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Use of Sunflower and Cottonseed Oil to prepare Biodiesel by catalyst assisted Transesterification

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Abstract

Environmental concerns and energy crisis of the world has led to the search of viable alternatives to the fossil fuel, FAME (Fatty Acid Methyl Ester) is environment friendly, alternative, and nontoxic, safe, biodegradable has a high flash point and is also termed as Bio-Diesel. It is commonly produced by the process transesterification. For its production, establishment of suitable process, selection of proper feedstock and reaction parameters is of utmost importance in present scenario. This paper is an attempt to compare two production process viz. base catalyzed and two stage acid-base catalyzed for two possible feedstock viz. sunflower oil and cottonseed oil. The transesterification was done for both feed stocks by varying the catalyst as sodium methoxide, NaOH and KOH. The change in catalyst and process was found to affect the conversion of feed stock into biodiesel using magnetic stirring assisted with microwave. It was found that for both the feed stocks, the two stage process gave greater conversion to biodiesel as compared to base catalyzed process. Using methoxide as catalyst, the cottonseed oil gave a conversion of 98% in base catalyzed process as compared to 98.89% in two stage process. Similarly, in case of sunflower oil, greater conversion of 99.05% was found using KOH as catalyst in using two stage processes than that of 98.9% using only base catalyzed process. The FFA content also showed higher reduction in FFA content of 0.34% in case of two stage transesterification as compared to 1.1% in base catalyzed transesterification using KOH with cottonseed oil. Hence it can be concluded that the two stage acid-base catalyzed transesterification is more efficient in producing biodiesel as compared to base catalyzed transesterification alone.

Keywords: Biodiesel, FAME, transesterification, FFA, catalyst, microwave.

Introduction

The petroleum fuels play a very important role in the development of industries, transportation, and agricultural sector and to meet many other basic human needs. However, these fuels are limited and depleting day by day as the consumption is increasing very rapidly. Moreover, their use is increasing pollution at an alarming rate. India is importing more than 80% of its fuel demand [1]. It is becoming an increasingly popular alternative fuel for diesel engines. Biodiesel is a clean renewable fuel, and hence has recently been considered as the best substitute for a diesel fuel because it can be used in any compression ignition engine without the need for modification[2]. Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids. It is produced from renewable biological sources such as vegetable oils and animal fat by simple transesterification reaction. More than 95% of biodiesel production feedstocks come from edible oils[3,4,5].

However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel[6]. In order to overcome these disadvantages, many researchers are interested in non-edible oils which are not suitable for human consumption because of the presence of some toxic components in the oils[4,7,8]. Since the cost of raw materials accounts about 60–80% of the total cost of biodiesel production, choosing a right feedstock is very important. The technique and technology of production also plays very important role in its production as the yield varies from process to process. A number of methods are currently available and have been adopted for the production of biodiesel fuel. The most commonly used method for converting oils to biodiesel is through the transesterification of animal fats or vegetable oils[4,9].

Objective: The objective of this paper is to give an overview of trans-esterification process for the production of biodiesel using homogenous catalysis and the advantage of having a two stage transesterification process for the same.

Chemical Reactions: To make a biodiesel molecule, oil must undergo transesterification enabling a fatty acid to undergo esterification. Transesterification and esterification of oils and fatty acids can be accomplished in the presence of an alcohol and a catalyst. The overall stoichiometric view of this process is shown in the reaction below. Common alcohols used in this process are short chain alcohols, most notably methanol and ethanol. The catalysts commonly used for this process are chemical catalysts, biocatalysts, and non-enzymatic heterogeneous catalysts[10,11].

$$\begin{array}{lcl} CH_2\text{-}COOR^1 & & R^1COOCH_3 \quad CH_2\text{-}OH \\ CH\text{-}COOR^2 + 3CH_3OH & \longrightarrow & R^2COOCH_3 + CH\text{-}OH \\ CH_2\text{-}COOR^3 & & R^3COOCH_3 \quad CH_2\text{-}OH \end{array}$$

Triglyceride Methanol Methyl ester Glycerol

Overall Reaction of Triglyceride Transesterification: A major problem in carrying out the alcoholysis of oil is to limit the presence of water and free fatty acids (FFA) in the oils. The excess presence of FFA may lead to formation of soap in presence of certain catalyst, hence decreasing the yield, as shown by the following reaction.

