“To Study the Effect of Various Catalyst Types & their Concentration on Biodiesel Production”

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IN
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Submitted By
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UNDER THE GUIDANCE
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CERTIFICATE

This is to certify that the thesis entitled ***"TO STUDY THE EFFECT OF VARIOUS CATALYST TYPES AND THEIR CONCENTRATION ON BIODIESEL PRODUCTION"*** which is being submitted by Mr. Anand Prakash Mall to the Department of Mechanical Engineering, Delhi Technological University, Delhi for the award of ***"Master of Technology in Thermal Engineering"*** *de*gree, is a record of bonafide research work carried out by him under my guidance and has fulfilled the requirements for the submission of thesis, which is to my knowledge has reached requisite standard.

To the best of my knowledge, the results contained in this dissertation have not been submitted in part or in full to any university or institute for the award or any degree.

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DECLARATION

I, ***Anand Prakash Mall*** (Roll No: 2K13/THE/05), belonging to Master of Technology, Thermal Engineering, Delhi Technological University (Formerly Delhi College of Engineering) hereby certify that the work which is being presented in the dissertation entitled "***TO STUDY THE EFFECT OF VARIOUS CATALYST TYPES AND THEIR CONCENTRATION ON BIODIESEL PRODUCTION***" submitted to the Department of Mechanical Engineering, in partial fulfillment of the requirements for the award of *"**Master of Technology in Thermal Engineering**"* degree from ***Delhi Technological University,*** *is an authentic record of my own work carried under the supervision of* ***Dr. Amit Pal, Associate professor, Mechanical Engineering Department, Delhi.***

I have not submitted the matter embodied in this major project as whole or in part to any university or institute for the award of any other degree.

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NOMENCLATURE

FAME = Fatty Acid Methyl Ester

FFA = Free Fatty Acids

NOx = Nitrogen Oxides

SAC = Solid Acid Catalyst

SBC = Solid Base Catalyst

SOx = Sulfur Oxides

WCO = Waste Cooking Oil

RSO = Rape Seed Oil

NOME = Neem Oil Methyl Ester

JCO = Jatropha Curcas Oil

ANOVA = Analysis of Variance Table

ASTM = American Society for Testing Materials

EN = European Standard

h = Hour

ABSTRACT

Biodiesel is a low-emissions diesel substitute fuel made from renewable resources and waste lipid. The most common way to produce biodiesel is through transesterification, especially alkali-catalyzed transesterification. When the raw materials (oils or fats) have a high percentage of free fatty acids or water, the alkali catalyst will react with the free fatty acids to form soaps. The water can hydrolyze the triglycerides into diglycerides and form more free fatty acids. Both of the above reactions are undesirable and reduce the yield of the biodiesel product. In this situation, the acidic materials should be pretreated to inhibit the saponification reaction.

Homogeneous basic catalyst like sodium hydroxide and potassium hydroxide are generally used for biodiesel production at industrial scale due to short reaction time and mild reaction conditions. However, the use of this catalyst leads to soap formation due to reaction of alkaline catalyst with free fatty acids. It is very difficult to remove catalytic species after reaction and to large extent formation of waste water streams. An alternative way to process vegetable oils, is the utilization of a solid state catalyst which will cope with the most economical and environmental draw back. The main hurdle for biodiesel preparation is the process economics which arises from the catalytic system. All these have been taken care by solid state catalyst.

Currently, most of the biodiesel is produced from the edible/refined type oil using methanol and alkaline catalyst. However, large amount of non-edible type oils and fats are available in our country. In this study, crude neem oil is used as alternative fuel for biodiesel production. The difficulty with alkaline transesterification of these oils has contained large amounts of free fatty acids (FFA). These free fatty acids quickly react with the alkaline catalyst to produce soaps that inhibit the separation of the ester and glycerin.

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 H_2SO_4 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 (Meher et al., 2006) (Table 1 shows the physicochemical properties of some feedstocks). 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 (Table 2.1(a) shows the physicochemical properties of biodiesel produced from different oil source).

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 (Meher et al., 2006). 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.

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 (Hanna et al.,2005). 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 (Demirbas, 2009). 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].

Table1 Feedstocks for biodiesel production and their physicochemical properties. (Leung et al., 2010)

Species	Main chemical composition (fatty acid composition wt. %)	Density (g/cm^3)	Kinematic viscosity (cst, at 40ºC)
I. Edible Oils			
Soybean	C16:0, C18:1, C18:2	0.91	32.9
Rapessed	C16:0, C18:0, C18:1, C18:2	0.91	35.1
Sunflower	C16:0, C18:0, C18:1, C18:2	0.92	32.6
Palm	C16:0, C18:0, C18:1, C18:2	0.92	39.6 a
Peanut	C16:0, C18:0, C18:1, C18:2, C20:0, C22:0	0.9	22.72

Species	**Main chemical composition (fatty acid composition wt. %)**	**Density (g/cm^3)**	**Kinematic viscosity (cst, at 40ºC)**
Corn	C16:0, C18:0, C18:1, C18:2, C18:3	0.91	34.9 a
Camelina	C16:0, C18:0, C18:1, C18:2 C18:3, C20:0, C20:1, C20:3	0.91	–
Canola	C16:0, C18:0, C18:1, C18:2 C18:3	–	38.2
Cotton	C16:0, C18:0, C18:1, C18:2	0.91	18.2
Pumpkin	C16:0, C18:0, C18:1, C18:2	0.92	35.6
II. Non Edible Oils			
Jatropha curcas	C16:0, C16:1, C18:0, C18:1, C18:2	0.92	29.4

Species	Main chemical composition (fatty acid composition wt. %)	Density (g/cm^3)	Kinematic viscosity (cst, at 40ºC)
Sea mango	C16:0, C18:0, C18:1, C18:2	0.92	29.6
Palanga	C16:0, C18:0, C18:1, C18:2	0.9	72
Tallow	C14:0, C16:0, C16:1, C17:0, C18:0, C18:1, C18:2	0.92	–
Nile tilapia	C16:0, C18:1, C20:5, C22:6, other acids	0.91	32.1 b
Poultry	C16:0, C16:1, C18:0, C18:1, C18:2, C18:3	0.9	–
Used cooking oil	Depends on fresh cooking oil	0.9	44.7

[a] Kinematic viscosity at 38ºC, mm^2/s.

[b] Kinematic viscosity at 37ºC, mm^2/s.

1.1. Catalysis:

1.1.1. Homogeneous Catalysis

Homogeneous catalysis is a type of catalysis process in which the phases of the catalyst is the same as the phase of the reactant. Homogeneous catalysis processes provide higher reaction rates without increasing temperature but due to their difficult recoverability process, heterogeneous catalyst are used if possible. Homogeneous catalysis can be found in many processes such as acid catalysis, organometallic chemistry and enzyme secretion process.

1.1.2. Heterogeneous Catalysis

Heterogeneous catalysis is a type of catalysis process in which the phase of the catalyst is different from the phase of the reactants. The term “phase” here not only extends references to solid, liquid or gas but also to immiscible liquids. Major percentages of the heterogeneous catalysts are solids with liquids or gasses as the reactants. Solid heterogeneous catalysts have found great importance in many industries due to their regenerative and reusability properties. The adsorption process plays a very important role in the process of heterogeneous catalysis. Adsorption is a phenomenon in which a molecule in gaseous or liquid phase sticks or binds itself to the surface of other solid or liquid. The substance that binds itself on some other support is known as the adsorbate and the substance providing the binding surface is called as the adsorbent. In Heterogeneous catalysis, the reactant acts as the adsorbate and the catalyst act as adsorbents. Based on the nature of interactions between the adsorbate and adsorbent, the adsorption can be classified into two parts called Physisorption and Chemisorption.In Physisorption, the major cause of the binding force between the adsorbent and adsorbate interaction are vanderwaals forces. On the other hand, in Chemisorptions, the interaction takes place due to stronger chemical bonds. Physisorption process is usually relatively low energy processes varying from 2 to 10 kcal/mol compared to values as high as 100 kcal/mol for chemisorptions. In heterogeneous catalysis, the adsorption process is a chemisorptions process.

