
“ECO- FRIENDLY PROCESS FOR THE PREPARATION OF BIO DIESEL USING SUPPORTED SOLIID ACID CATALYST”

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My family & Department of Industrial Chemistry

*Without their love, support and constant
encouragement
this would not have been possible.*

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DECLARATION

We undersigned, hereby declare that the work assimilated in the dissertation thesis entitled “ECO- FRIENDLY PROCESS FOR THE PREPARATION OF BIO DIESEL USING SUPPORTED SOLIID ACID CATALYST USING B-ADSA-SI” has been carried out by us at Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India, under the supervision and Guidance of **Dr. Mehul L. Savaliya, Assistant Professor, Faculty of Science, Department of Industrial Chemistry, Atmiya University, Rajkot, Gujarat, India.**

To the best of our knowledge and belief, the work included in this thesis is quite original and has not submitted to any other Institution or University for the award of any degreeeither in this or any other form.

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Abstract:

Biodiesel production was carried out by using cotton seed oil and catalyst B-ADSA-Si (B-Alanine di sulfonic acid Silica). To characterize the biodiesel and catalyst B-ADSA-Si produced, different standard tests were carried out. Besides standard tests, FTIR spectroscopy of biodiesel and catalyst was also performed. Results reveal that characteristics of biodiesel depend on the feed stock and characteristic of catalyst. The best combination of properties is obtained from Cotton seed oil-based Biodiesel. Biodiesel produced from waste vegetable oil was also found very convenient to be used and properties were comparable to an ordinary diesel fuel.

1.0 Introduction

Biodiesel falls in the category of the biofuels. Biofuels were introduced decades ago to overcome the environmental pollution caused by the use of ordinary fuels i.e. Sulphur and heavy metals oxide. Biodiesel is free of lead, contains almost no sulfur or aromatics and substantially reduces emissions of unburned hydrocarbons, carbon monoxide and particulate matter (soot), which have been linked to respiratory disease, cancer and other adverse health conditions. It has been found that NO_x in exhaust is very high if biodiesel is used. However it can be controlled and reduced by adjusting the engine timing. Some types of catalyst exhaust tips are also developed to capture the NO_x in the exhaust system, while CO_x production rate is very low as compared to ordinary diesel fuel. Also there are no emissions of the sulfur compounds. Sulfur compounds cause acid rain which is the main cause of soil erosion. Another reason for the research on biofuels is to meet the world's requirement of fuel. Fossil fuel reserves are decreasing due to increase in fuel demands. The basic idea of researches is to go for alternative which yields as good efficiency as fossil fuels and economical as well. Many kinds of biofuels are used these days, among them ethanol based fuel is used as an alternative of gasoline and biodiesel is used as an alternative of diesel fuels. Biodiesel is the cleaner fuel and it requires no engine modification. It can directly be used in diesel engines. It has also been reported that diesel engines run longer with biodiesel. 75% less pollution is caused by biodiesel compared to ordinary diesel (Canakc et Journal of Quality and Technology Management al.,2006). The most important is that biodiesel can be produced from any vegetable oil including waste vegetable oil (Zhang et al.,2003). Biodiesel can be blended with ordinary diesel with no additive required for making them miscible. Better lubrication is achieved by using biodiesel in the engine (Schumacher et al., 2001). As far as fuel economy is concerned, biodiesel's fuel economy is same as conventional diesel. Biodiesel is environmental friendly and is biodegradable. Chemical reaction for the manufacturing of biodiesel using vegetable oil is as follows:

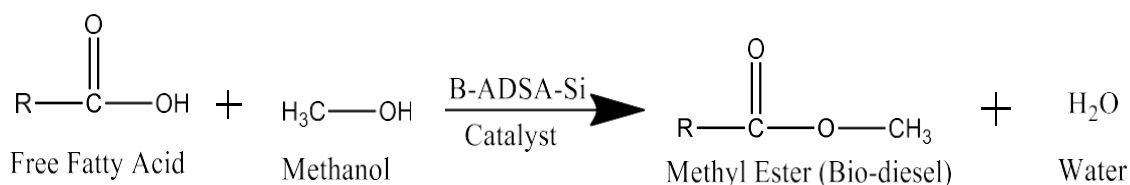


Figure .1 Reaction of FAME(Bio-diesel)

This increase of energy demand has been supplied by the use of fossil resources, which caused the crises of the fossil fuel depletion, the increase in its price and the serious environmental impacts as global warming, acidification, deforestation, ozone depletion, Eutrophication and photochemical smog. As fossil fuels are limited sources of energy, this increasing demand for energy has led to a search for alternative sources of energy that would be economically efficient, socially equitable, and environmentally sound. Two of the main contributors of this increase of energy demand have been the transportation and the basic industry sectors, being the largest energy consumers. The transport sector is a major consumer of petroleum fuels such as diesel, gasoline, liquefied petroleum gas(LPG) and compressed natural gas (CNG)'(Demirbas, 2006). Demand for transport fuels has risen significantly during the past few decades. (IEA, 2008). The demand for transport fuel has been increasing and expectations are that this trend will stay unchanged for the coming decades. In fact, with a world-wide increasing number of vehicles and a rising demand of emerging economies, demand will probably rise even harder. Transport fuel demand is traditionally satisfied by fossil fuel demand. However, resources of these fuels are running out, prices of fossil fuels are expected to rise and the combustion of fossil fuels has detrimental effects on the climate. The expected scarcity of petroleum supplies and the negative environmental consequences of fossil fuels have spurred the search for renewable transportation biofuels' (Hil , Nelson ,Tlman, Polasky& Tiffany, 2006).Biofuels appear to be a solution to substitute fossil fuels because, resources for it will not runout (as fresh supplies can be regrown), they are becoming cost wise competitive with fossil fuels, they appear to be more environmental friendly and they are rather accessible to distribute and use as applicable infrastructure and technologies exists and are readily available. Forecasts are that transport on a global scale will increase demand for conventional fuels with up to a maximum annual growth of

1.3% up to 2030. This would result in a daily demand of around 18.4 billion litres (up from around 13.4 billion litres per day in 2005) (The Royal Society, 2008). Conventional fuels, however, are predicted to become scarce (The Royal Society, 2008) as 'petroleum reserves are limited' (Demirbas, 2006), for this reason these fuels are set to become increasingly costly in the coming decades. Renewable fuels, made from biomass, 'have enormous potential and can meet many times the present world energy demand' (IEA, 2008). 'Biomass can be used for energy in several ways; one of these is the conversion into liquid or gaseous fuels such as ethanol and bio-diesel for use in mobile source combustion' (Marshall, 2007). In fact 'global demand for liquid biofuels more than tripled between 2000 and 2007. And future targets and investment plans suggest strong growth will continue in the future' (IEA, 2008). The potential of biofuels appears to be enormous from an economical, political and environmental perspective. Speaking in terms of advantages, much heard is that they, as an alternative fuel, could solve several issues as the increasing energy prices worldwide, the increasing need of energy imports, the negative environmental consequences of fossil fuel combustion and the security of national energy supply for many countries.