$$R_1\text{-}COOH + NaOH \longrightarrow R_1COONa + H_2O$$

FFA Sodium Hydroxide Soap Water

Reaction of soap formation (Saponification): This can also be linked to the quality of product obtained. Water in the reaction system retards the rate of transesterification by hydrolysis of triglyceride, increasing the FFA content of the system.

$$\begin{array}{lcl} CH_2\text{-}O\text{-}CO\text{-}R_1 & & CH_2\text{-}OH \\ CH\text{-}O\text{-}CO\text{-}R_2 + H_2O & \longrightarrow & CH\text{-}O\text{-}CO\text{-}R_2 + R_1\text{-}COOH \\ CH_2\text{-}O\text{-}CO\text{-}R_3 & & CH_2\text{-}O\text{-}CO\text{-}R_3 \end{array}$$

Triglyceride Water Diglyceride FFA

Hydrolysis of triglyceride forming acid molecules: This in turns results in soap production.However; the FFA in the acid-catalyzed system can react with alcohol, resulting in esters. Hence creating the need for two stage catalyzed process. Generally, for oils having FFA content greater than 2.5%, an acid catalyzed treatment in a necessity [3,4,12].

Catalysts: Acid Catalyst: The use of an acid catalyst is observed to be more effective than alkali catalysts when the concentration of free fatty acids is high. Also the performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock. In fact, acid catalysts can simultaneously catalyze both esterification and transesterification. Thus, a great advantage with acid catalysts is that they can directly produce bio-diesel from low-cost lipid feedstocks, generally associated with high FFA concentrations (low-cost feedstocks, such as used cooking oil and greases, commonly have FFAs levels of >6%)[3]. However, Homogeneous acid catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction. Acids used in the catalysis of the transesterification of biodiesels are usually either hydrochloric acid or sulfuric acid. Though these two acids are the most common, any Bronsted acid can be used in this reaction. The Biodiesel samples produced here are catalyzed using sulfuric acid.

Base catalyst: Transesterification reaction can be catalyzed by both homogeneous (alkalies and acids) and heterogeneous catalysts. The used alkali catalysts are NaOH, CH_3ONa, and KOH for producing biodiesel[13,14]. The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed. But the use of base catalyzed transesterification is only limited to oil having low water and FFA content. This reaction is the most widely used process for production of biodiesel worldwide. To keep check on the water and FFA content of the oil, they are first pretreated with an acid catalyzed transesterification process, which converts the FFA to esters[15,16].

Material and Methods

Experimental work- Biodiesel Production process: The production of biodiesel has been conducted using two main oil samples, sunflower and cottonseed oil. The parameter that has been varied is the mode of the trans-esterification reaction using base catalysis and then two stage acid-base catalysis. The different base catalysts employed are sodium hydroxide, potassium hydroxide and sodium Methoxide.

A Two stage transesterification process chiefly consists of an acid catalyzed alcoholysis, often termed as pre-treatment of oil and followed by base catalyzed alcoholysis[13,14,17]. The glycerol and biodiesel produced then undergo phase separation followed by their individual purification.

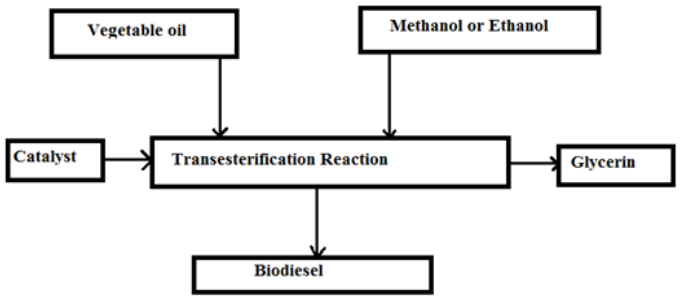

Figure-1
Biodiesel Production Process

Acid Catalyzed Trans-esterification and Pretreatment of acidic feedstocks: Also known as in-situ transesterification, it is one of the most important steps for the production of biodiesel. In *situ* transesterification differs from the conventional reaction, in that the oil-bearing material contacts acidified alcohol directly instead of reacting with purified oil and alcohol. That is, extraction and transesterification proceed within the same process, the alcohol acting both as an extraction solvent and an esterification reagent.

The two main processes which undergo during the process are :
i. Alcoholysis, ii. Esterification of FFA.

