Synthesis of Biodiesel from Linseed Oil by Using Acid and Base Catalysts

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Abstract- *Biodiesel synthesized by the transesterification of vegetable oils and animal fat. It is a promising alternative fuel to diesel due to inadequate fossil fuel resources and environmental concerns. In the present work biodiesel synthesized from linseed oil through transesterification process by using the acid catalyst (HCl) and base catalyst (KOH). Important experimental variables like amount of catalyst, reaction temperature, reaction time and methanol oil molar ratio were analyzed. The fatty acid methyl ester composition in biodiesel was confirmed by GC-MS techniques. The maximum biodiesel yield found at 86%, the optimized variable found at reaction time 4 hours, reaction temperature 65^{o}C and methanol oil ratio 10:1.*

Keywords- Transesterification, Biodiesel, Fatty acid methyl ester, Vegetable oil, Linseed oil.

I. INTRODUCTION

There is growing attention in developing alternative energy resources. An instantly applicable possibility is a replacement of diesel fuel by means of biodiesel, which consists of the methyl esters of fatty acids. Biodiesel contribution to greenhouse gasses is insignificant since the emitted CO_2 is equal to the CO_2 absorbed by the plants to generate the triglyceride. Biodiesel is renewable, non-toxic, sulfur free, clean burning fuel and also a suitable alternate for internal combustion engines instead of conventional diesel [1-14]. Biodiesel is typically produced by the transesterification of vegetable oil, algal oil or animal fat as a feedstock. The most frequently used alcohol is methanol or ethanol to produce fatty acid methyl esters or fatty acid ethyl esters. It is generally referred as fatty acid methyl esters (FAME). Currently, there are four different methods are available to reduce the viscosity of vegetables such as blending of oil with petroleum diesel, emulsification, pyrolysis, and transesterification. Biodiesel can be mixed with petroleum at any percentage. However directly used as a fuel which is called as B100[15]. It has similar properties (physical and chemical) of petroleum diesel fuel. However, properties the biodiesel has been found to be superior when compared to conventional fossil fuel. It has a higher flash point, better cetane number and specific gravity, ultra-low sulfur concentration, and better lubricating efficiency [16].The combustion engines to be modified to avoid the carbon deposition, when the vegetable oil is used directly or mixed along with petroleum diesel. The pyrolysis and emulsification procedures are producing unwanted sense carbon deposits, increase lubricating oil viscosity, incomplete combustion and undesirable side products such as aliphatic and aromatic compounds and carboxylic acids.

Recently, transesterification has been reported as the most common way to produce biodiesel from vegetable or animal fats with alcohol usually methanol or ethanol, in the presence of an acid or base catalyst [17]. Transesterification involves a numeral of consecutive and reversible reactions. Triglycerides are converted in stepwise into diglycerides, monoglycerides and finally glycerol. In each step, a mole of fatty acid methyl ester liberated. Since last few decade various biodiesel production plants have been initiated in India. These plants are operated as per the availability of feedstock, the price of crude vegetable oils. The potential biodiesel feed stock is castor oil, cottonseed oil, Jatropha, Karanja, Mahua, Neem, Palm oil, Rice bran oil, Soap nut, Tumba, Waste cooking oil and Algae. These plants grow in adverse agro-climatic conditions, least gestation period and their fatty acid composition suitable for producing good quality biodiesel. In this research work linseed oil is chosen as a biodiesel feedstock.

Biodiesel synthesis commonly carried out by catalytic, non-catalytic transesterification reaction, ultrasound systems, microwave treatment and also supercritical conditions. The catalyst presence is essential to increase the reaction rate and increase conversion yield of biodiesel. Linseed oil, also known as flaxseed oil is made from the seeds of the flax plant, colorless to yellowish oil. The oil contains substances which stimulate good health for human beings.

II. MATERIALS AND METHODS

In this research work, biodiesel is produced by transesterification method. Linseed oil is purchased from the local market. Chemicals like Methanol, HCl and KOH were

Purchased from Merck. The entire chemicals used were analytical grade.

2.1 Biodiesel Production Process

Free fatty acid value (FFA) of vegetable oil selects the transesterification process. If the free fatty acid content of the oil is lower than 3%, a single process is carried out. If it is greater than 3%, double stage process is carried out.

