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Biodiesel Production from Waste Cooking Oil over Acid and Base Catalysts in a Green Way

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Abstract : Waste vegetable oil of mustard and soyabean oil are used as a feedstock for biodiesel production; as these are natural products, they are mixtures of several component oils and fats. These oils/fats are triglyceride molecules (glycerin esterified with three fatty acids) through transesterification and only creates glycerine as a byproduct. 100ml of wasted cooking oil was treated with acid catalyst (HCl, H_2SO_4) and base (KOH, NaOH)found that base catalyst are more promising. Gas chromatography confirms the hydrocarbon fractions are of the product was diesel-like properties.

Keywords : Biodiesel, Catalyst, Transesterification.

1. Introduction

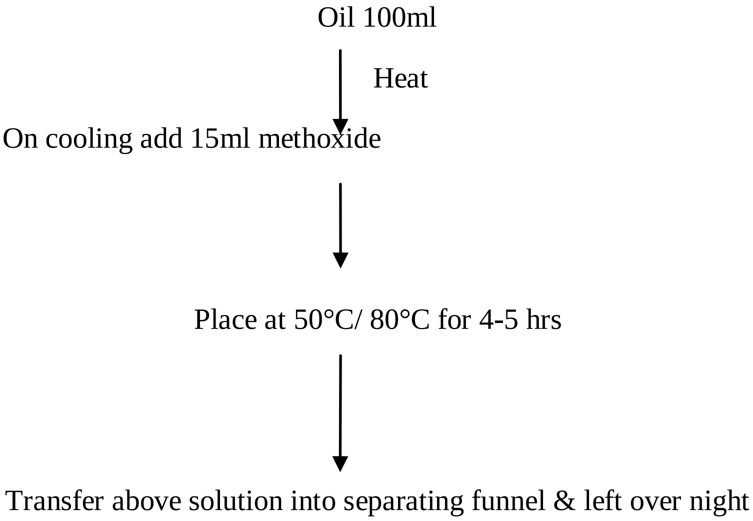
The price of feedstock oil is one of the most significant factors affecting the economic viability of biodiesel manufacturer. Many approaches were investigated toreduce the biodiesel production cost. The present work gave a preliminary study of two approaches to economically produce biodiesel. One was the use of waste cooking oil (WCO) as raw material.The transesterification reaction of used waste vegetable oils to convert biodiesel by homogenous and heterogeneous catalyst. However a high molar ratio of alcohol to oil, large amount of catalyst and high temperature and pressure are required when utilizing heterogeneous catalyst to produce biodiesel [1]. Transesterification has been used in the biodiesel production process since its beginning. It is required to store stock of enough supply to feed to the production line throughout its production to be fed into the system at required rate [2].

Biodiesel is a renewable substitute fuel for petroleum diesel fuel which is made from nontoxic, biodegradable, renewable sources such as refined and used vegetable oils and animal fats. Biodiesel is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. The process of transesterification is affected by the mode of reaction, molar ratio of alcohol to oil, type of alcohol, nature and amount of catalysts, reaction time, and temperature. Various studies have been carried out using different oils as the raw material and different alcohols (methanol, ethanol, butanol), as well as different catalysts, notably homogeneous ones such as sodium hydroxide, potassium hydroxide, sulfuric acid, and supercritical fluids or enzymes such as lipases. The present study focuses on the application of heterogeneous catalysts to produce biodiesel, because of their environmental and economic advantages [3]. NaOH and KOH are the most common homogeneous base catalyst in biodiesel production [4]. The highest biodiesel yield produced by *Calophyllum inophyllum* was report with 98.53% by using 1wt% KOH and 9:1 methanol to oil ratio [5]. 95% production of biodiesel yield from soybean oil by using NaOH with 1.3wt% catalyst loading and ethanol to oil ratio of 9:1 [6]. The present research work, is to produce a biodiesel from economic way by using low cost catalysts i.e. acid (H_2SO_4) and base (NaOH, KOH) from waste cooking oil.