Biofuels appear to be more environment friendly in comparison to fossil fuels considering the emission of greenhouse gases when consumed. Examples of those gases are carbon-dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). Those gases pose risks as they tend to warm the earth's surface'. The energy content of biofuels differs from conventional fuels. Total energy output per liter of biofuel is determined by the feed stock used, region where the feedstock is grown and production techniques applied. Biodiesel, for example, provides energy contents of biodiesel and bio-ethanol. Its energy contents are 87% of those of diesel. Bioethanol has an energy ratio compared to gasoline of 1.42 (67% of gasoline)'. The amount that is similar to the amount of energy content of one litre gasoline is referred to as gasoline equivalent. Biodiesel production is a very modern and technological area for researchers as an alternative fuel for diesel engines because of the increase in the petroleum price, its renewability and the environmental advantages. Biodiesel can be produced from renewable sources such as vegetable oil, animal fat and used cooking oil. Currently, the cost of biodiesel is high as compared to conventional diesel oil because most of the biodiesel is produced from pure vegetable oil.

Extensive use of edible oils may cause other significant problems such as starvation in developing countries. However, the cost of biodiesel can be reduced by using low cost feedstock such as animal-fat and used cooking oil. It is estimated that the cost of biodiesel is approximately 1.5 times higher than that of diesel fuel due to the use of food grade oil for biodiesel production. The term “waste vegetable oil” (WVO) refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. Waste vegetable oil arises from many different sources, including domestic, commercial and industrial. Waste vegetable oil is a potentially problematic waste stream which requires to be properly managed. The disposal of waste vegetable oil can be problematic when disposed, incorrectly, down kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies. Properties of degraded used frying oil after it gets into sewage system are conducive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent or pollutes water ways. The use of used cooking oil as feedstock reduces biodiesel production cost by about 60–70% because the feedstock cost constitutes approximately 70–95% of the overall biodiesel production cost. It is reported that the prices of biodiesel will be reduced approximately to the half with the use of low cost feedstock. Moreover used cooking oils can be a workable feedstock for biodiesel production as they are easily available. The use of non-edible plant oils when compared with edible oils is very significant because of the tremendous demand for edible oils as food, and they are far too expensive to be used as fuel at present. The land use for growing oilseeds as feedstocks for the biodiesel production competes with the use of land for food production.

2.0 Literature review:

Factor affecting the production of biodiesel from waste cooking oil

Effect of molar ratio of alcohol

Molar ratio of alcohol plays a vital role in biodiesel yield (Leung and Guo, 2006; Zhang *et al.*, 2003; Ma and Hanna, 1999; Freedman *et al.*, 1986). Normally the transesterification reaction requires 8 mol of alcohol for one mol of fatty acid to three mol of fatty acid ester and three mol of water. So the yield of biodiesel depends upon the concentration of alcohol up to certain concentration. However further increase of alcohol content does not increase the yield of biodiesel but it also increases the cost of alcohol recovery (Leung and Guo, 2006). In addition to this the ratio of alcohol content may vary with catalyst used, i.e. when we use alkali catalyst the reaction requires 6:1 ratio of alcohol to catalyze the transesterification of oils or fats (Zhang *et al.*, 2003; Freedman *et al.*, 1986). In case the oil samples contain high free fatty acid (FFA) such reaction does not respond to acid catalyst. In that situation acid catalyst will be effective to catalyze the reaction and the reaction requires higher amount of alcohol than acid catalyst. This is due to the fact that acid catalyst tolerates the FFA content and water content present in the oil samples.

Effect of water and FFA contents:

The water and Free Fatty Acid (FFA) contents are critical factors for transesterification reaction. Acid-catalyzed transesterification reaction requires water free and high acid value (< 1) raw materials (Demirbas, 2009) for biodiesel production. If the oil samples have high FFA content (more than 1%) then the reaction requires more acid catalyst to neutralize the FFA. Presence of water gives greater negative effect than that of FFAs because water can cause soap formation and frothing which can cause increase in viscosity. In addition formation of gels and foams hinders the separation of glycerol from biodiesel (Demirbas, 2009 and 2005). Water and FFA also leads to the reduction of

by Kusdiana and Saka (2004) which was compared to alkaline and acid-catalyzed method. It may be noted that water has less influence in supercritical methanol method

Reaction time:

Freedman et al (1986) observed the increase in fatty acid esters conversion when there is an increase in reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol and oil. After that the reaction proceeds very fast. However the maximum ester conversion was achieved within < 8hr. Further increase in reaction time does not increase the yield product i.e. biodiesel/mono alkyl ester (Leung and Guo, 2006; Alamu *et al.*, 2007). Besides, longer reaction time leads to the reduction of end product (biodiesel) due to the reversible reaction of transesterification resulting in loss of esters as well as soap formation (Eevera *et al.*, 2009; Ma *et al.*, 1998).

Reaction temperature:

Reaction temperature is another important factor that will affect the yield of biodiesel. For example higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. However, Leung and Guo (2006) and Eevera *et al.*, (2009) found that increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides. Usually the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of optimal reaction temperature may vary from 60°C to 65°C depends upon the oils or fats used (Leung and Guo, 2006; Ma and Hanna, 1999; Freedman *et al.*, 1984).

Catalyst concentration:

Biodiesel formation is also affected by the concentration of catalyst. we used catalyst for biodiesel production is B-Alanine Di Sulphonic Acid (BADSA) However, Freedman found that the sodium methoxide would be more effective because mixing of sodium hydroxide with methanol produce little amount of water which inhibit the formation of end product

(Biodiesel) due to the hydrolysis reaction (Guo, 2005). This is one of the reason for mixing of catalyst with methanol first and then added to the oil or fats. In addition to this when the concentration of catalyst is increases with oil samples, the conversion of triglycerides into biodiesel is also increases. On the other hand insufficient amount of catalyst leads to the incomplete conversion of triglycerides into fatty acid esters (Leung and Guo, 2006; Guo, 2005). However, optimal product yield (biodiesel) was achieved when the concentration of NaOH reaches 1.5 wt.% at the same time further increase of catalyst concentration proved to have negative impact on end product yield. Because addition of excess amount of alkali catalyst react with triglycerides to form more soap (Leung and Guo, 2006; Gabelman and Hwang, 1999).