1.2. Various Catalysts for Biodiesel Production:

1.2.1. Homogeneous Acid Catalysts

Commercial biodiesel is typically produced using non-reusable homogeneous catalysts resulting in corrosion of equipment, additional processing steps and wastewater disposal problems. Homogeneous acidic catalysts such as sulfuric acid, sulfonic acid, phosphoric acid or hydrochloric acid are commonly applied in transesterification.Acidic catalysts are insensitive to free fatty acid content of low quality feedstock and are less sensitive to water content. Acid catalyzed reactions require higher oil to methanol ratio (1:9 compared to 1:3) to achieve conversions similar to basic catalysts. The rates of reaction of acidic catalysts in transesterification are slower than with basic catalysts, so the time required for the reaction to proceed to completion is longer (3 h to 48 h) Homogeneous acid catalysts are not ideal for biodiesel production due to the slow reaction rates requiring lengthy reaction times. The ability of homogeneous catalysts to simultaneously catalyze esterification and transesterification, as well as their demonstrated tolerance to water content, are desirable qualities.

1.2.2. Homogeneous Base Catalysts

Basic catalysts are more common in industry because they have a higher reaction rate compared to acid catalysts. However ,basic catalysts require anhydrous condition and the feedstock must have low levels of free fatty acids(FFA) to prevent saponification.This side reaction occur when an ester is hydrolyzed to a salt and the catalyst is consumed.Saponification lowers ester yield, reduces the ease of separation of the ester and glycerol product layers and cause difficulty during product washing. Some work suggests that a two stage process can be employed. Homogeneous acid pretreatment followed by homogeneous base catalysis aids in the processing of low quality feedstock,however the problems associated with homogeneous catalysts remain an issue.Homogeneous catalysts can’t be reused, they present corrosion issues with equipment and the products require neutralization and washing with water to remove caustic substances.Removal of the catalyst from product stream is a technical challenge and adds cost to the process.In addition feedstock oils and methanol must be anhydrous when using homogeneous base catalysts to avoid saponification ,which causes difficulties in the separation of products.Homogeneous bases are the most commonly used catalysts for biodiesel production.However,homogeneous catalysts are not reusable , they are associated with corrosion issues of processing equipment,require hazardous waste disposal and require additional washing stages for purification.Homogeneous basic catalysts are not tolerant to water or free fatty acids typically present in low-quality feedstocks.Due to the issues involved in the continued use of homogeneous catalysts,there is a need for the development of a suitable heterogeneous catalyst for use in the biodiesel production industry.

1.2.3. Heterogeneous Acid Catalysts

Heterogeneous catalysts have the potential to replace homogeneous catalysts and circumvent some of the problems associated with conventional production methods. Solid acid catalysts (SAC) have been reported to simultaneously catalyze the esterification and transesterification reactions. Both Bronsted and Lewis acid sites are capable of catalyzing the esterification reaction. Previous research has shown that sulfated material had the highest catalytic activity, but they are subject to poisoning effects. Other heterogeneous catalysts such as sulfonated solids, metal oxides and supported heteropolyacids have been examined in transesterification.Many of the catalysts were unable to achieve conversion to FAME approaching ASTM standards. Several of the catalysts that were highly active were subject to sulfate leaching and deactivation in successive reactions. Supported heteropolyacids, zirconia titania and zirconia alumina were the most active and stable catalysts. Organically functionalized solid acid catalysts have demonstrated high catalytic activities in both esterification and transesterification.Additional work is required to increase stability and longevity of these catalysts. Example of solid acid catalysts reviewed are zeolite, heteropoly acids, functionalized zirconia and silica, tungsten oxide, ion exchange resins and sulfonated saccharides.Due to the low activity of SAC at conventional temperatures used in biodiesel production they are largely dismissed. Jothiramalingam concludes that ‘an ideal…solid acid catalyst should posses interconnected large porous texture with moderate to high concentration of acid sites and a hydrophobic surface’. A hydrophobic surface is essential to promote preferential adsorption of oily hydrophobic species on the catalyst surface and to avoid possible deactivation of catalytic sites by the strong adsorption of polar byproducts such as water and glycerol.

Singh examined numerous metal oxides as solid Lewis acid catalysts for transesterification of soybean oil. Catalysts examined were magnesium oxide (MgO),calcium oxide (CaO),lead oxide (PbO),lead dioxide(PbO_2),lead tetra oxide(Pb_2O_4),titanium trioxide(Ti_2O_3) and zinc oxide (ZnO).Several temperature were examined :75°C,150°C and 225°C. Catalyst loading was 2 wt% using an oil to methanol ratio 1:7. A yield of 89% was reported with PbO and PbO_2 after two hours. A significant quantity of metal leaching was detected in both the glycerol and biodiesel products.

1.2.4. Heterogeneous Base Catalysts

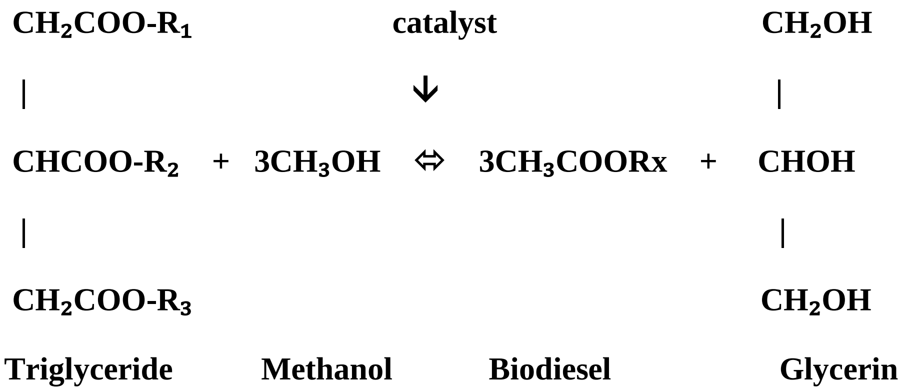
Solid basic catalysts have faster reaction times when compared to solid acid catalysts. Catalyst efficiency is reported to depend on physical surface properties such as surface area, pore size, pore volume and active site concentration. Most heterogeneous base catalysts were tested at the boiling point of methanol. The mechanism of heterogeneous Bronsted basic catalysis, relying on the formation of the alkoxide cation (CH_3O-) bonded to the catalyst surface. Solid base catalysts and enzymatic lipases including alkali metal, alkali earth metals,hydrotalcites and transition metals on various supports,hydrotalcites and alkali oxides, have been examined by previous research.Manycatalysts achieved reported conversion above 90%. A conversion of 99% has been reported using calcium oxide on calcium carbonate. Temperature was 65°C and reaction time was 2 hours. Alcohol molar ratio was 1:6 and catalyst loading 13% by weight. Lipase catalyst reported yields up to 94% and are stated to be a promising candidate for future research in biodiesel production. Ebuira examined alumina loaded with alkali metal in solid base catalysis of triolein in transesterification. Metal salts such as potassium carbonate(K_2CO_3),lithium nitrate($LiNO_3$) and sodium nitrate($NaNO_3$)were doped on alumina(Al_2O_3). Reaction conditions were as follows: temperature of 60°C ,1:24 oil to methanol ratio,5 wt% catalyst loading and tetrahydrofuran(THF) as a co-solvent over a reaction time of one hour. Potassium carbonate was found to be the most highly active catalyst. The highest reported yield of methyl oleate (FAME) was 94 mol%.