Though the rate of esterification in an acid catalyzed medium is extremely low, it provides an advantage of converting glycerides with high acid content to biodiesel. The FFA reacts with the alcohol present in presence of the acid catalyst to give an ester (biodiesel). Hence at the end of the reaction, biodiesel is obtained by the above mentioned reactions. However, the oil still consists of large quantities of unreacted glycerides, which are processed using a base catalyst.

Mixing of Alkali catalyst and Alcohol: This is a step of preparing the catalyst mixture of the base catalyzed alcoholysis of the glycerides. The alcohol methanol is used here with a combination of three different catalysts namely NaOH, KOH and CH_3ONa. The purpose of mixing the two together is to produce methoxide ions, which react with the base oil. Many catalyst like NaOH are in solid form, and hence not readily soluble in methanol. Hence, they are introduced in the alcohol with simultaneously agitating the solution. Once it is completely dissolved, the mixture is send to oil container, where two reactions take place. i. Some part of the base catalyst reacts with residual acid from the pre-treatment step, or ii. It reacts with the free fatty acids in the oil producing soap.

The rest of the base is consumed in catalyzing the alcoholysis.

Base Catalyzed Transesterification: When the catalyst, alcohol, and oil are mixed and agitated in a reaction vessel, a transesterification reaction will start. The experiments for production of biodiesel have been conducted from different oil samples and catalysts using microwave irradiation. The vegetable oil has been taken and catalyst is added to it. Taking the molar ratio of alcohol to catalyst as 9:1, methanol is added. The mixture is kept on a magnetic stirrer cum hot plate for proper mixing. The uniformly mixed mixture is then placed in microwave oven. It is then placed in the separating funnel for separating the layers of biodiesel and glycerin impurities. The upper layer is biodiesel and lower layer is that of glycerin. The method is repeated for different catalyst sodium hydroxide, potassium hydroxide and sodium methoxide for Sunflower and Cottonseed Oil samples. The results are shown in table 1.

Table–1

Percentage Conversion of Oil Samples using Base Catalysis

Oil	Catalyst	%TG	% Conversion
Sunflower	NaOH	0.9	99.1
	KOH	1.099	98.9
	CH_3ONa	1.11	98.89
Cottonseed	NaOH	0.75	99.25
	KOH	0.299	99.7
	CH_3ONa	1.11	98.89

As has been inferred from our experiments, two-stage acid-base catalyzed transesterification is used for vegetable oils having high FFA content as it minimizes the saponification reaction to form the unwanted byproduct, soap. A vegetable oil sample is measured. Taking molar ratio of methanol to acid catalyst as 12:1, methanol and concentrated sulfuric acid are mixed well. This mixture is then added to the oil sample which is then kept on the magnetic stirrer cum hot plate. Then it is placed in the microwave oven [18]. It is then placed in the separating funnel which is then followed by the base catalyzed procedure. For this, the lower layer is separated and is neutralized by addition of sodium hydroxide which is then subjected to transesterification[19, 20]. The required amount of catalyst is taken. Taking the molar ratio of alcohol to catalyst as 9:1, methanol is added and the above mentioned steps are repeated again to get the upper layer as biodiesel and lower layer of that of glycerin. The method is repeated for different catalysts- sodium hydroxide, potassium hydroxide and sodium methoxide for Sunflower and Cottonseed Oil samples. The results obtained are shown in table 2.

Table–2

Comparison of Percentage of oils through Single Stage and Two Stage Catalysis

Oil	Catalyst	% Conversion acid-base catalysis	%Conversion base catalysis
Sunflower	NaOH	99.45	99.1
	KOH	99.05	98.9
	CH_3ONa	98.95	98.89
Cottonseed	NaOH	99.25	98.95
	KOH	99.7	99.4
	CH_3ONa	98.89	98

Separation: On completion of the esterification process, two major products are obtained: esters (biodiesel) and glycerol. The glycerol phase is much denser than the biodiesel phase and settles at the bottom of the reaction vessel, allowing it to be separated from the biodiesel phase. Phase separation can be observed within 10 min and can be completed within several hours of settling. Both the biodiesel and glycerol are contaminated with an un-reacted catalyst, alcohol, and oil during the transesterification step. Soap that may be generated during the process also contaminates the biodiesel and glycerol phase. Therefore, crude biodiesel needs to be purified before use[21].