Agitation speed:

Agitation speed plays an important role in the formation of end product (mono alkyl ester or biodiesel), because agitation of oil and catalyst mixture enhances the reaction. For example the mixing intensities chosen were 200 rpm, 400 rpm, 600 rpm and 800 rpm for 60 min while other parameters were kept constant. At 400 rpm higher conversion of end product were obtained. Because, lower stirring speed shows lower product formation. On the other hand higher stirring speed favors formation of soap. This is due to the reverse behavior of transesterification reaction (Knothe *et al.*, 2005; Demirbas, 2008; Eevera *et al.*, 2009; Rashid and Anwar, 2008).

2.2.0 Biodiesel synthesis under supercritical methanol conditions:

Recent increases in liquid fossil fuel prices and uncertainties in its availability have stimulated interest in renewable liquid fuels. One of these attractive fuels is biodiesel, which can be made from triglycerides of various biomass sources such as plant oils (e.g., corn, palm) (Rathore & Madras, 2007), animal fats (Marulanda, Anitescu, & Tavlarides, 2010b), rapeseed oil (Bajaj, Lohan, Jha, & Mehrotra, 2010; Saka & Kusdiana, 2001), soybean oil (He et al., 2007; He, Wang, & Zhu, 2007; Silva et al., 2007), and microalgae oil (M. F. Demirbas, 2010). The chemical process to produce biodiesel is called transesterification in which triglycerides are reacted with methanol or ethanol to give methyl or ethyl esters of fatty acids and glycerol.

Commercial biodiesel is currently produced through transesterification reactions using acid or alkali solutions as catalysts. However, these conventional processes require a high purity of feedstock with very low free fatty acid and water content. Furthermore, the complexity of separation steps to remove catalyst, glycerol and excess alcohol from biodiesel drives up biodiesel cost (Warabi, Kusdiana, & Saka, 2004). Another enzyme-catalyzed process is more tolerant of impurities and has simple post reaction separations, but is relatively expensive to implement (Bajaj et al., 2010).

A catalyst-free method for the transesterification of plant oils and animal fats at supercritical alcohol conditions has been proposed (A. Demirbas, 2002; A. Demirbas, 2007; Kusdiana & Saka, 2001; Marulanda, Anitescu, & Tavlarides, 2010a; Saka & Kusdiana, 2001). The non-catalytic process has significant advantages over conventional catalytic methods to treat various low-quality feedstocks. Transesterification of nonpolar triglycerides with a polar alcohol is usually a heterogeneous, two liquid phase reaction at conventional processing conditions (Madras et al., 2004). This process characteristic is due to incomplete miscibility of the nonpolar and polar reactants. According to mixing ratio, at appropriate temperatures and pressures, the

methanol and triglycerides binary system can mix and form a homogeneous phase which will accelerate the transesterification reactions due to removal of the oil-alcohol interphase that limits mass transfer and hence reaction rates (Srivastava & Prasad, 2000).

Furthermore, separating biodiesel product from glycerol byproduct is simple, because the products are immiscible at ambient temperature and no soap or other side products need to be removed (Pinnarat & Savage, 2008).

There have been several studies of transesterification under supercritical methanol conditions. Reaction temperatures of 300 to 350 °C and alcohol-to-oil molar ratio of 42 were often suggested to be the best set of conditions for non-catalytic biodiesel production (Hawash, Kamal, Zaher, Kenawi, & El Diwani, 2009). It was considered that large excess of alcohol is required to shift the reaction equilibrium toward biodiesel product. However, a major drawback that hampers the industrial application of this method is the extremely high alcohol-to-oil molar ratio (i.e., 42:1) which will cause additional preheating, pumping, and separation costs (Marulanda, Animescu, & Tavlarides, 2010a). Some recent work shows that non-catalytic biodiesel synthesis can be performed at much lower molar ratios (e.g. 9:1 and 11:1) and higher temperatures (e.g. 385 °C) (Animescu, Deshpande, & Tavlarides, 2008; Marulanda, Animescu, & Tavlarides, 2010a)

In order to achieve a homogeneous reaction phase to avoid other issues such as interphase mixing and mass transfer, the pressure-temperature relationships of triglyceride-alcohol mixtures were studied by using Peng Robinson equation of state. It was found that higher alcohol-to-oil ratios actually reduce the critical temperature of the reactant mixture.

One major concern about transesterification in supercritical methanol is the extent to which biodiesel components decompose at the high reaction temperatures. The decomposition of methyl esters was assumed to occur at temperatures above 350 °C. From the recent study, decomposed products such as smaller molecular compounds from unsaturated and saturated FAMEs, and glycerol will improve some biodiesel qualities such as volatility, cold flow properties and viscosity (Marulanda, Animescu, & Tavlarides et al., 2010b).

Materials and Methods :

Raw Materials:-

The raw materials used for the production of biodiesel are waste vegetable oils, methanol/Ethanol, Chloro sulfonic acid, B-Alanine, silica gel, etc.

- **Waste Vegetable Oil:** waste vegetable (waste of cottonseed) oil was obtained from –Gondal.
- **Catalyst:** It was prepared in lab. By using chloro-sulphonic acid and B-Alanine. Resulting catalyst powder formed mixed with silica gel.
- **Solvent:** The solvent used for synthesis of bio-diesel are methanol and ethanol.

Preparation of Catalyst:-

B-Alanine Di-sulphonic acid is taken 13.87gm in RBF and kept under 65° c temperature controlled magnetic stirrer. to this chloro sulphonic acid is added 10ml. The reaction carried out at 0-5°C. after completion of reaction wash with solvent the resulting reaction mass dried and mixed with silica gel. A figure (2) of preparation of catalyst shown below.