2. LITERATURE REVIEW

(Biodiesel production with catalyzed transesterification)

2.1. Basic chemical reactions

Common vegetable oils or animal fats are esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride. These esters are called triglycerides, which can react with alcohol in the presence of a catalyst, a process known as transesterification. The simplified form of its chemical reaction is presented in equation.



$$\begin{array}{ccccccc} CH_2COO\text{-}R_1 & & & \text{catalyst} & & & CH_2OH \\ | & & & \downarrow & & & | \\ CHCOO\text{-}R_2 & + & 3CH_3OH & \Leftrightarrow & 3CH_3COORx & + & CHOH \\ | & & & & & & | \\ CH_2COO\text{-}R_3 & & & & & & CH_2OH \\ \text{Triglyceride} & & \text{Methanol} & & \text{Biodiesel} & & \text{Glycerin} \end{array}$$

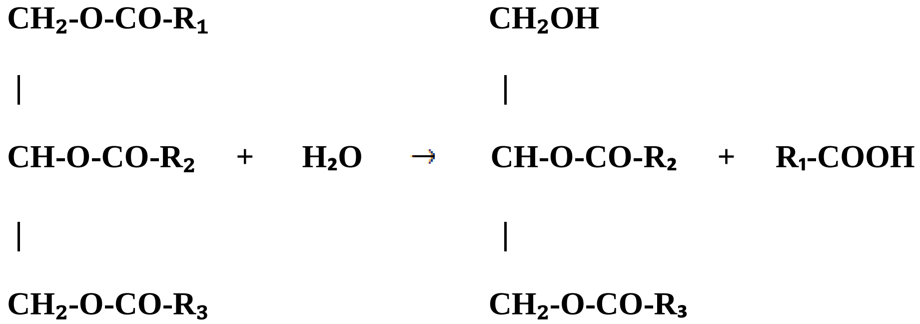
Where R_1, R_2, R_3 are long-chain hydrocarbons, sometimes called fatty acid chains. Normally, there are five main types of chains in vegetable oils and animal oils: palmitic, stearic, oleic, linoleic, and linolenic. When the triglyceride is converted stepwise to diglyceride, monoglyceride, and finally to glycerol, 1 mol of fatty ester is liberated at each step. Usually, methanol is the preferred alcohol for producing biodiesel because of its low cost.

Vegetable oils and fats may contain small amounts of water and free fatty acids (FFA). For an alkali catalyzed transesterification, the alkali catalyst that is used will react with the FFA to form soap. The below Eq. shows the saponification reaction of the catalyst (sodium hydroxide) and the FFA, forming soap and water.

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

(FFA) (Sodium Hydroxide) (Soap) (Water)

This reaction is undesirable because the soap lowers the yield of the biodiesel and inhibits the separation of the esters from the glycerol. In addition, it binds with the catalyst meaning that more catalyst will be needed and hence the process will involve a higher cost. Water, originated either from the oils and fats or formed during the saponification reaction, retards the transesterification reaction through the hydrolysis reaction. It can hydrolyze the triglycerides to diglycerides and forms more FFA. The typical hydrolysis reaction is shown in Eq. below.



$$\begin{array}{lcccccc} CH_2\text{-}O\text{-}CO\text{-}R_1 & & & & CH_2OH & & \\ | & & & & | & & \\ CH\text{-}O\text{-}CO\text{-}R_2 & + & H_2O & \rightarrow & CH\text{-}O\text{-}CO\text{-}R_2 & + & R_1\text{-}COOH \\ | & & & & | & & \\ CH_2\text{-}O\text{-}CO\text{-}R_3 & & & & CH_2\text{-}O\text{-}CO\text{-}R_3 & & \end{array}$$

(Triglyceride) (Water) (Diglyceride) (FFA)

However, the FFA can react with alcohol to form ester (biodiesel) by an acid-catalyzed esterification reaction. This reaction is very useful for handling oils or fats with high FFA, as shown in the equation below:

$$\underset{\textbf{(FFA)}}{\mathbf{R_1—COOH}} \quad + \quad \underset{\textbf{(Alcohol)}}{\mathbf{ROH}} \quad \xrightarrow{H^+} \quad \underset{\textbf{(Fatty Acid Ester)}}{\mathbf{R—O—CO—R_1}} \quad + \quad \underset{\textbf{(Water)}}{\mathbf{H_2O}}$$

Normally, the catalyst for this reaction is concentrated sulphuric acid. Due to the slow reaction rate and the high methanol to oil molar ratio that is required, acid-catalyzed esterification has not gained as much attention as the alkali catalyzed transesterification. (Gerpen, 2005)

Table 2.1(a) physicochemical properties of biodiesel from different oil source (Wu et al., 2010)

Feedstock	**Kinematic Viscosity (cst,at 40 ⁰C)**	**Density (g/cm^3)**
Soybean	4.08	0.885
Rapeseed	5.83	0.88
Sunflower	4.9	0.88
Palm	4.42	0.86
Peanut	4.42	0.883
Camelina	6.12	0.882
Canola	3.53	0.88

Feedstock	**Kinematic Viscosity (cst,at 40 ºC)**	**Density (g/cm^3)**
Cotton	4.07	0.875
Pumpkin	4.41	0.8837
Jatropha curcas	4.78	0.8636
Pongamina pinnata	4.8	0.883
Palanga	3.99	0.869
Tallow	–	0.856
Nile tilapia	–	–
Used cooking oil	4	–

Table 2.1(b) Different methods of biodiesel production

(D.Y.C. Leung et al.,2010)

Methods	Definition	Advantage	Disadvantage	Problems of using in engines
Direct use and blending	Direct use as diesel fuel or blend with diesel fuel	Liquid nature portability Heat content (80% of diesel fuel) Readily available; renewability	Higher viscosity Lower volatility Reactivity of unsaturated Hydrocarbon chains	Coking and trumpet Formation Carbon deposits Oil ring sticking; thickening and gelling of the lubricating oil
Micro-emulsions	A colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two immiscible liquids and one or more ionic or non-ionic amphiphiles	Better spray patterns during combustion Lower fuel viscosities	Lower cetane number Lower energy content	Irregular injector needle sticking; incomplete combustion Heavy carbon deposits; increase lubrication oil viscosity
Thermal cracking (pyrolysis)	The conversion of long-chain and saturated substance (biomass basis) to biodiesel by means of heat	Chemically similar to petroleum-derived gasoline and diesel fuel	Energy intensive and hence higher cost	–
Transester-ification	The reaction of a fat or oil with an alcohol in the presence of catalyst to form esters and glycerol	Renewability; higher cetane number; lower emissions; higher combustion efficiency	Disposal of by-product (glycerol and waste water)	–

2.2. Biodiesel production processes:

2.2.1. Process flow chart

Today, most of the biodiesel is produced by the alkali catalyzed process. Fig.1(a) shows a simplified flow chart of the alkali-catalyst process. As described earlier, feedstocks with high free fatty acid will react undesirably with the alkali catalyst thereby forming soap. The maximum amount of free fatty acids acceptable in an alkali catalyzed system is below 2.5 wt. % FFA. If the oil or fat feedstock has FFA content over 2.5 wt. %, a pretreatment step is necessary before the transesterification process.

2.2.2. Raw materials treatment

The raw materials, which can be vegetable oils, animal fats, or recycled greases, used in the production of biodiesel contain triglycerides, free fatty acids, water, and other contaminants in various proportions. Some crude vegetable oils contain phospholipids that need to be removed in a degumming step. Phospholipids can produce lecithin, a commercial emulsifier. Liu et al. compared the different degumming methods, such as membrane filtration, hydration, acid micelles degumming, supercritical extraction, etc. The characteristics of the raw oils should be investigated before choosing the suitable degumming method because different degumming methods have their advantages and disadvantages. The oil can be separated through membrane filtration according to the average molecular weight or the particle size of phospholipids. Although degumming method can solve the problem,