Table–3

Variations in density of Biodiesel with change in catalyst

Oil	Catalyst	Density
Sunflower	NaOH	0.8238
	KOH	0.8285
	CH_3ONa	0.8262
Cottonseed	NaOH	0.8231
	KOH	0.8292
	CH_3ONa	0.8269

Factors affecting yield of Biodiesel: Base catalyzed transesterification process is more sensitive to reaction conditions as compared to acid catalyzed. Some chief factors affecting the yield of reaction are as follows:

FFA content and Moisture: For alkali catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water causes a partial reaction change to saponification, which produces soap. The soap consumes the catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol. Hence, it is suggested that a pretreatment by acid catalyzed transesterification be done in order to reduce the effect of FFA and moisture, which also results in increase in yield. The results are shown in table 4.

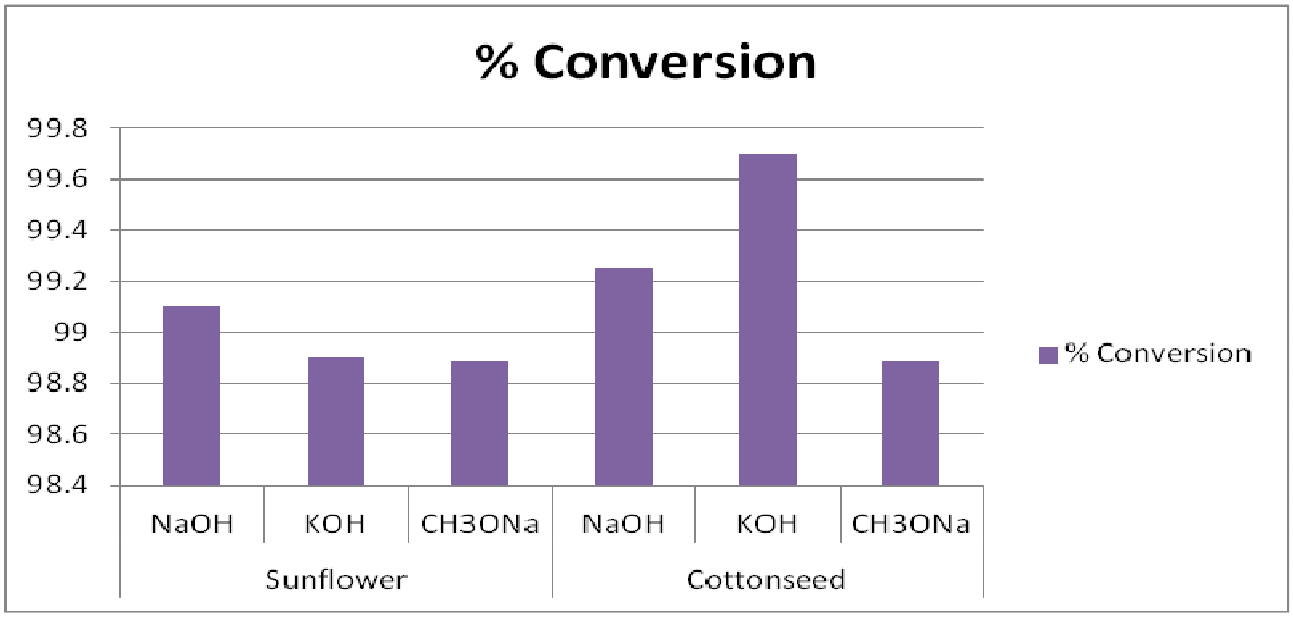

Figure-2
Comparison of Percentage Conversion of oil samples using Base Catalysis

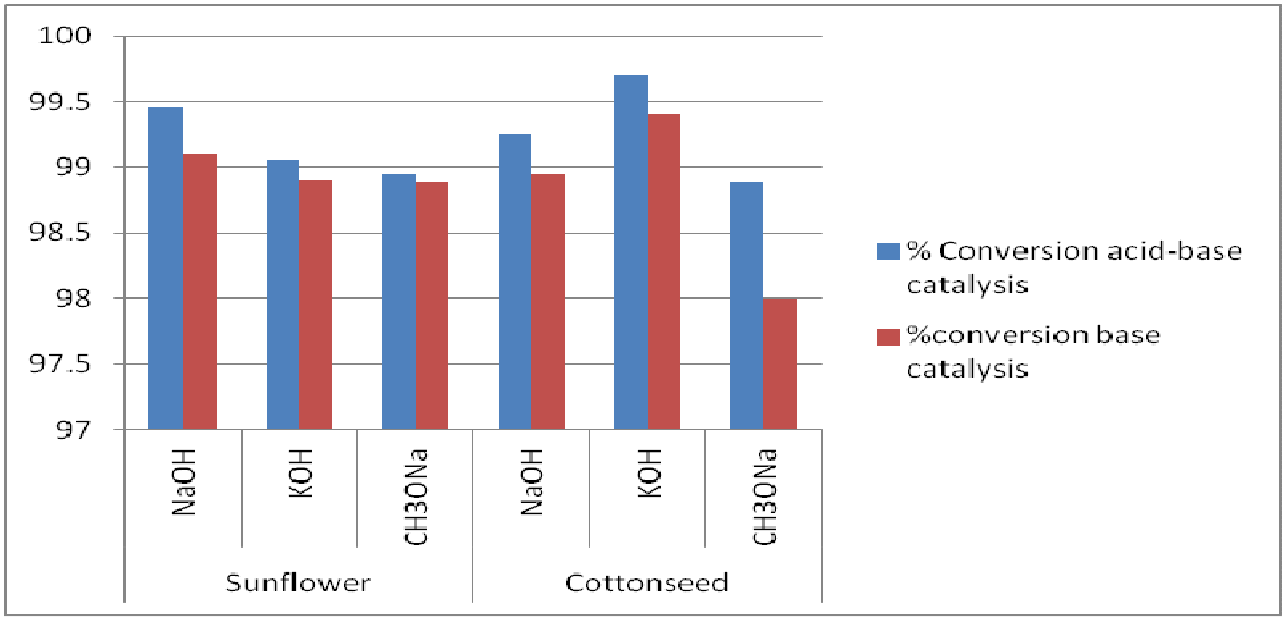

Figure-3
Comparison of Percentage Conversion of oils through Single Stage and Two Stage Catalysis

Table-4
FFA Content of the Used Oil Samples in Combination With Different Catalysts

Oil	Catalyst	%FFA
Sunflower	NaOH	1.116
	KOH	1.113
	CH_3ONa	0.974
Cottonseed	NaOH	1.112
	KOH	1.116
	CH_3ONa	1.127

Analysis of the Biodiesel product: Total glycerin analysis (TGA) is a test used to find the amount of glycerin content present in the test sample. The % content of the presence of glycerin in the sample is obtained as a result of the titration process carried out. From this value of % of total glycerin in the sample the value of amount of conversion can be calculated as per the formula:

Conversion = 100 - %TGA value (1)

Since % TGA value is the unconverted biodiesel content, this value on subtracting from 100 gives the value of the conversion. For this process of TG analysis, alcoholic KOH is mixed with the weighed sample. The mixture is heated and then sample is allowed to cool for 5-10 minutes, and then titrated against sodium thiosulphate