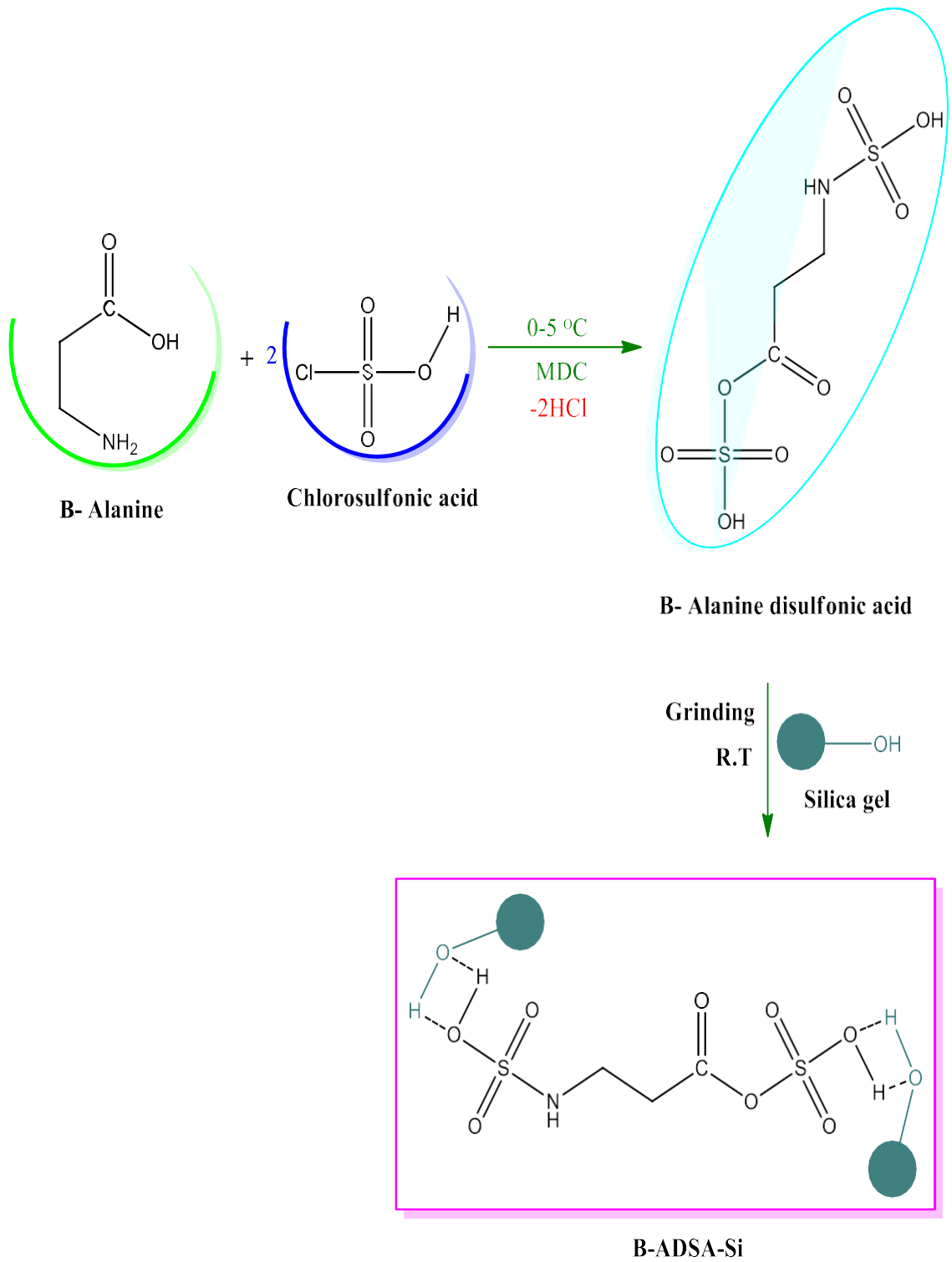


Figure-2 Synthesis of B-ADSA-Si



Figure .3 Image of catalyst preparation

Bio-diesel production

Methanol and Catalyst were mixed in a closed CSTR. Waste vegetable oil was filtered to remove inorganic residues and added into a CSTR. The mixture was heated up to 60-70 °C to remove the water contents present in the oil. The temperature was maintained below the boiling temperature of methanol for 40-60 min. After completion of the reaction, binary mixture (Biodiesel and Glycerol) was produced. Biodiesel and glycerol have different specific gravities and separated using gravity Filtration. The biodiesel was washed with hot water till no more alkali was found. Recovered alkali could be recycled while glycerol was the byproduct of the process.