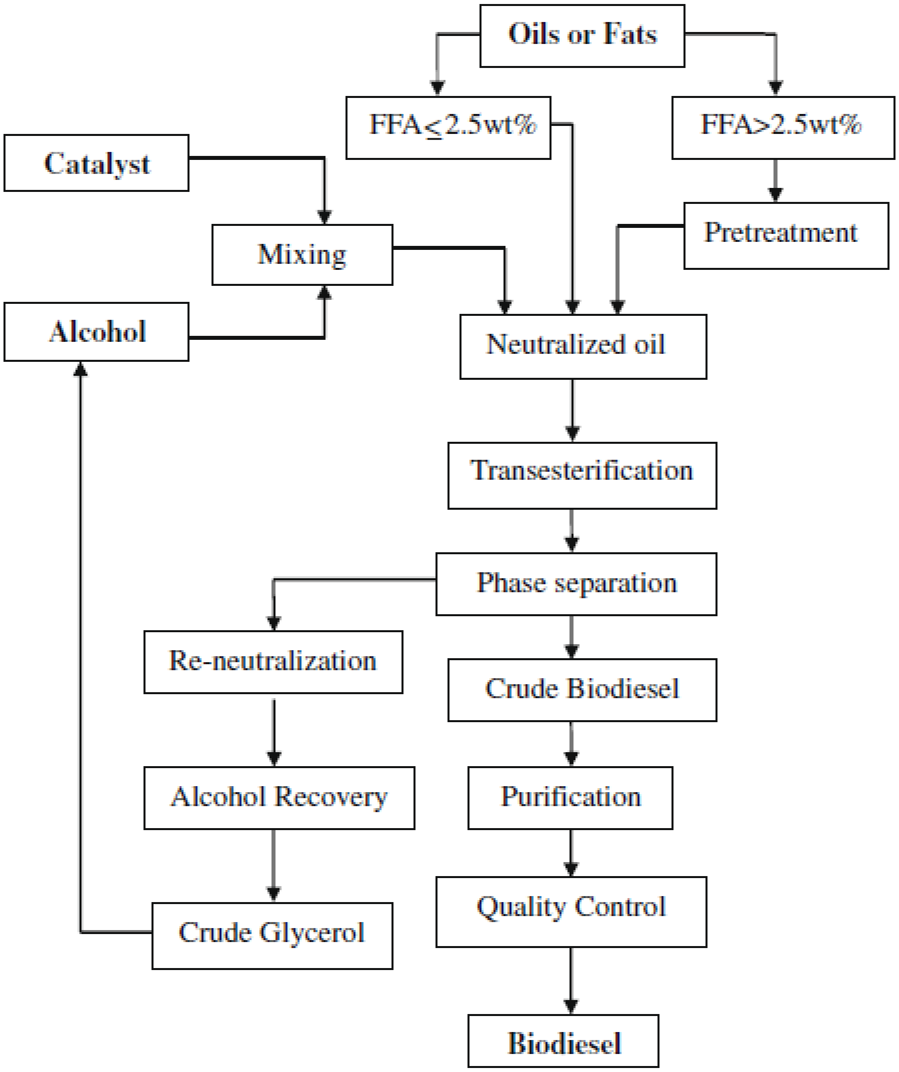


Fig.1(a) Simplified process flow chart of alkali – catalyzed biodiesel production (D.Y.C. Leung et al., 2010)

Its process involves two steps with the use of an organic solvent. Therefore, this method has no superiority on cost because of its complicated processing. In the hydration process, because of phospholipids hydrophilicity, hot water can be added into the oil with stirring. The phospholipids solubility will be significantly reduced, so it could be separated from the oil by natural settlement. The hydration method features a simple process, easy operation, and high yields refining, but nonhydratable phospholipids cannot be removed by this method. For removing nonhydratable phospholipids, critic acid or phosphoric acid can be added into the oil which is heated to 70ºC, this is called the special micelles degumming method. It is found that the reaction time for this method is about 5 min, followed by neutralization through dilute lye. The supercritical extraction method is employed to separate the phospholipids. Moreover, by refining with supercritical CO_2 extraction, it can effectively remove the free fatty acids and the peroxidation products that are in the crude oil. However, the high pressure required in this process will be the biggest challenge in its industrial application.

The free fatty acids are removed in a refining step and excess free fatty acids can be removed as soaps in a later pretreatment step. In addition, deodorization is another important step in the raw material treatment. During this step, steam, at 1–6 mm Hg pressure, is injected into the oil at 490–550 K in order to eliminate free fatty acids, aldehydes, unsaturated hydrocarbons, and ketones, all of which cause undesirable odors and flavors in the oil. Next, in order to determine the percentage of FFA in the oils or fats, titration is performed. As described above, if the percentage of FFA is over 2.5 wt. %, pretreatment is necessary to reduce the content of FFA. This step also determines the amount of caustic soda required in the neutralization step.

2.2.3. Pretreatment of acidic feedstocks

Many pretreatment methods have been proposed for reducing the high free fatty acid content of the oils, including steam distillation, extraction by alcohol, and esterification by acid catalysis. However, steam distillation for reducing high free fatty acids requires a high temperature and has low efficiency. Because of the limited solubility of free fatty acids in alcohol, extraction by alcohol method needs a large amount of solvent and the process is complicated. Compared with the two former methods, esterification by acid catalysis makes the best use of the free fatty acids in the oil and transforms it into biodiesel. The common pretreatment is esterification of the FFA with methanol in the presence of acidic catalysts (usually sulphuric acid). The catalysts can be homogeneous acid-catalysts or solid acid catalysts. Compared with the former one, solid acid catalysts offer some advantages for eliminating separation, corrosion, toxicity, and environmental problems, but the reaction rate is slower. As described earlier, free fatty acids will be converted to biodiesel by direct acid esterification and the water needs to be removed. If the acid value of the oils or fats is very high, one step esterification pretreatment may not reduce the FFA efficiently because of the high content of water produced during the reaction. In this case, a mixture of alcohol and sulphuric acid can be added into the oils or fats three times (three-step pre-esterification). The time required for this process is about 2 h and water must be removed by a separation funnel before adding the mixture into the oils or fats for esterification again. Moreover, some researchers reduce the percent of FFA by using acidic ion exchange resins in a packed bed. Strong commercial acidic ion exchange resins can be used for the esterification of FFA in waste cooking oils but the loss of the catalytic activity maybe a problem.

An alternative approach to reduce the FFA is to use iodine as a catalyst to convert free fatty acids into biodiesel. An obvious advantage of this approach is that the catalyst (iodine) can be recycled after the esterification reaction. It is found through orthogonal tests, under the optimal conditions (i.e. iodine amount: 1.3 wt. % of oils; reaction temperature: 80ºC; ratio of methanol to oils: 1.75:1; reaction time: 3 h) that the FFA content can be reduced to <2%.

Another new method of pretreatment is to add glycerol into the acidic feedstock and heat it to a high temperature of about 200ºC, normally with a catalyst such as zinc chloride. The glycerol will react with the FFA to form monoglycerides and diglycerides. Then the FFA level will become low and biodiesel can be produced using the traditional alkali catalyzed transesterification method. The advantage of this approach is that no alcohol is needed during the pretreatment and the water formed from the reaction can be immediately vaporized and vented from the mixture. However, the drawbacks of this method are its high temperature requirement and relatively slow reaction rate.

2.2.4. Catalyst and alcohol

In general, there are three categories of catalysts used for biodiesel production: alkalis, acids, and enzymes. Enzyme catalysts have become more attractive recently since it can avoid soap formation and the purification process is simple to accomplish. However, they are less often used commercially because of the longer reaction times and higher cost. To reduce the cost, some researchers developed new biocatalysts in recent years. An example is so called whole cell biocatalysts which are immobilized within biomass support particles. An advantage is that no purification is necessary for using these biocatalysts. Compare with enzyme catalysts, the alkali and acid catalysts are more commonly used in biodiesel production. The alkali and acid catalysts include homogeneous and heterogeneous catalysts. Due to the low cost of raw materials, sodium hydroxide and potassium hydroxide are usually used as alkali homogeneous catalysts and alkali catalyzed transesterification is most commonly used commercially. These materials are the most economic because the alkali catalyzed transesterification process is carried out under a low temperature and pressure environment, and the conversion rate is high with no intermediate steps. However, the alkali homogeneous catalysts are highly hygroscopic and absorb water from air during storage. They also form water when dissolved in the alcohol reactant and affect the yield. Therefore, they should be properly handled. On the other hand, some heterogeneous catalysts are solid and it could be rapidly separated from the product by filtration, which reduces the washing requirement. In addition, solid heterogeneous catalysts can stimulatingly catalyze the transesterification and esterification reaction that can avoid the preesterification step, thus these catalysts are particularly useful for those feedstocks with high free fatty acid content. However, using a solid catalyst, the reaction proceeds at a slower rate because the reaction mixture constitutes a three-phase system, which, due to diffusion reasons, inhibits the reaction. Tab.2.2 classifies the three categories of catalysts with their advantages and disadvantages.

The alcohol materials that can be used in the transesterification process include methanol, ethanol, propanol, butanol, and amyl alcohol. Among these alcohols, methanol and ethanol are used most frequently. Methanol is especially used because of its lower cost and its physical and chemical advantages.Hanna et al. reported that methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it. However, due to its low boiling point, there is a large explosion risk associated with methanol vapors which are colorless and odorless. Both methanol and methoxide are extremely hazardous materials that should be handled carefully. It should be ensured that one is not exposed to these chemicals during biodiesel production.