solution. When the sample is cooled it is mixed with glacial acetic acid and chloroform which is then poured into flask filled with distilled water .This mixture is then allowed to settle for 6-7 hours. When the above mixture settles down properly, the denser chloroform content settles at the bottom, from the upper layer 100ml of solution is taken in which per iodine solution is added and then kept for 30 minutes. After this, iodometric titration is carried out.

In the sample solution KI solution is added which gives red color and is immediately titrated against sodium thiosulphate solution which gives yellow color. Then 2-3 drops of starch indicator is added which on further titration gives a colorless solution while the volume of titrant used is noted. The value of blank titration is obtained initially which is then used to calculate the % TGA value. The difference between the reading of blank titration and sample titration is used to calculate % TG value from the following formula:

$$\%TG = \left(\frac{(\text{difference in burette reading}) * (900) * (2.302) * (0.097)}{\text{actual weight of sample}}\right) * 100 \quad (2)$$

From this value, the conversion value is obtained from equation (1).

Results and Discussion

It was found that for both the feed stocks, the two stage process gave greater conversion to biodiesel as compared to base catalyzed process. Using methoxide as catalyst, the cottonseed oil gave a conversion of 98% in base catalyzed process as compared to 98.89% in two stage process. Similarly, in case of sunflower oil, greater conversion of 99.05% was found using KOH as catalyst in using two stage processes than that of 98.9% using only base catalyzed process. The FFA content also showed higher reduction in FFA content of 0.34% in case of two stage transesterification as compared to 1.1% in base catalyzed transesterification using KOH with cottonseed oil. Hence it can be concluded that the two stage acid-base catalyzed transesterification is more efficient in producing biodiesel as compared to base catalyzed trans-esterification alone.