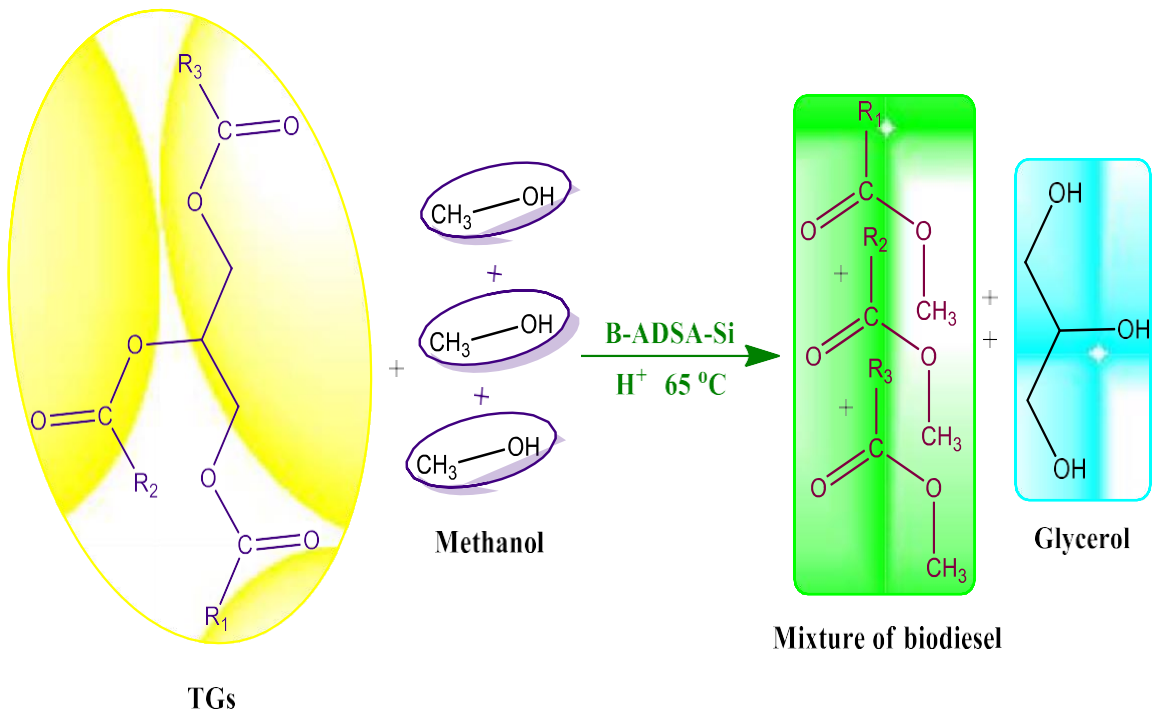


Figure 4: Synthesis of Bio-diesel via trans-esterification

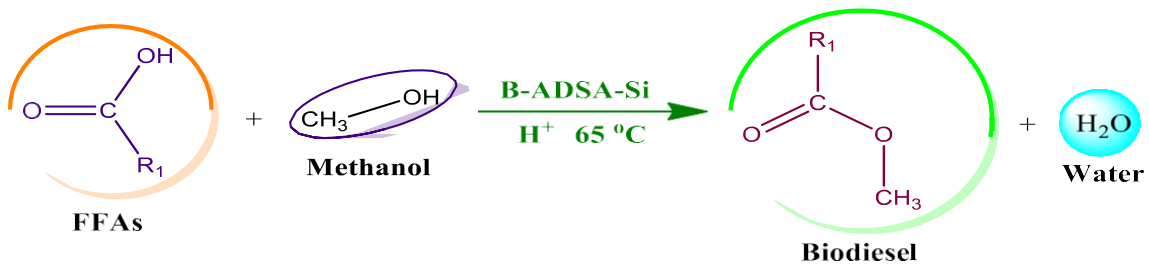


Figure 5: Synthesis of Bio-diesel via esterification

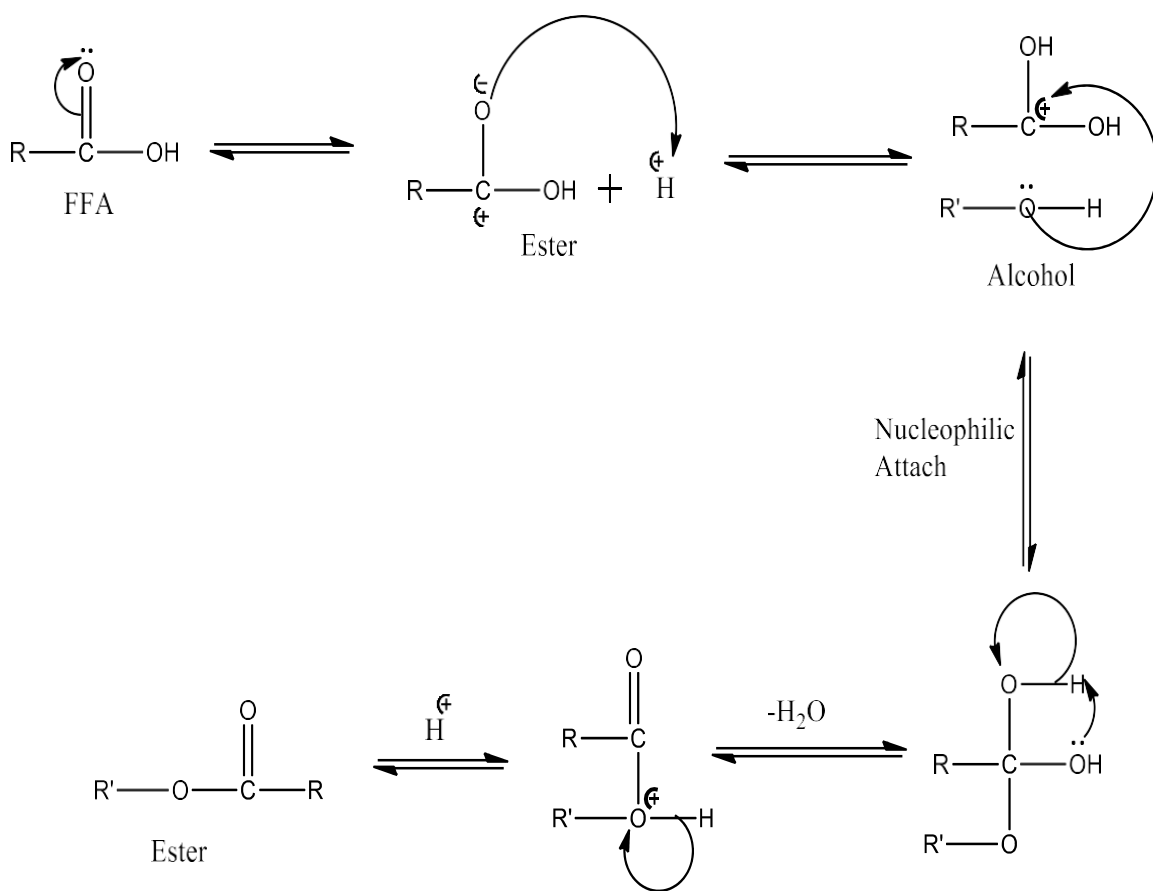


Figure .5 Mechanism of FAME Synthesis



Figure .7 Image of FAME (Bio-diesel) Synthesis

Transesterification of vegetable oil

Transesterification is the process of converting the fatty acids to form fatty acid esters (FAE) and free glycerol [Meher, et al., 2006; Morrison and Boyd, 2005; Abhullah, et al. 2007]. Fatty acid esters commonly known as biodiesel can be produced in batches or continuously by transesterifying free fatty acid such as animal fat or vegetable oil with lower molecular weight alcohols in the presence of an heterogeneous acid catalyst. The transesterification process of converting vegetable oils to biodiesel. The "R" groups are the fatty acids, which are usually long chain hydrocarbons in length. The large-vegetable oil molecule is reduced to about 1/3 its original size, lowering the viscosity making it

similar to diesel fuel. The resulting fuel operates similar to diesel fuel in an engine. The reaction produces three molecules of an ester fuel from one molecule of vegetable oil.

A free fatty acid is allowed to react with an excess of an alcohol such as ethanol or methanol, and this alcohol takes the place of the ester linkage to glycerol, yielding three fatty acid esters of the new alcohol and glycerol. Here three molecules of one alcohol are replacing glycerol, another alcohol, in the triglyceride.

Vegetable oils have to undergo the process of transesterification to be usable in internal combustion engines. Biodiesel is the product of the process of trans esterification. Trans esterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. Alcohol combines with the triglycerides to form glycerol and esters. A catalyst is usually used to improve their action rate and yield. Since the reaction is reversible, excess alcohol is required to shift the equilibrium to the product side. Among the alcohols that can be used in the trans esterification process are methanol, ethanol, etc.

Formula for calculation:-

Biodiesel Yield (%) estimation:

The biodiesel yield (%) has been calculated using acid value estimation of waste Cotton seed oil and biodiesel as given in equation

$$\% \text{FFA Conversion (ppm)} = \frac{\text{AV}_i - \text{AV}_F}{\text{AV}(I)} \times 100 \quad (1)$$

Where: FFA –Free Fatty Acid,

AV_i- Acid value initial,

AV_F- Acid value final

The determination of free fatty acid:-

10 grams of the filtered rapeseed oil was put in 250 ml Erlenmeyer flask, and then 50 ml of diethyl ether and ethanol were added. Stirring was done until the oil was completely dissolved in the solvent mixture. A burette was filled with about 10-15 ml of ethanolic KOH solution, 3-4 drops of phenolphthalein (1% in ethanol) and a magnetic stir bar were given to the solution in the Erlenmeyer flask, and then the KOH solution was added to the mixture (mixture titration). When the color of the mixture changed, the mixture was left another 30 seconds to be sure of the new color. - A formula was used to determine the concentration of free fatty acid i

$$\text{Waste vegetable oil: \% free fatty acid} = a * \text{avg.mol.wght.} / 10 * E$$