Table 2.2 Advantages and disadvantages at different types of catalysts used in the biodiesel production (D.Y.C. Leung et al.,2010)

Type	Example	Advantages	Disadvantages
Alkali Catalysts			
Homogeneo -us	NaOH, KOH	High catalytic activity, low cost, favorable kinetics, modest operation conditions	Low FFA requirement, anhydrous conditions, saponification, emulsion formation, more wastewater from purification, disposable
Heterogene- ous	CaO, $CaTiO_3$, $CaZrO_3$, CaO–CeO_2, $CaMnO_3$,$Ca_2Fe_2O_5$, KOH/Al_2O_3, KOH/NaY, Al_2O_3/KI,ETS-10 zeolite, alumina/silica supported K_2CO_3	Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes	Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, high reaction temperature and pressure, diffusion limitations, high cost
Acid Catalysts			
Homogene- ous	Concentrated sulphuric acid	Catalyze esterification and Transesterification simultaneously, avoid soap formation	Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity
Heterogen- eous	ZnO/I_2, ZrO_2/SO_4^{2-}, TiO_2/SO_4^{2-}, carbon-based solid acid catalyst, carbohydrate-derived catalyst, Vanadyl phosphate, niobic acid, sulphated zirconia, Amberlyst-15, Nafion-NR50	Catalyze esterification and Transesterification simultaneously, recyclable, eco-friendly	Low acid site concentrations, low microporosity, diffusion limitations, high cost
Enzymes	Candida antarctica fraction B lipase, Rhizomucor mieher lipase	Avoid soap formation, nonpolluting, easier purification	Expensive, denaturation

2.2.5. Mixing and neutralization

The purpose of mixing methanol with the catalyst is to produce methoxide which reacts with the base oils. Most of the catalysts (e.g. NaOH, KOH) are in solid form and do not readily dissolve into methanol, it is best to start agitating the methanol in a mixer and add the catalyst slowly and carefully. Once the catalyst completely dissolves in the methanol, the methoxide is ready to be added to the oil. Once the methoxide is added into the oil, a neutralization reaction will immediately start. Some alkali catalysts will react with rudimental acids during the pretreatment step or will react with the free fatty acids from the oil. Therefore, more catalyst needs to be added to complete the reaction.

2.2.6. Transesterification and separation

When the catalyst, alcohol, and oil are mixed and agitated in a reaction vessel, a transesterification reaction will start. A stirred reactor is usually used as the reaction vessel for continuous alkali catalyzed biodiesel production. Recently, there is an increased interest in new technologies related to mass transfer enhancement. Biodiesel is produced from vegetable oils assisted by ultrasound which is a useful tool for strengthening the mass transfer of immiscible liquids. Ultrasonic irradiation causes cavitation of bubbles near the phase boundary between immiscible liquid phases. The asymmetric collapse of the cavitation bubbles disrupts the phase boundary and starts emulsification instantly. Micro jets, formed by impinging one liquid to another, lead to intensive mixing of the system near the phase boundary. With the use of ultrasound biodiesel can be produced without heating because the cavitation may lead to a localized increase in temperature at the phase boundary and enhance the reaction. Moreover, Wen et al. fabricated a new reaction vessel Zigzag micro-channel reactor in recent years and found that less energy consumption for biodiesel synthesis can be achieved by using this reactor.

Leung studied the effect of operating conditions on the product yield and pointed out that heating the oil prior to the mixing can increase the reaction rate and hence shorten the reaction time. During this step, in order to speed up the reaction, mixing brings the oil, the catalyst, and the alcohol into intimate contact while the temperature is kept just below the boiling point of the alcohol (i.e. 64.5⁰C for methanol). Normally, the reaction pressure is close to the atmospheric pressure to prevent the loss of alcohol, and excess alcohol is used to ensure total conversion of the oil to its esters. As previously mentioned, if the free fatty acid level or water level is too high, it may cause problems downstream with the saponification and the separation of the glycerol byproduct. Therefore, the amount of water and free fatty acids in the feedstock oil should be monitored during the reaction.

Once the transesterification reaction is completed, two major products exist: 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. The reaction mixture is allowed to settle in the reaction vessel in order to allow the initial separation of biodiesel and glycerol, or the mixture is pumped into a settling vessel. In some cases, a centrifuge may be used to separate the two phases.

Both the biodiesel and glycerol are contaminated with an unreacted catalyst, alcohol, and oil during the transesterification step. Soap that may be generated during the process also contaminates the biodiesel and glycerol phase. Schumacher suggested that although the glycerol phase tends to contain a higher percentage of contaminants than the biodiesel, a significant amount of contaminants is also present in the biodiesel. Therefore, crude biodiesel needs to be purified before use.

2.2.7. Refining crude glycerol

Although biodiesel is the desired product from the reactions, the refining of glycerol is also important due to its numerous applications in different industrial products such as moisturizers, soaps, cosmetics, medicines, and other glycerol products. It is one of the few products that has a good reactivity on sump oil, and is extremely effective for washing shearing shed floor, so it can be used as a heavy duty detergent and degreaser. Whittington reported that glycerol can even be fermented to produce ethanol, which means more biofuel can be produced.

According to the statements of Van Gerpen, typically produced glycerol is about 50% glycerol or less in composition and mainly contains water, salts, unreacted alcohol, and unused catalyst. The unused alkali catalyst is usually neutralized by an acid. In some cases, hydrochloric or sulphuric acids are added into the glycerol phase during the re-neutralization step and produce salts such as sodium chloride or potassium sulphate, the latter can be recovered for use as a fertilizer. Generally, water and alcohol are removed to produce 80–88% pure glycerol that can be sold as crude glycerol. In more sophisticated operations, the glycerol is distilled to 99% or higher purity and sold in different markets.

After the re-neutralization step, the alcohol in the glycerol phase can be removed through a vacuum flash process or by other types of evaporators. Usually, the alcohol vapor is condensed back into liquid and reused in the process. However, the alcohol may contain water that should be removed in a distillation column before the alcohol is returned to the process. The alcohol recovery step is more difficult when the alcohol that is used, such as ethanol or isopropanol, forms an azeotrope with the water. Gerpen proposed the use of a molecular sieve to remove the water generated.

2.2.8. Purification of crude biodiesel

After separation from the glycerol phase, crude biodiesel is mainly contaminated with residual catalyst, water, unreacted alcohol, free glycerol, and soaps that were generated during the transesterification reaction. Normally, crude biodiesel enters a neutralization step and then passes through an alcohol stripper before the washing step. In some cases, acid is added to crude biodiesel to neutralize any remaining catalyst and to split any soap. Soaps react with the acid to form water soluble salts and free fatty acids. Gerpen stated that neutralization before the washing step reduces the materials required for the washing step and minimizes the potential for emulsions being formed during the washing step. Unreacted alcohol should be removed with distillation equipment before the washing step to prevent excess alcohol from entering the wastewater effluent. The primary purpose of this step is to wash out the remnants of the catalyst, soaps, salts, residual alcohol, and free glycerol from the crude biodiesel. Generally, three main approaches are adopted for purifying biodiesel: water washing, dry washing, and membrane extraction. These approaches are briefly shown in Table 2.3(a) and discussed in detail as follows.

2.2.8(i) Water washing.

Since both glycerol and alcohol are highly soluble in water, water washing is very effective for removing both contaminants. It also can remove any residual sodium salts and soaps. The primary material for water washing is distilled warm water or softened water (slightly acidic). Warm water pre-vents the precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action. Softened water (slightly acidic) eliminates calcium and magnesium contamination and neutralizes any remaining alkali catalysts. After washing several times, the water phase becomes clear, meaning that the contaminants have been completely removed. Then, the biodiesel and water phases are separated by a separation funnel or centrifuge. Moreover, because of the immiscibility of water and biodiesel, molecular sieves and silica gels, etc., can also be used to remove water from the biodiesel. The remaining water can be removed from the biodiesel by passing the product over heated Na_2SO_4 (25 wt. % of the amount of the ester product) overnight and then be removed by filtration. However, there are many disadvantages to this method, including an increased cost and production time, polluting liquid effluent, product loss, etc. Moreover, emulsions can form when washing the biodiesel made from waste cooking oils or acidic feedstocks because of the soap formation.

2.2.8(ii) Dry washing.

Dry washing is used by replacing the water with an ion exchange resin or a magnesium silicate powder in order to remove impurities. These two dry washing methods can bring the free glycerol level down and is reasonably effective for removing soaps. Both the ion exchange process and the magnesol process have the advantage of being waterless and thus eliminate many of the problems outlined above. Although the magnesol process has a better effect on the removal of methanol than the ion resins, none of the products from this process fulfill the limits specified in the EN Standard.

