production. It has been found that the feedstock with high FFA its could not be transesterified with alkaline catalyst because the alkaline catalyst react with FFA to form soap. So in this study, two step processes 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 H_2SO_4) reaction with methanol (0.45 v/v) at 50˚C temperature and 45 min reaction time. After acid treatment alkaline transesterfication reaction was carried out at 1% w/w KOH, 4.5 methanols to oil molar ratio, 50˚C and 75 min reaction time. The maximum yield is 70±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 and it leads to more production cost.

5. Cost Analysis

Sl. No	**Component**	**Cost (Rs.)**
1	Sodium Hydroxide (Catalyst)	23/kg
2	Potassium hydroxide (Catalyst)	36/kg
3	Neem oil (Feedstock)	150/ litre
4	Methanol (Alcohol)	35/ litre
5	Glycerin (By product of Biodiesel)	75/ litre
Sl. No.	**Component**	**Cost (Rs.)**
1	Neem Oil – 100 ml	15
2	Two step transesterification Cost - 65 ml(45 ml + 20 ml) of Methanol [4.5 Methanol/Oil Molar Ratio]	2.275
3	Catalyst KOH 1.0 gm	0.036
4	Recovery (Glycerin 50 ml)	3.75
5	Total Cost (1 + 2 + 3 – 4)	17.311 – 3.75 = 13.561

Biodiesel production from 1 litre Neem Oil=0.70 Litre
So Cost of Biodiesel per litre = [(13.561 /100)*1000] / 0.70 = 193.73 Rs.

The cost of the biodiesel production can be minimized as possible to recover the used methanol. Recycling of methanol again and again in mass production and commercial use, the cost must be come to the lowest amount. Also the by-product such as glycerin and soap play an important role to minimize the cost.

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