2.1.1 Acid Esterification Procedure

100ml of Linseed oil (FFA>3%) was taken in a clean conical flask. The moisture content of the oil was removed by heating at 90°C for 2 hours. Then the oil cooled, 30ml of methanol and hydrochloric acid was added (volume of HCl = FFA value x 0.05). It was continuously stirred for 2 hours at 70°C. This mixture was separated by separating funnel for overnight. A Top layer consisting of acid esterified oil and bottom layer contain residues. The bottom layer was separated out from acid esterified oil and used for transesterification process.

2.1.2. Base Transesterification Procedure

The required volume of methanol was added to the acid esterified oil (FFA < 3%). The resultant mixture was then heated at various temperature ranges under maximum agitation and various amounts of KOH catalysts were added. After several hours, the reaction mixture was cooled slowly to room temperature and separated by filtration. The filtrate was settled down to separate into two layers. The top layer consisted of fatty acid methyl esters (biodiesel) and unreacted triglycerides, while the bottom layer primarily contained methanol and glycerol. Experiments were carried out by changing different parameters like reaction temperature, reaction time, and methanol/oil molar ratio.

Biodiesel yield can be calculated by

Biodiesel Yield (%)=(Grams of Biodiesel Produced)/(Grams of Vegetable Oil Taken)×100

III. RESULTS AND DISCUSSION

3.1 Effect of Acid Catalyst on Biodiesel Yield

The hydrochloric acid, the amount was varied in the range of 2 to 10 ml. These requirements are based on the volume of the oil used for the acid esterification reaction [18]. The pretreatment of high FFA Linseed oil using an acid-catalyzed esterification was shown in Figure 1. It was also observed during the experiments that addition of excess hydrochloric acid darkens the color observed in the product but yields remain the same for oil.

3.2 Effect of Base Catalyst on Biodiesel Yield

Transesterification of oil was carried out with KOH as a catalyst at 3 to 16 ml. Figure 2 shows the yield of biodiesel versus KOH concentration. The lower catalytic concentration of 3 ml was insignificant to complete the reaction. It was originated that the biodiesel yield increased with the increase of catalyst concentration from 3 to 9 ml. A Maximum biodiesel yield of 86% found at 9 ml of KOH concentration. The excess amount of catalyst was rapid to form an emulsion which improves the viscosity and led to the gel formation. The physico chemical properties of linseed oil show in Table 1. The formation of emulsion hinders the transesterification reaction [19].

3.3 Effect of Reaction Time

Figure 3 shows the effect of reaction time on biodiesel yield. The rate of reaction is strongly influenced by reaction time. The conversion of biodiesel increased gradually with increasing reaction time and then achieved a plateau value. The maximum conversion reached in 4 hour reaction time; after 4 hour reaction time the reaction reversed and also the yield of biodiesel were decreased (formation of triglycerides).

3.4 Effect of Reaction Temperature

The effect of reaction temperature related to biodiesel conversion was investigated and the corresponding graph presented in Figure 4. The conversion initiated slowly at low temperature (45^{o}C). The maximum ester conversion of 86 % was found at 65^{o}C, which was near the boiling point of methanol. The conversion dropped beyond the 65^{o}C, since the molar ratio of methanol to oil decreased when methanol vapourised into the gas phase above 65^{o}C.

3.5 Effect of Methanol Oil Ratio on Biodiesel Yield

The molar ratio of methanol to oil is the most significant variable influencing the biodiesel yield [20].The influence of the methanol oil ratio on conversion of biodiesel is shown in Figure 5. The stoichiometric requirement for the transesterification reaction involves 3 moles of alcohol and 1 mole of triglyceride to yield 3 moles of biodiesel and 1 mole of glycerol. However, this reaction is an equilibrium reaction in which a large amount of alcohol is required for initiating the reaction in the forward direction. This experiment were carried out with the methanol oil ratio 5:1, 10:1, 15:1, 20:1 under the reaction temperature 65°C and 4 hours of reaction time. In the beginning, the conversion was increasing trend with methanol. Maximum yield was obtained at 10:1 molar ratio of methanol to oil. Beyond the molar ratio of 10:1, the added methanol does not pointedly enhance the ester conversion. However, a further rise in oil to methanol ratio did not promote the reaction. It is assumed that the glycerol would dissolve in excessive methanol, since inhibiting the reaction of methanol with the reactants, catalyst and also difficult to the separation of glycerin, since lowers the biodiesel conversion by shifting the equilibrium in the reverse direction [21]. Hence the methanol to oil ratio 10:1 was considered as optimized ratio.