2.2.8(iii) Membrane extraction

It is proved that the contaminants can be removed by using a hollow fiber membrane extraction, such as polysulfone. In this method, a hollow fiber membrane (1 m long, 1 mm diameter) filled with distilled water is immersed into the reactor (20^{o}C). The crude biodiesel is pumped into the hollow fiber membrane (flow rate: 0.5 ml/min; operating pressure: 0.1 MPa). Following this step, biodiesel is passed over heated Na_2SO_4 and then filtered to remove any remaining water. This approach effectively avoids emulsification during the washing step and decreases the loss during the refining process. The purity of the biodiesel obtained is about 90% and the other properties conform to the ASTM standards. It is a very promising method for purifying biodiesel.

2.2.9. Quality control

For commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets international standards. A few specifications have been set but the ASTM D 6751 and EN 14214 standards are the most commonly used standards. Even in blends with conventional diesel fuel, Mittelbach stated that most people in the industry expect the biodiesel blending stock to meet the relevant standard before being blended. Some properties in the standard, such as the cetane number or density, can reflect the properties of the chemical compounds that make up the biodiesel, and other properties provide an indication of the quality of the production process. Generally, biodiesel standards identify the parameters that pure biodiesel must meet before being used as a pure fuel or being blended with distillate fuels .

To ensure safe operation in diesel engines, the most important aspects of the biodiesel product are the completion of the reaction, the removal of the free glycerol, residual catalyst and alcohol, and the absence of free fatty acids. As mentioned before, if the transesterification reaction is not complete then triglycerides, diglycerides, or monoglycerides may be left in the final product. Chemically, each of these compounds contains a glycerol molecule. Fuel with excessive free glycerol may plug the fuel filters and cause combustion problems in the diesel engine. Therefore, the ASTM standard requires the total glycerol to be <0.24% of the final biodiesel product. On the other hand, since residual methanol, even as little as 1%, can lower the flash point of the final biodiesel product from 170ºC to < 40ºC, the EN 14214 standard limits the amount of alcohol to a very low level. Finally, although a specific value for the residual catalyst is not included in the ASTM standard, it is limited by the specification on levels of sulfated ash, which may lead to engine deposits and high abrasive wear levels.

Because the European specification for sulfur content (i.e. EN 14214) is much tighter than the US requirement, it is reported that a number of producers in

Europe are resorting to the use of vacuum distillation for the removal of sulfur compounds from the final biodiesel product. In addition, some vegetable oils, yellow greases, and brown greases leave an objectionable color in the biodiesel. Although there is no color specification in the ASTM standard, in some cases, an activated carbon bed, which is an effective method for the removal of excessive color, is used to produce a colorless biodiesel.

2.3. Storage of biodiesel product

Biodiesel is safe to store and the properties of biodiesel should conform to respective standards after it has been stored for a long time. Table 2.3(b) shows the ATSM D 6751 and EN 14214 standards.

There are several key factors that need to be considered for the storage of biodiesel, including exposure temperature, oxidative stability, fuel solvency, and material compatibility. Lee stated that the temperature of stored biodiesel should be controlled so as to avoid the formation of crystals which can plug fuel lines and fuel filters. For this reason, the storage temperature of most pure biodiesel is generally kept between 7 and 10ºC. Even in extremely cold climates, underground storage of pure biodiesel usually provides the storage temperature necessary for preventing crystal formation.

Bondioli noted that the stability of biodiesel is an important property when it is to be stored for a prolonged period. Poor stability can lead to an increased acid value and fuel viscosity and to the formation of gums and sediments. Therefore, if the duration of storing biodiesel or biodiesel blends is more than 6 months, it should be treated with an antioxidant additive. Moreover, because water contamination will lead to biological growth in the fuel, it should be minimized in the stored fuel by using biocides. Biodiesel storage tanks made of aluminum, steel, Teflon, and fluorinated polyethylene or polypropylene should be selected.

The tanks should minimize the possibility of water contamination and should be cleaned prior to use for biodiesel storage.

Table 2.3(a) Different approaches for purifying crude biodiesel (Wu et al.,2010)

Approaches	Primary material used	Function	Phases separation	Advantage	Disadvantage
Water washing	Distilled Warm water Softened water	Prevents precipitation of saturated fatty acid esters. Retards the emulsion formation. Eliminates calcium and magnesium Contamination	Separation funnel, centrifuge, molecular sieves, silica gels, etc.	Very effective in removing contaminants	Increased cost and production time, liquid effluent, product loss, emulsions formation
Dry washing	Ion exchange resin Magnesium Silicate powder	Brings the free glycerol level down and removing soaps	–	Waterless	Overruns the limit in the EN Standard
Membrane extraction	Polysulfone	Remove the Contaminants	–	Avoids the emulsion formation and decreases the refining loss	Probably high cost and low throughput due to contaminants existed

Table 2.3(b) Specifications and test methods of ASTM D6751 and EN 14214 standards [EN, 2003; ASTM]

Property	Unit	Limits	
		ASTM D6751	EN 14214
Flash point	⁰C	130.0 min	101.0 min
Kinematic viscosity at 40 ⁰C	mm^2/s	1.9–6.0	3.5–5.0
Cetane number	–	47	51
Sulphated ash content	% (m/m)	0.020 max	–
Copper strip corrosion	–	No. 3 max	Class 1
Acid value	mg KOH/g	0.80 max	0.5 max
Free glycerol	% (m/m)	0.020 max	–
Total glycerol	% (m/m)	0.240 max	0.25 max
Phosphorous content	% (m/m)	0.001 max	0.01 max
Carbon residue	–	–	–
ASTM D6751 (100% sample)	% (m/m)	0.050 max	–
EN 14214 (10% bottoms)	–	–	0.3 max
Cloud point	⁰C	Report customer	–
Density at 15 LC	kg/m^3	–	860–900
Distillation T90 AET	⁰C	360 max	–
Sulfur (S 15 Grade)	ppm	0.0015 max	–
Sulfur (S 500 Grade)	ppm	0.05 max	–
Sulfur content	mg/kg	–	10 max
Water and sediment	%vol.	0.050 max	–
Water content	mg/kg	–	500 max
Total contamination	mg/kg	–	24 max
Oxidation stability at 110 ⁰C	h	–	6 min
Iodine value	–	–	120 max
Linolenic acid methyl ester	% (m/m)	–	12 max
Ester content	% (m/m)	–	96.5 min
Methanol content	% (m/m)	–	0.2 max
Monoglyceride content	% (m/m)	–	0.8 max
Diglyceride content	% (m/m)	–	0.2 max
Triglyceride content	% (m/m)	–	0.2 max
Alkaline metals (Na + K)	mg/kg	–	5 max

2.4. Main factors affecting the yield of biodiesel

2.4.1. Alcohol quantity

Many researchers recognized that one of the main factors affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Theoretically, the ratio for transesterification reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. The yield of biodiesel is increased when the alcohol triglyceride ratio is raised beyond 3 and reaches a maximum. Further increasing the alcohol amount beyond the optimal ratio will not increase the yield but will increase cost for alcohol recovery. In addition, the molar ratio is associated with the type of catalyst used and the molar ratio of alcohol to triglycerides in most investigations is 6:1, with the use of an alkali catalyst. When the percentage of free fatty acids in the oils or fats is high, such as in the case of waste cooking oil, a molar ratio as high as 15:1 is needed when using acid catalyzed transesterification.

2.4.2. Reaction time

Freedman found that the conversion rate of fatty acid esters increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of <90 min, and then re-mains relatively constant with a further increase in the reaction time. Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps.

2.4.3. Reaction temperature

Temperature clearly influences the reaction and yield of the biodiesel product. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. However, it is found that when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides. The reaction temperature must be less than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization. Depending on the oil used, the optimal temperature ranges from 50ºC to 60ºC.

2.4.4. Catalyst concentration

Catalyst concentration can affect the yield of the biodiesel product. As mentioned before, the most commonly used catalyst for the reaction is sodium hydroxide. However, Freedman found that sodium methoxide was more effective than sodium hydroxide because upon mixing sodium hydroxide with methanol a small amount of water will be produced, which will affect the product yield because of the hydrolysis reaction. This is the reason why the catalyst should be added into the methanol first and then mixed with the oil. As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel in-crease. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters. Usually, the yield reaches an optimal value when the catalyst (NaOH) concentration reaches 1.5 wt. % and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap.