2. Experimental

2.1 Biodiesel Preparation From Soyabean Oil or Mustard Oil by Potassium methoxide/ Sodium methoxide

100ml of soyabean oil or mustard oil was taken in a conical flask and heated for 5mins at 100°C. At temperture of 70°C, 15ml of potassium methoxide/sodium methoxide was added then incubated at 50°C for 4~5h. Later the flask was transferred into separating funnel and left overnight at room temp.Next day two layers were seen to be separated in separating funnel. The upper layer consisted of biodiesel and the lower layer consisted of the byproduct of crude glycerol.



2.2 Biodiesel Preparation From Soyabean Oil or Mustard Oil by Sulphuric acid/ Hydrochloride acid

100ml of soyabean oil or mustard oil of 100ml was taken in a conical flask and heated at for 5mins at 100°C.18ml methoxide was prepared with methanol and sulphuic acid/hydrochloric acid in a ratio of 6:1.After boiling of the oil it was cooled to 80°C and 15ml acid methoxide was added. Flask was incubated at 50°C in case of sulphuric acid and 80°C in case of hydrochloric acid for 4-5h.After 4-5h the whole content of flask was transferred into separating funnel and left overnight at room temp.Next day two layers were seen to be separated in separating funnel. The upper layer consisted of biodiesel and the lower layer consisted of the byproduct i.e. crude glycerol.

2.3 Biodiesel Preparation From by sulphuric acid/ Hydrochloric acid

100ml of Soyabean oil was heated for 5 mins at 100°C in a conical flask.18ml methoxide was prepared with methanol & sulphuic acid / Hydrochloric acid in 6:1 ratio. Flask was incubated at 50°C in case of sulphuric acid and 80°C in case of hydrochloric acid for 4-5h.After 4-5h the whole content of flask was transferred into separating funnel and left overnight at room temp.Next day two layers were seen to be separated in separating funnel. The upper layer consisted of biodiesel and the lower layer consisted of the byproduct: crude glycerol.

2.4 Prepared biodiesel from mustard and soyabean oil using base catalyst

Alkaline catalysteither sodium hydroxide (NaOH) or potassium hydroxide (KOH)are shown to be more effective in promoting the reaction and strength of 85% of purity or greater is adequate. The KOH used rather than NaOH as a catalyst, approximately 1.5 times more KOH will be needed compared to using NaOH [7]. In this process, the sodium methoxide/potassium methoxide prepared was mixed with the heated mustard oil/soyabean oil and stirred until it was completely mixed. It was kept for 4-5h and was later transferred to a separating funnel and left for a day.

The acid catalysis gave 97% of biodiesel formation while base catalysis gave 94%-97% biodiesel formation. When the chromatographic analysis was done many of the biodiesel peaks obtained were similar to the standard pure diesel peaks. The similar Hydrocarbons peaks have been shown in the same color in the Table 1. The table gives a glimpse of all the hydrocarbons present in the different biodiesel which are prepared from different oils and different catalysts. When we analyse the GC peaks it was observed that the biodiesel formed from NaOH and KOH have higher no. of peaks which are similar to pure diesel [8]. Thus the quality of biodiesel produced from base catalysis is better than the other forms of catalysis. Table 1 shows that hydrocarbons from C_{10} to C_{21} are present in the Biodiesel obtained from KOH catalyst. Thus it proves that KOH is the best used catalysts even when the type oil is changed. Thus for all different types of oils: used or unused KOH seems to be the best cost effective and best catalysts.For the present study when base catalysts were used, it was observed that the KOH seemed to be a better technique for biodiesel formation [9].

2.5 Prepared biodiesel from mustard/soyabean oil using H_2SO_4 and HCl (acid catalyzed)

The catalyst sulfuric acid, and hydrochloric acid, all of which are dangerous chemicals and dangerous to handle. In addition, the water formed during the esterification process will inhibit the reaction (making your own biodiesel) [10]. The reaction can be extended to diglycerides and monoglycerides. The main concern when acid catalysed transesterification is employed as the reaction method is the formation of carboxylic acid as the by-product when water is present in the reaction mixture. The methoxide was made with H_2SO_4 the other sample was made using HCl. It was then mixed with the heated soyabean/mustard oil and left for 5h and was later transferred in to a separating funnel and left overnight [11]. Two layers were found in the samples containing H_2SO_4 acid catalyst in both the soyabean and mustard oil. However, the sample containing HCl acid catalyst was found unseparated.When the acid catalysts was used, there was separation only in the case of H_2SO_4. However while using HCl as catalyst, though different methoxide volumes was used, there was no separation at all.