Where: a: volume [ml] of KOH * 0.1 [mol / ml]

avg.mol.wght.: 314 g / mol E: initial weight in gram

5.0 Results and Discussion

Table1. the result of %FFA Conversion with different reaction parameters

Sr No.	O:M Molar ratio	Reaction Time (hr)	% W/W Catalyst	% Free Fatty Acid
1	1:9	6	5%	71.10%
2	1:9	7	5%	65.5%
3	1:9	8	5%	61.51%
4	1:9	9	5%	38.5%
5	1:9	10	5%	38.5%
6	1:10	6	5%	24.3%
7	1:10	7	5%	21.5%
8	1:10	8	5%	19.2%
9	1:10	9	5%	14.2%
10	1:10	10	5%	11.03%
11	1:11	6	5%	11.02%
12	1:11	7	5%	8.2%
13	1:11	8	5%	7.3%
14	1:11	9	5%	6.2%
15	1:11	10	5%	5.4%
16	1:12	6	5%	5.3%
17	1:12	7	5%	5.3%
18	1:12	8	5%	7.3%
19	1:12	9	5%	5.04%
20	1:12	10	5%	5.04%
21	1:11	10	1%	5.01%
22	1:11	10	2%	6.3%
23	1:11	10	3%	7.88%
24	1:11	10	4%	8.99%
25	1:11	10	6%	9.12%

It has been found from the experimental result; the 38.5% biodiesel yield has been obtained with 1:9 oil molar ratio, 5% (w/w) catalyst, 65⁰c reaction temperature and 6hr reaction time. However, it has also been obtained from the experimental result, the 11.03% biodiesel yield has been obtained with 1:10 oil molar ratio, 5%(w/w) catalyst, 65⁰c reaction temperature and 10hr reaction timer. However, ithas been found from the experimental result; the 5.4% biodiesel yield has been obtained with 1:11 oil molar ratio, 5% (w/w) catalyst, 65⁰c reaction temperature and 8hr reaction time. It has been found from the experimental result; the 5.1% biodiesel yield has been obtained with 1:12 oil molar ratio, 2% (w/w) catalyst, 65⁰c reaction temperature and 10hr reaction time. It has been found from the experimental result; the 5.01% biodiesel yield has been obtained with 1:11 oil molar ratio, 1% (w/w) catalyst, 65⁰c reaction temperature and 10hr reaction time. It has been found from the experimental result; the 6.3% biodiesel yield has been obtained with 1:11 oil molar ratio, 2% (w/w) catalyst, 65⁰c reaction temperature and 10hr reaction time. It has been found from the experimental result; the 7.88% biodiesel yield has been obtained with 1:11 oil molar ratio, 3% (w/w) catalyst, 65⁰c reaction temperature and 10hr reaction time. It has been found from the experimental result; the 8.99% biodiesel yield has been obtained with 1:11 oil molar ratio, 4% (w/w) catalyst, 65⁰c reaction temperature and 10hr reaction time. It has been found from the experimental result; the 9.12% biodiesel yield has been obtained with 1:11 oil molar ratio, 6% (w/w) catalyst, 65⁰c reaction temperature and 10hr reaction time.

Spectral characterization:-

FT-IR analysis of B-Alanine Di sulfonic Acid –Silica (B-ADSA-Si) :

FT-IR spectrum of B-Alanine di sulfonic acid silica confirm with the presence of 3595.43 cm^{-1} (Si-OH stretching , H-Bond) , 3039.91 cm^{-1} (NH-Stretching) , 1874.87 cm^{-1} (indicates the presence of molecule of water) , 1720.56 cm^{-1} (SO_2 asymmetrical vibration provided by presence of SO_3H group) , 1049.31 cm^{-1} (c=s stretching) respectively. FTIR Spectrum of B-Alanine di sulfonic acid silica in fig 8.

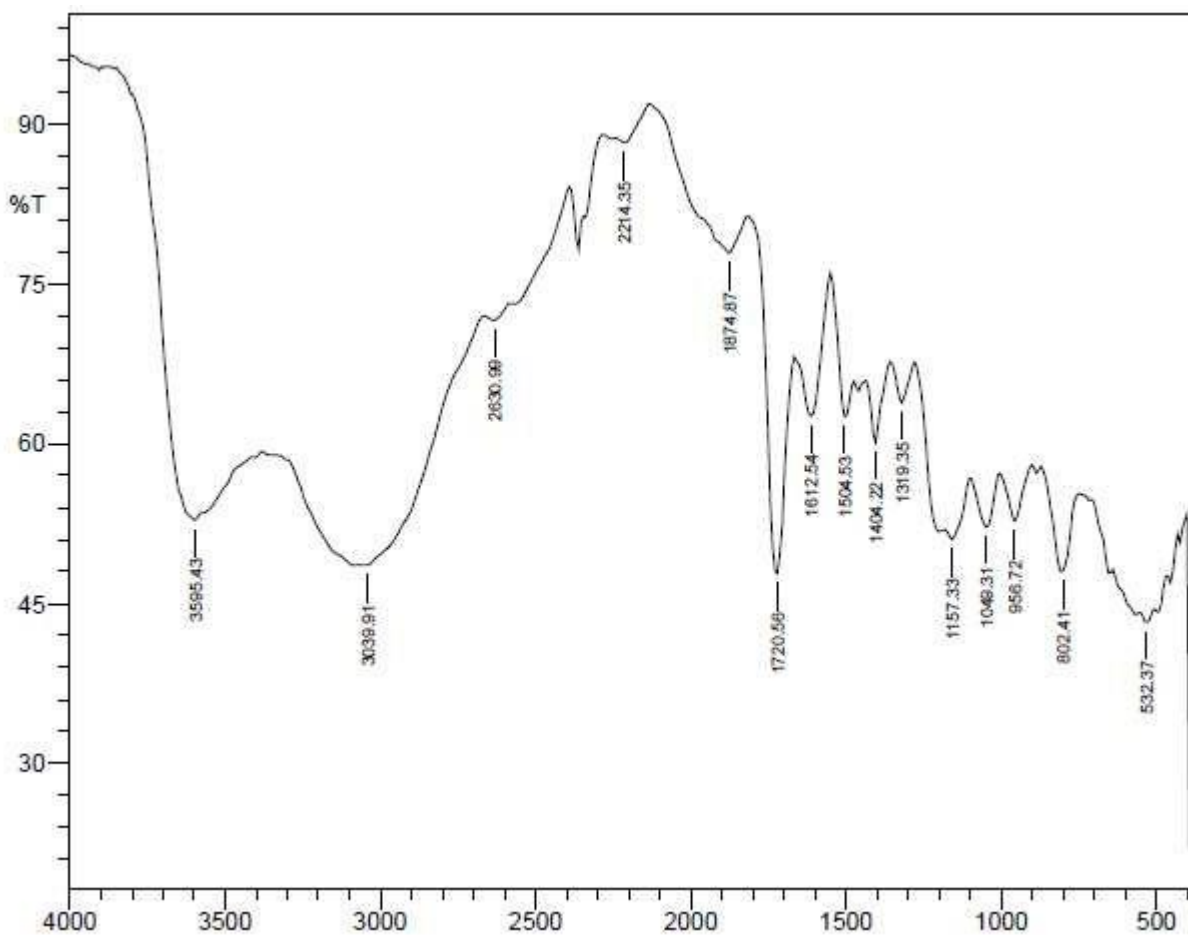


Figure 8 FT-IR of B-ADSA-Si catalyst

FT IR analysis of Cottonseed-oil (CO).