2.5. Other processes of biodiesel production

2.5.1. Biox cosolvent process

The Biox cosolvent process was developed by Boocock et al. in 1996. In this process, triglycerides are converted to esters through the selection of inert cosolvents that generate a one phase oil rich system. Cosolvent options are available to overcome slow reaction times caused by the extremely low solubility of the alcohol in the triglyceride phase. Tetrahydrofuran (THF) is used as a cosolvent to make the methanol soluble. After the completion of the reaction, the biodiesel–glycerol phase separation is clean and both the excess alcohol and the tetrahydrofuran cosolvent can be recovered in a single step. However, because of the possible hazard and toxicity of the cosolvents, they must be completely removed from the glycerol phase as well as the biodiesel phase and the final products should be water free. The unique advantage of the Biox cosolvent process is that it uses inert, reclaimable cosolvents in a single pass reaction that takes only seconds at ambient temperature and pressure, and no catalyst residues appear in either the biodiesel phase or the glycerol phase. This process can handle not only grainbased feedstocks but also waste cooking oils and animal fats. Van Gerpen found, however, that the recovery of excess alcohol is difficult when using this process because the boiling point of the THF cosolvent is very close to that of methanol.

2.5.2. Supercritical alcohol process

As is known, when a fluid or gas is subjected to temperatures and pressures in excess of its critical point, a number of unusual properties are exhibited. Under such conditions, a distinct liquid and vapor phase no longer exist. Instead, a single fluid phase is formed. Therefore, a process for biodiesel production has been developed by a non-catalytic supercritical methanol method. Because of the lower value of the dielectric constant of methanol in the supercritical state, this approach is believed to be able to solve the problems associated with the two-phase nature of normal methanol/triglyceride mixtures by forming a single phase, and the reaction is completed in a very short time (Deshpande et al., 2011). Supercritical transesterification is carried out in a high pressure reactor, with heat supplied from an external heater. Reaction occurs during the heating period. After the reaction is complete, the gas is vented and the product in the reactor is poured into a collecting vessel. The remaining contents are removed from the reactor by washing it with methanol. During the whole process, several variables (i.e. reaction pressure and temperature) affect the yield of the biodiesel product and the highest yield can be obtained under the optimal conditions. In contrast to the common alkali catalyzed method, this process has advantages in terms of reaction time and purification but requires a high temperature and pressure, hence requiring a high amount of energy.

2.5.3. In situ biodiesel process

The in situ biodiesel production is a novel approach for converting oil to biodiesel which was developed by Harrington and D’Arcy Evans in 1985. In this method, to achieve transesterification of its acyglycerols, the oilseeds are directly treated at ambient temperature and pressure with a methanol solution in which the catalyst has been previously dissolved. That means that the oil in the oilseeds is not isolated prior to transesterification to fatty acid esters. To reduce the alcohol requirement for high efficiency during in situ transesterification, the oilseeds need to be dried before the reaction takes place. Milled oilseeds are mixed with alcohol in which the catalyst had been dissolved and the mixture is heated under reflux for 1–5 h. Two layers are formed around the time of the completion of the reaction. The lower layer is the alcohol phase and can be recovered. The upper layer, including the crude biodiesel, is washed with water to remove the contaminants until the washing solution is neutral. After the washing step, the upper layer is dried over anhydrous sodium sulfate, then filtered, and the residual product is biodiesel. Haas and Scott found that the final biodiesel product can conform to the ASTM standard and the conversion of the oilseed is very high (about 98%). Since this method eliminates the need for the isolation of, and possibly for the refining of, the oilseed lipid, the process could reduce biodiesel production costs, reduce the long size of the production system associated with the preextraction, degumming, and maximize the yield of the biodiesel production. However, this process cannot handle waste cooking oils and animal fats, which can reduce the cost of feedstock.

2.6. Heterogeneous catalysis for biodiesel production

Homogeneous catalysts are commonly applied in the transesterification of vegetable oils. Base homogenous catalysts such as NaOH and KOH are the most active under mild reaction conditions. Acid homogeneous catalysts are also used but require longer reaction time as compared to the alkaline-based transesterification reaction. However, homogeneous catalysts are difficult to recover and lead to downstream waste treatment, increasing the cost of biodiesel production. Base catalysts have limitation for high FFA containing oils leading to soap formation and consumption of the catalyst. They are also sensitive to water content in the oil. Acid catalysts are usually used for oils with high FFAs.

The main mechanism of heterogeneous catalysis follows similarly the principle of homogeneous catalysis of either acid or base systems. The important factor in homogeneous base catalyzed reaction is to create nucleophilic alkoxide from the alcohol to attack the electrophilic part of the carbonyl group of the triglycerides while in acid catalysis the carbonyl group in triglycerides is protonated and the alcohol attacks the protonated carbon to create a tetrahedral intermediate. The breakdown of triglyceride requires three steps. The first step is to produce an intermediate tetrahedral and the second step is the breakdown of the unstable intermediate tetrahedral to diglyceride ion and fatty acid ester. The last step is the recovery of the catalyst by proton transfer. These three mechanisms are repeated for cleavage of each fatty acid ester and then finally three fatty acid esters and a glycerol are formed. Like homogeneous catalysis, acidic and basic characteristics of heterogeneous catalysis are important properties for transesterification of triglycerides. In heterogeneous catalysis contrary to the homogenous system, adsorption of reactants and desorption of products have to take place on the surface of the solid catalyst for the reaction to take place at increased rate.

Heterogeneous catalysts are promising candidates for biodiesel production from vegetable oils. Different types of heterogeneous catalysts and their activity for transesterification have been studied since more than a decade ago. Unlike homogeneous, heterogeneous catalysts can be recycled and used several times with better separation of the final product, are environmentally benign and can be used in a continuous process without the need for further purification steps. They are also potentially cheap. Heterogeneous catalysts can easily be tuned to include desired catalyst properties so that the presence of FFAs or water does not adversely affect the reaction steps during transesterification.

Unlike edible oils, nonedible oils have high FFA which greatly reduces the biodiesel yield during transesterification. To solve this problem, two step methods is most commonly used. The first step is the FFA esterification reaction. This reaction is commonly carried out using homogenous acid catalyst. The second step is transesterification reaction mostly using base catalysts. However, the two step method increases system complexity and the cost of production. Single step simultaneous esterification and transesterification using heterogeneous catalysts can be an ideal solution for biodiesel production from nonedible oils such as Jatropha curcas oil (JCO).

The performance of different solid acid catalysts for simultaneous esterification and transesterification of high FFA vegetable oils has been studied. Mesoporous Ta_2O_5/SiO_2 - [H3PW12O40/R] (R = Me or Ph) hybrid catalysts, sulfated zirconia, sulfated carbon base catalysts and ZnO-La_2O_3 catalysts are some of the results reported. However, acid solid catalyst requires high reaction temperatures, high alcohol to oil ratios and longer reaction time for complete conversion to biodiesel. Catalysis for esterification using solid acids proceeds at a faster rate than transesterification.

The objective of this work is to develop and test catalysts or mixture of catalysts, which catalyze a simultaneous esterification and transesterification of JCO with FFA content in a single step and compare with a reference sample of RSO. For this type of reactions, catalysts need to have both acidic and basic properties for esterification and transesterification to result in high conversions of the reactants to biodiesel. Metal oxide-based catalysts are known to have acidic or basic catalytic. Metal salts with acidic catalytic sites are known for their esterification reaction. In this study, rare earth metal oxide catalysts of La loaded on zinc oxide (La_2O_3-ZnO), on alumina (La_2O_3/Al_2O_3) and a perovskite catalyst (La0.1Ca0.9MnO3) were prepared and tested for transesterification and compared with a reference sample of RSO. Likewise, mixtures of alkaline earth metal oxide (CaO) or alkali doped alkaline earth metal oxide (Li-CaO) with iron(III) sulfate ($Fe_2(SO4)_3$) were also tested for simultaneous esterification and transesterification of JCO with high FFA content in a single step reaction for the first time in a batch reactor under mild conditions.