2.6. Estimation of Biodiesel factions by Gas Chromatography:

Gas chromatography is specifically gas-liquid chromatography-involves a sampling being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid. It exploits differences in the partition coefficients between a stationary liquid phase and a mobile gas phase of the volatilized analyzed they are carried through the column by the mobile gas phase .the temperature of the column is raised to 50-300°C volatilization. Gas chromatography is widely use for the qualitative and quantitative analysis of a large number of low polarity compounds because it has high sensitivity. The carrier gas must be chemically inert .the carrier gas consist of an inert gas as nitrogen gas packed columns or helium or argon for capillary columns .the gas passing through a verity of molecular serves to remove oxygen. The gas flow rate of 40-80 cm^3min^{-1} commonly used gases include nitrogen, helium, detector which is used. For optimum column efficiency, the sample should not be too large, and should be introduced onto the column as a “plug” of vapor – slow injection of large samples causes band broadening and loss of resolution. The most common injection method is where a micro syringe is used to inject sample through a rubber septum into a flash vaporizer port at the head of the column. The temperature of the sample port is usually about 50°C higher than the boiling point of the least volatile component of the sample**.** Capillary columns of 1.5-10m in length and have an internal diameter of 2-4mm is used. A column temperature slightly above the average boiling point of the sample results in an elution time of 2-30 minutes with flame ionization detector. The FID is a useful general detector for the analysis of organic compounds; it has high sensitivity, a large linear response range, and low noise. It is also robust.

3. Result and Discussion

Biodiesel is prepared by using two different waste and used oils (soyabean and mustard oil) by different types of catalyst include acid catalyst and base catalyst. The results are consistent by using two different waste and used oils (soyabean and mustard oil). Different types of catalyst was used in the preparation of biodiesel from these two different oil which include acid and base catalyst. Biodiesel prepared in the study was identified by direct comparison with the standard Pure Diesel. The percentage of individual peaks of hydrocarbons defining each Biodiesel formed was compared to the hydrocarbon peaks obtained for pure diesel which was accepted as the standard. As far as the different studied fatty acid methyl esters have similar carbon chain length, it was assumed that they have the same response factor and volatility, allowing making a direct comparison of the peak areas to determine the sample composition.

3.1 Prepared biodiesel from mustard and soyabean oil using base catalyst

Table 1 and Fig. 1 shows that the alkaline catalyst either sodium hydroxide (NaOH) or potassium hydroxide (KOH)has been shown to be more effective in promoting the reaction and strength in greater is adequate. The KOH usage shows approximately 1.5 times more activity than NaOH as a catalyst. In this process, the sodium methoxide/potassium methoxide prepared was mixed with the heated mustard oil/soyabean oil and stirred until it was completely mixed. It was kept for 4-5h and was later transferred to a separating funnel and left for a day.For the present study when base catalysts were used, it was observed that the KOH seemed to be a better technique for biodiesel formation.

Table 1 Comparative volume of biodiesel prepared from waste mustard and soyabean oil using KOH and NaOH

Waste Cooking Oil (100ml)	Tempe -rature	Catalyst	Methoxide	Biodiesel	Crude Glycerol Byproduct
Mustard oil	70°C	NaOH	15ml	91ml	14ml
Mustard oil	70°C	KOH	15ml	94ml	12ml
Soyabean oil	70°C	NaOH	15ml	95ml	10ml
Soyabean oil	70°C	KOH	15ml	97ml	9ml