FT IR Spectrum of Cottonseed oil is confirmed with the presence of 2947.33 cm^{-1} (CH_3 stretching), 2870.17 cm^{-1} (CH_2 stretching), 1751.42 cm^{-1} ($\text{C}=\text{O}$) 1473.66 cm^{-1} (CH bending), 1118.75 cm^{-1} ($\text{C}-\text{O}$) and 740.69 cm^{-1} (CH rocking) respectively. FTIR spectrum of Ground nut oil is given figure 9.

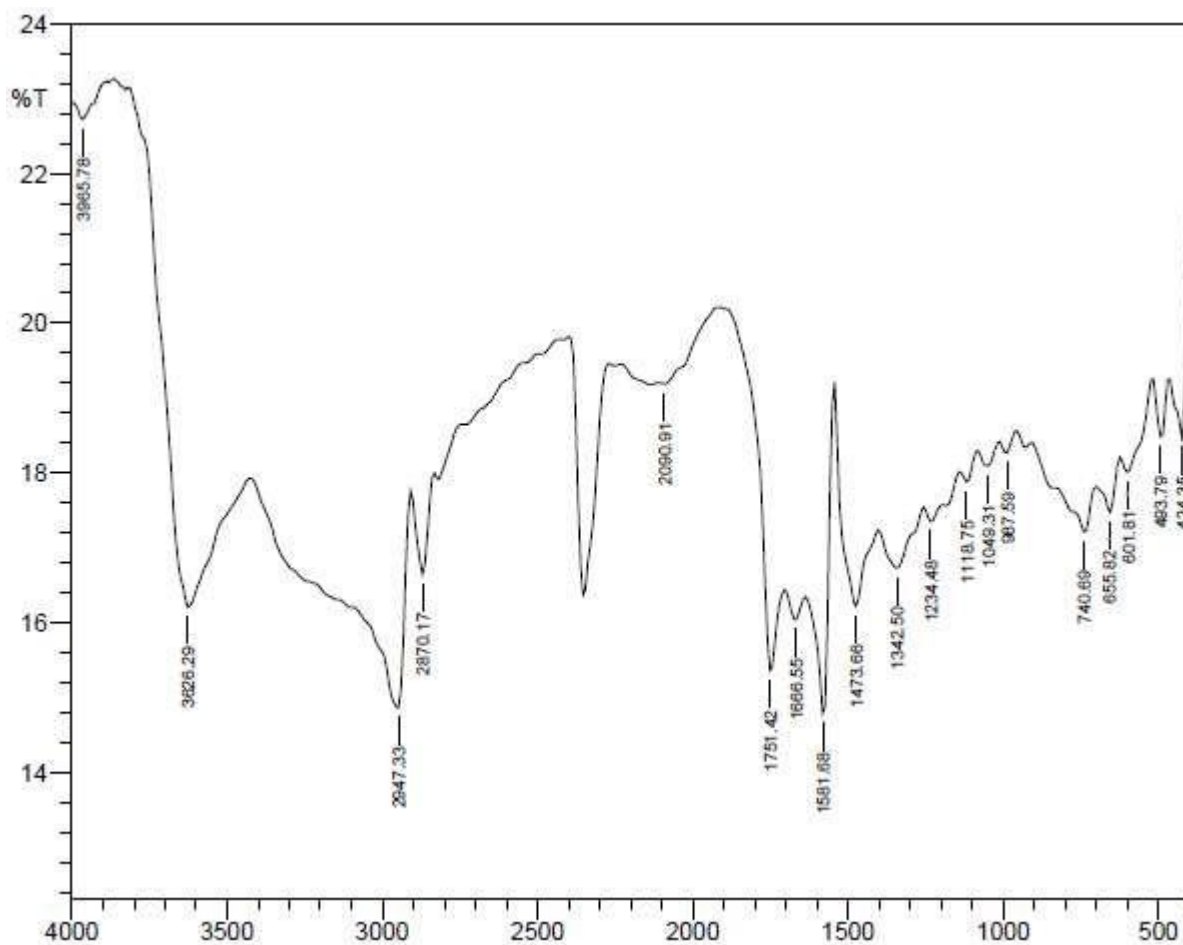


Figure .9 FT-IR of waste Cottonseed Oil

FT-IR analysis of synthesized Cottonseed Oil Bio-diesel :

FTIR spectrum of synthesized Cottonseed oil bio diesel is confirmed with the presence of 2931.90 cm^{-1} (CH₃ stretching) , 2854.74 cm^{-1} (CH₂ stretching) , 1735.99 cm^{-1} (C=O) , 1450.52 cm^{-1} (CH bending) , 1103.32 cm^{-1} (C-O) & 709.83 cm^{-1} (CH-rocking) respectively . FT-IR spectrum of cotton seed bio diesel is given in fig 10.