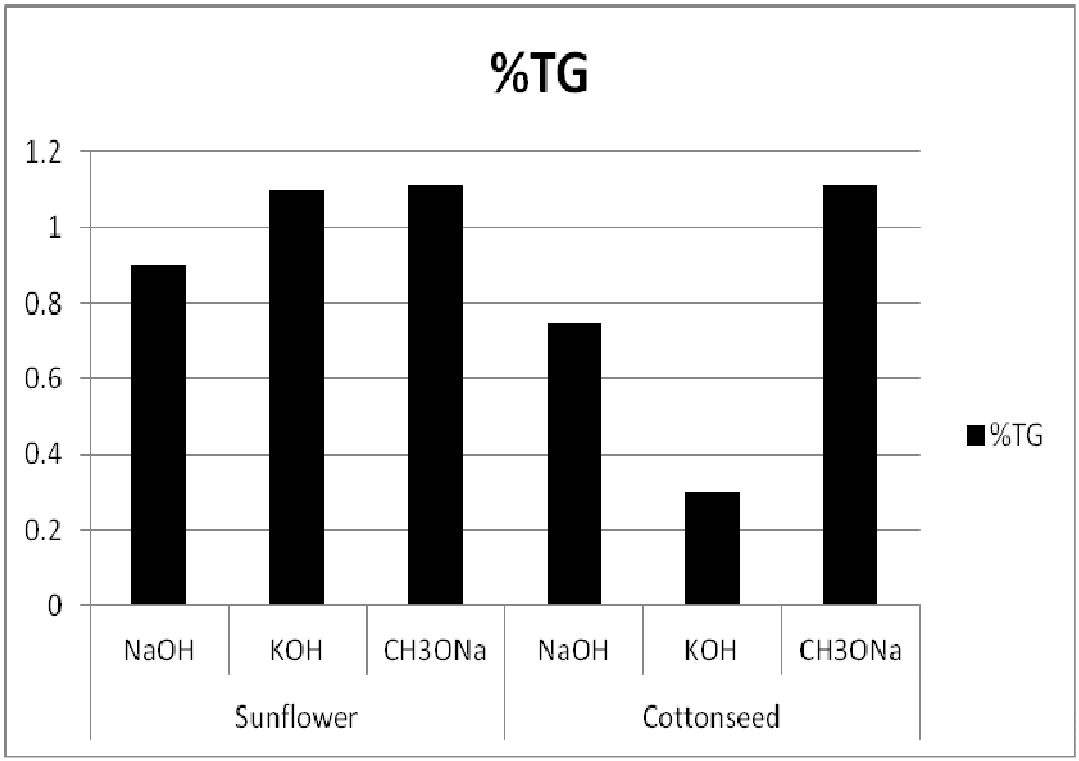

Figure-4
Total glycerin analysis of various biodiesel samples

Conclusion

Biodiesel is a clean-burning diesel fuel with a chemical structure of fatty acid alkyl esters. Of the various methods available for producing biodiesel, the alkali-catalyzed transesterification of vegetable oils and animal fats is currently the most commonly adopted method[3,4]. However, when the raw materials (oils or fats) contain a high percentage of free fatty acids or water, the alkali catalyst will react with the free fatty acids to form soaps and the water can hydrolyze the triglycerides into di-glycerides and form more free fatty acids. Therefore, after refining the raw materials, the acidic feedstocks should be pre-treated to inhibit the saponification reaction[17]. Hence, the oils are undertaken the process of Acid catalyzed alcoholysis, where FFA is decreased by esterification, and alcoholysis occurs. The transesterification reaction requires an alcohol as a reactant and a catalyst. The most commonly used alcohol is methanol while sodium hydroxide and potassium hydroxide are the most commonly used catalysts. During the reaction, glycerol will be produced as a by-product. The separation may take up several hours, but can be accelerated using a centrifuge. Because of its numerous industrial applications, the crude glycerol should be refined with purity higher than 99% to make it usable. The biodiesel produced contains many impurities and hence needs further processing.

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