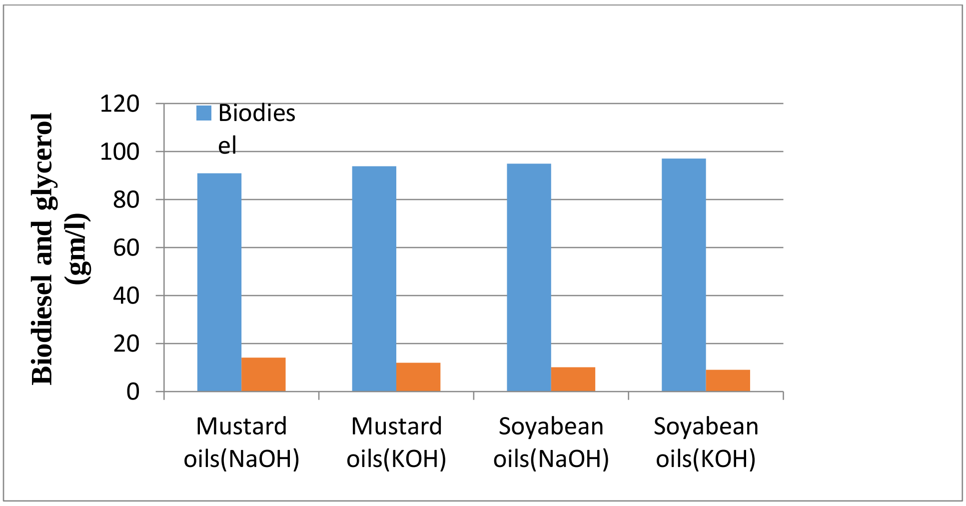


Fig .1Production of biodiesel from mustard and soyabean oils by base catalyst

3.2 Prepared biodiesel from mustard/soyabean oil using H_2SO_4 and HCl (acid catalysed)

The catalyst sulfuric acid, and hydrochloric acid, all of which are dangerous chemicals and dangerous to handle. In addition, the water formed during the esterification process will inhibit the reaction (making your own biodiesel). Table 2 and Fig. 2 reveals that the reaction can be extended to diglycerides and monoglycerides. The main concern when acid catalyzed transesterification is employed as the reaction method is the formation of carboxylic acid as the byproduct when water is present in the reaction mixture. The methoxide was made with H_2SO_4 the other sample was made using HCl. It was then mixed with the heated soyabean/mustard oil and left for 5h and was later transferred in to a separating funnel and left over night. Two layers were found in the samples containing H_2SO_4 acid catalyst in both the soyabean and mustard oil. However, the sample containing HCl acid catalyst was found unseparated. When the acid catalysts was used, there was separation only in the case of H_2SO_4. However while using HCl as catalyst, though different methoxide volumes was used, there was no separation at all. Fig. 3 shows that hydrocarbon factions well closer with recent reports [12].

Table 2 Comparative volume of biodiesel produced from mustard and soyabean oil using HCl and H_2SO_4

Waste Cooking Oil (100ml)	**Tempera-ture**	**Catalyst**	**Methoxide (ml)**	**Biodiesel (ml)**	**Crude Glycerol byproduct (ml)**
Mustard oil	90°C	H_2SO_4	18ml	97ml	14ml
Mustard oil	90°C	HCl	18ml	No Separation of byproduct	No Separation of byproduct
Soyabean oil	90°C	H_2SO_4	18ml	99ml	10ml
Soyabean oil	90°C	HCl	18ml	No Separation of byproduct	No Separation of byproduct