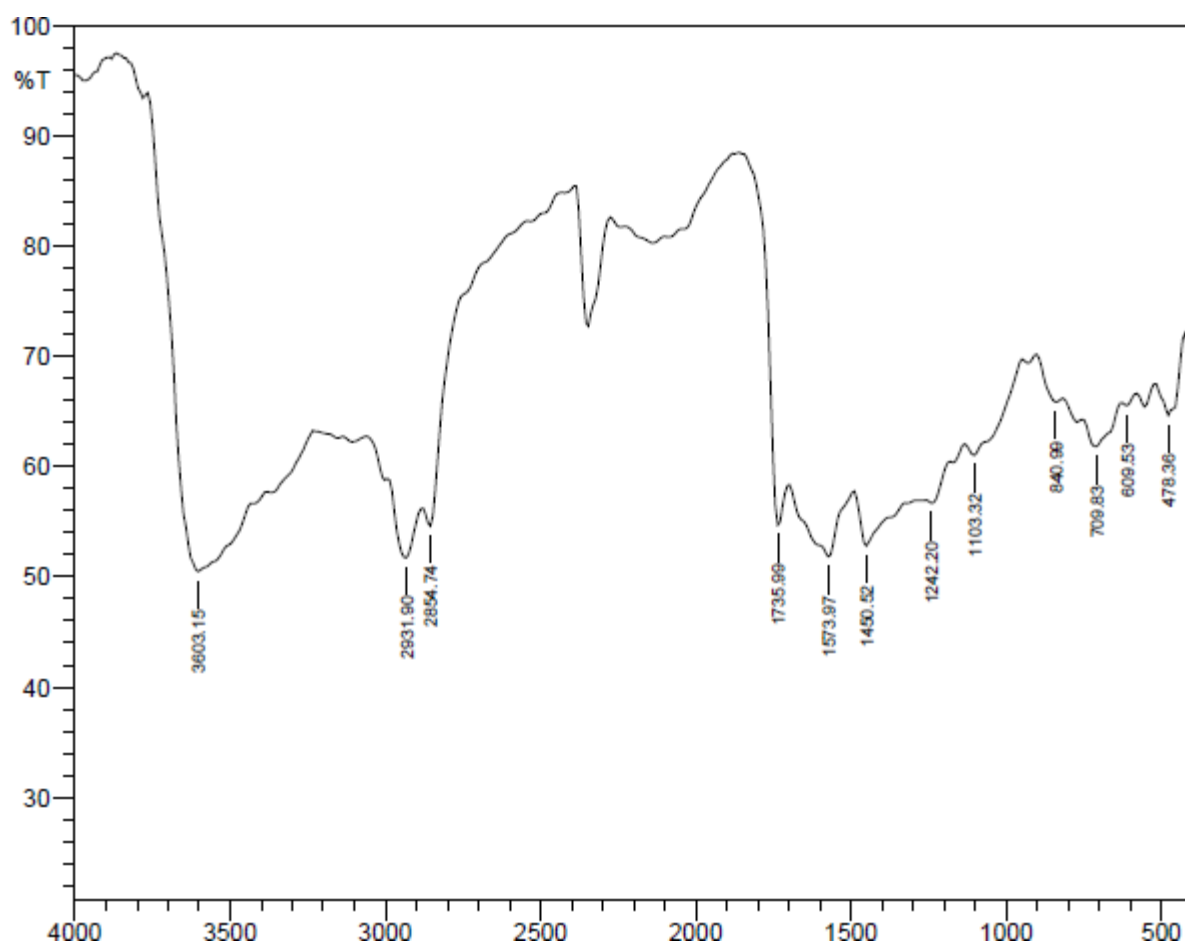


Figure .10 FT-IR of waste Cottonseed Bio-Diesel

Physical properties of biodiesel:

Table 2: some properties of cottonseed oil biodiesel

Properties	Biodiesel
Density(g/cm ³)	0.895
Specific gravity	0.896
Cloud point(° C)	-2
Pour point(° C)	-5
Carbon residue(%)	0.14
Flash point(° C)	104

The Bio-diesel Sample was prepared from waste vegetable oil. Specific gravity of the samples was obtained at 15° C and density of water was taken 0.997 from literature. Cloud point is the lowest temperature at which the first cloudy layer appears on the surface of fuel. From the cloud points of the Bio-diesel samples, The sample of Bio-diesel was more appropriate to be used as a fuel. Flash point calculation were also done, and were used as selection criteria in compression ignition engines. Since biodiesel is free from sulfur hence less sulfate emissions and particulate reduction is reported in the exhaust. Due to near absence of sulfur in biodiesel, it helps reduce the problem of acid rain due to transportation fuels. The lack of aromatic hydrocarbon (benzene ,toluene etc.) in biodiesel reduces unregulated emissions as well like ketone,

benzene etc. Breathing particulate has been found to be hazard for human health, especially in terms of respiratory system problem. PM consists of elemental carbon (~31%), sulfates and moisture(~14%), unburnt fuel (~7%), unburnt lubricating oil (~40%) and remaining may be metals and others substances. Smoke opacity is a direct measure of smoke and soot. Various studies show that smoke opacity for biodiesel is generally lower. Several experimental investigations are performed on 4-stroke DI diesel engines with vegetable oil methyl esters and found that hydrocarbon emissions are much lower in case of biodiesel compared to diesel. This is also due to oxygenated nature of biodiesel where more oxygen is available for burning and reducing hydrocarbon emissions in the exhaust. CO is a toxic combustion product resulting from incomplete combustion of hydrocarbons. In presence of sufficient oxygen, CO is converted into CO₂. Biodiesel is an oxygenated fuel and leads to more complete combustion; hence CO emissions reduce in the exhaust. reported that CO emission for biodiesel is marginally higher in comparison to diesel.

7.5 Environmental Benefits of Biodiesel Fuel

The steadily rising price of petroleum products and the environmental impact of procuring, manufacturing, and using them create the need for alternate energy sources. Biodiesel, fuel that is chemically prepared from vegetable oil, provides an environmentally friendly substitute for diesel fuel. It is classified as a biofuel because it originates from a biological source. Its biological origin makes it biodegradable and nontoxic. Other advantages of biodiesel fuel over petroleum diesel are the increased oxygen content, no sulfur content, increased lubricity, and lower emissions of particulate matter upon combustion. The Clean Air Act of 1990 mandates oxygenated additives to be added to gasoline in cities with excessive levels of ozone and carbon monoxide pollution because they lead to a reduction in carbon monoxide emissions. Biodiesel contains about 11% oxygen by mass so no additional oxygenated additives are necessary. A later ruling by the Environmental Protection Agency in 1994 required that 30% of the oxygenated additives to reformulated gasoline (gasoline whose composition has been altered to reduce concentrations of undesirable substances) be from renewable resources, and the most popular additive, methyl tertiary- butyl ether, MTBE, is made from methanol, a nonrenewable source. This ruling supports the use of ethanol, which is produced largely from corn, in place of the methanol, but biodiesel is an other renewable source of an oxygenated additive. Absence of sulfur

Conclusion:

The Biggest advantages of biodiesel are it is environmental friendly over gasoline and petroleum diesel. The advantages of biodiesel as a diesel fuel were its probability, easy availability, renewability, higher combustion efficiency and biodegradable. Its potential for reducing a given economy's dependency on important petroleum biodegradability, high flashpoint and inherent lubricates in the heat form.

Hence, the main objective of the study was to produce biodiesel from cotton seed oil and to use esterification and transesterification with solvents Ethanol and B-ADSA-Si Catalyst method. The optimum parameters which gave maximum conversion of 71.10% using 5% w/w catalyst, 1:9 oil to alcohol molar ratio, at 65 °C in 6 hours.

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