IV. GAS CHROMATOGRAPHY – MASS SPECTROSCOPY ANALYSIS OF BIODIESEL (GC-MS)

Fatty acid methyl ester profile of the biodiesel prepared from linseed oil was investigated by GC-MS analysis. The individual peaks of the gas chromatogram shown in Figure 6 and fatty acid compositions presented in Table 2. Biodiesel from Linseed oil consists of Palmitic acid (C16:0), Palmitoleic acid (C16:1), Stearic acid (C18:0), Oleic acid (C18:1), Linoleic acid (C18:2) and Linolenic acid (C18:3). The major fatty acid is Oleic acid followed by Linoleic acid, Palmitic acid and Stearic acids. Linolenic acid, Palmitoleic acids are present as minor constituents.

V. CONCLUSIONS

This research work investigates the synthesis of biodiesel from linseed oil by using acid and base catalyst. The effects on biodiesel production on methanol/oil molar ratio, reaction temperature, reaction time and catalysts amount were studied. The optimum reaction conditions were found to be temperature 65°C, reaction time 4 hours, and methanol to oil molar ratio was 10:1. The maximum biodiesel yield found to be 86%. GC-MS analyses prove the fatty acid methyl ester compositions in produced biodiesel sample.

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Figures:

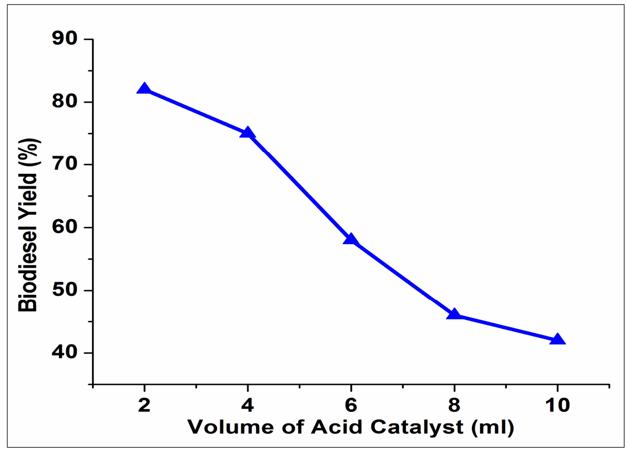

Figure.1: Effect of Volume of Acid Catalyst on Biodiesel Yield

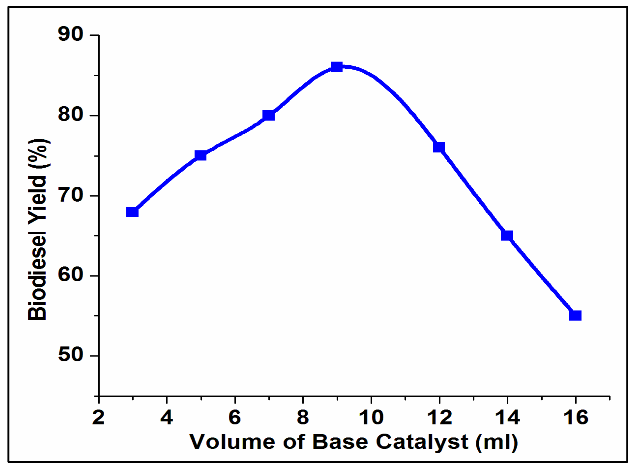

Figure.2: Effect of Volume of Base Catalyst on Biodiesel Yield

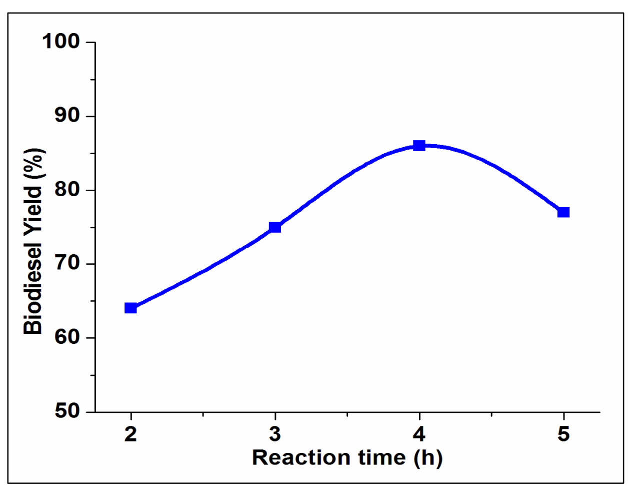

Figure.3: Effect of Reaction Time on Biodiesel Yield

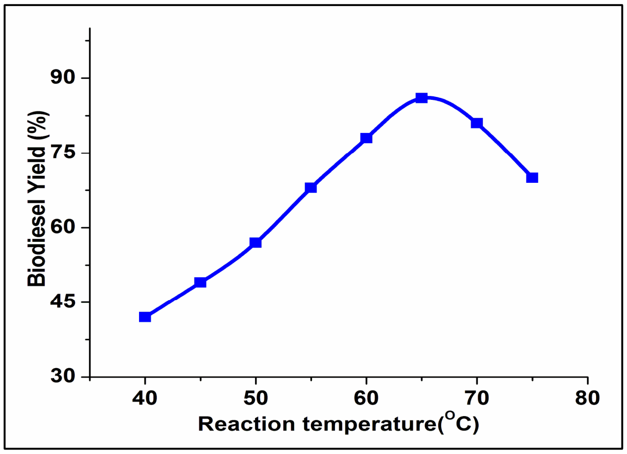

Figure.4: Effect of Reaction Temperature on Biodiesel Yield

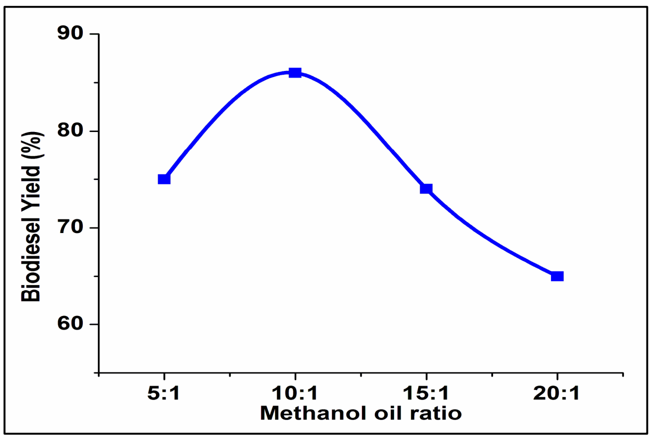

Figure.5: Effect of Methanol Oil Ratio on Biodiesel Yield

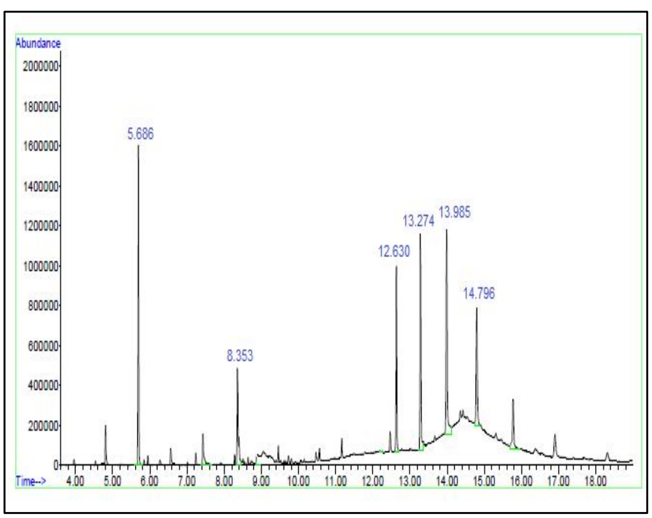

Figure.6: GC Chromatogram of Biodiesel Produced From Linseed Oil

Tables:

Parameter	Characteristic
Moisture	0.09 (%)
Density	921 (kg/m^3)
Iodine Value	93 (gram of iodine /100g)
Saponification value	178 (mg of KOH/g)
Kinetic Viscosity at 40°C	27.5 (mm^2/s)
Acid Value	10.5 (mg of NaOH/g)
Free Fatty Acid Value	5.5 (%)

Table. 1: Physico-Chemical Properties of Linseed Oil

Fatty Acids	Composition (wt. %)
Palmitic acid (C16:0)	14.82 wt.%
Palmitoleic acid (C16:1)	0.87 wt.%
Stearic acid (C18:0)	9.32 wt.%
Oleic acid (C18:1)	45.43 wt.%
Linoleic acid (C18:2)	28.74 wt.%
Linolenic acid (C18:3)	1.54 wt.%

Table 2: Fatty Acid Profile of Biodiesel Produced from Linseed Oil