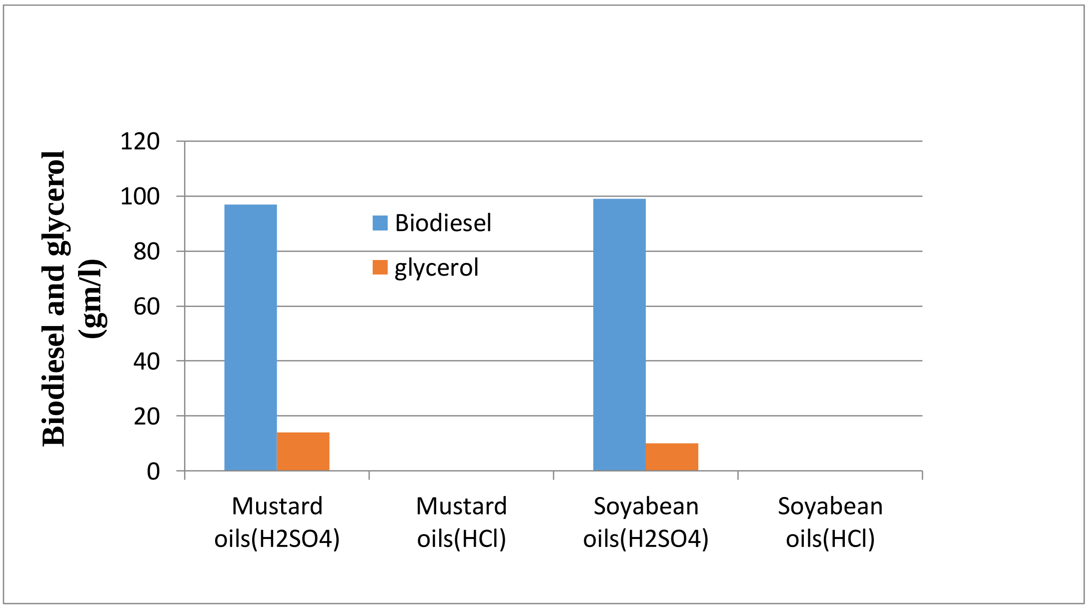


Fig .2Production biodiesel from mustard and soyabean oils by acid catalyst

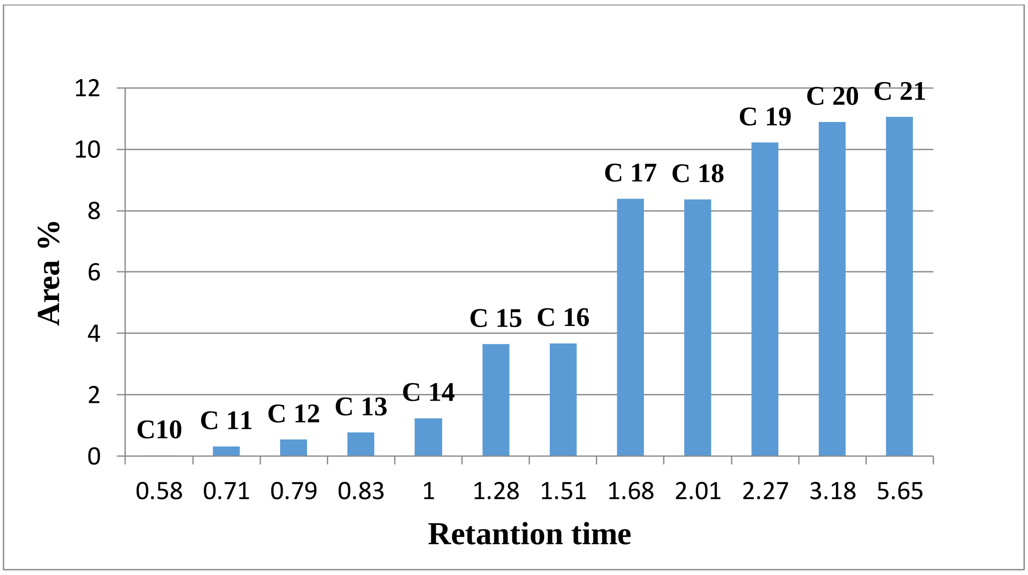


Fig. 3 Gas chromatography analysis of hydrocarbon fractions of biodiesel prepared.

4. Conclusion

The dwindling reserve of conventional energy resources and their associated environmental problems have increased the awareness to seek for alternative renewable and sustainable resources for fuel production. The production of biofuel is now escalating as a replacement of fossil fuel. Biodiesel has become beguiling nowadays for its environmental benefits and it seems an alternative fuels for future. It is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and also environmentally beneficial.

The present study deals with analyzing the best method for preparing higher amount of Biodiesel from vegetable oils which are waste and discarded. The results showed higher levels of Biodiesel formation from acid catalysis and enzymatic usage. But it was seen that in all the cases heat is required for the transesterification to occur. To further prove the formation of Biodiesel, gas chromatography was used to analyze and compare the hydrocarbon peaks obtained.

The study finally concluded that waste oils can be definitely used for biodiesel production in larger scale and the quality of the Biodiesel formed is also comparable to the pure diesel.

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