2.6.1. Methods

2.6.1(i) Materials

Crude JCO and RSO. $CaCO_3$ (99.9% purity), $LiNO_3$ (99.9% purity), ZnO (99% purity) and Al_2O_3 (70-230 mesh size) and methanol (extra pure). La $(NO_3)_3.6H_2O$ (99.9% purity) and Fe_2 $(SO4)_3$.

2.6.1(ii) Catalyst preparation and characterization

Calcium oxide (CaO) was prepared by decomposing pulverized $CaCO_3$ at 960°C for 3½ h. Lithium doped calcium oxide (Li-CaO) was prepared by the incipient wetness or impregnation method: 7 g of $LiNO_3$ was dissolved in water and 10 g of CaO was added and stirred by magnetic stirrer. The solution was dried in oven at 120°C for 3 h and calcined at 550°C for a duration of 3 h. Lanthanum loaded on zinc oxide (La_2O_3-ZnO) and supported on alumina (La_2O_3/Al_2O_3) catalysts were also employed as heterogeneous catalysts for transesterification. Incipient wetness impregnation followed by oven drying and calcinations was used to prepare these catalysts (Ibrahim et al., 2013). A 10 g of $La(NO_3)_3.6H_2O$ was dissolved in water and 7.5 g of ZnO added to the solution. The solution was stirred and oven dried at 150ºC for 3 h. The catalyst was calcined at 470ºC for 3 h. La supported on alumina (Al_2O_3) was also prepared by the same method. A 5 g of $La(NO_3)_3.6H_2O$ was dissolved in water and 20.3 g of Al_2O_3 was added and stirred using magnetic stirrer. The mixture was dried in oven at 150 ºC for 3 h followed by calcinations at 600ºC for 3 h. Anhydrous iron(III) sulfate ($Fe_2(SO4)_3$) was dried in oven to remove any trace of moisture at 110ºC for 3 h prior to use as a catalyst. $La0.1Ca0.9MnO_3$ catalyst was prepared by the precipitation method and was calcined at 650ºC.

Catalyst samples and supports were characterized according to the BrunauereEmmetteTeller (BET) analysis method of the surface area as well as porosity by Micrometrics ASAP 2010. Isotherms were recorded to obtain several point BET-surface areas. Micropore, mircopore volume and pore size were also analyzed. Samples were degassed overnight at 250ºC drying temperature with liquid nitrogen trap. N2 adsorptions at 77 K were used for surface characterization.

2.6.1(iii) Transesterification

A three-necked glass reactor in a hot thermostat bath system as shown in Fig. 1(b) was used as a batch reactor to test the activity of the catalysts. Test of the catalysts and transesterification were carried out under reaction conditions of 60ºC reaction temperature, 3 h of reaction time,

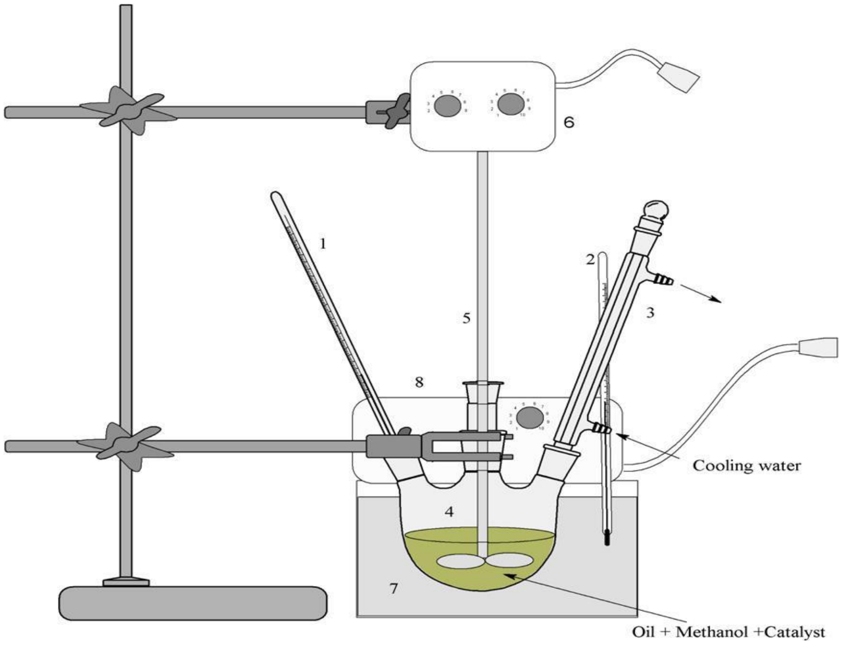


Fig.1(b) Schematic reaction apparatus for batch production of biodiesel (A.K.Endalew et al., 2011).
1 and 2- thermometers, 3-condenser,4-glass reactor,5-Teflon stirrer,6-agitation motor,7-hot water bath,8-thermostat heat control unit.

6:1 molar based alcohol to oil ratio, 5 wt. % catalysts (based on the amount of oil) and an agitation speed of 300 revolutions per min (rpm). In order to increase the miscibility of the oil and methanol as well as the mass transfer rate, the mixing intensity was kept constant throughout the reaction time. A mixture of catalyst and methanol was stirred and heated to the reaction temperature. 90 ml of oil was heated separately to reach the reaction temperature. Oil and catalyst methanol mixture were introduced to the reactor. Cooling was done through tap water piping through the condenser. Thermometers were inserted to measure the reaction and water bath temperatures, respectively. Reaction agitation was made by Teflon stirrer driven by an electrical motor. Centrifugation of samples was done at 5700 rpm for 30 min and a clear phase separation was obtained. After centrifugation, the sample due to differences in densities is separated into four distinct phases according to the following sequence from top to the bottom: methanol, biodiesel, glycerol and solid catalyst, respectively. Samples for further analysis were prepared from the upper part of the clear biodiesel phase.

A GC (Agilent 6890) fitted with split inlet and flame ionization detector (FID) and an HP-FAAP polyethylene glycol TPA column was used for quantitative analysis of the samples. Propyl acetate was used as a GC internal standard, while the GC was calibrated for methyl ester content using a solution containing carbon numbers ranging from C8 to C24. Acid based titrations were performed to determine the FFA content of JCO and RSO. A 0.46 M KOH was prepared to analyze the FFA content of the oils. 5 ml of oil was added to 40 ml of propanol and was well stirred. The oil was titrated three times for its acidity and an average value was obtained. The viscosity of the oil and biodiesel was measured on Brookfield (KF 10) falling body viscometer at room temperature. The viscometer was calibrated for a known viscosity of ethanol.

2.6.2. CaO

CaO is the best known solid base catalyst for transesterification of low FFA content oils. It is relatively cheap and non toxic. CaO has been tested for transesterification of many vegetable oils. However, like most alkaline catalysts, soap formation is the main problem consuming and deactivating the catalyst for transesterification of high FFA content vegetable oils (Rane et al., 2008). The morphology of CaO catalyst from $CaCO_3$ greatly depends on the treatment temperature and time. Granados treated pulverized $CaCO_3$ at 800 ⁰C for 1 h and found a BET-surface area of 43 m^2/g, pore diameter of 24 nm and a pore volume of 0.3 cm^3/g.The catalyst was used for transesterification of sunflower oil and a FAME yield of 90% was obtained for 14:1 methanol to oil ratio, 5 h of reaction time and at 60ºC. Kouzu treated $CaCO_3$ at 900ºC for 1.5 h and a surface area of 13 m^2/g was measured. The catalyst was used in transesterification of soybean oil (SBO) with more than 12:1 methanol to oil ratio and at 65ºC. Nearly complete conversion was obtained for 2 h of reaction time.

Fortunately, increasing the calcinations temperature (up to decomposition temperature of $CaCO_3$) for CaO increases the basicity of the catalyst which is an important property for the catalyst activity in transesterification (Rane et al., 2008). In this study, high treatment temperature and longer time of treatment reduced the surface area to 2 m^2/g. The catalyst is expected to have high surface basicity due to increased treatment temperature and time.

The CaO with such surface properties was tested for its activity in transesterification of JCO and only 18% FAME yield was obtained and much soap was formed as shown in Fig. 2(a) Although CaO is very active catalyst for transesterification of low FFA oils, the activity of the catalyst is highly affected by the presence of FFA and favors unwanted side reactions. The same catalyst was also tested for its activity for commercial RSO under the same reaction conditions. A complete conversion was obtained after 3 h of reaction time as shown in Fig.2(b).c

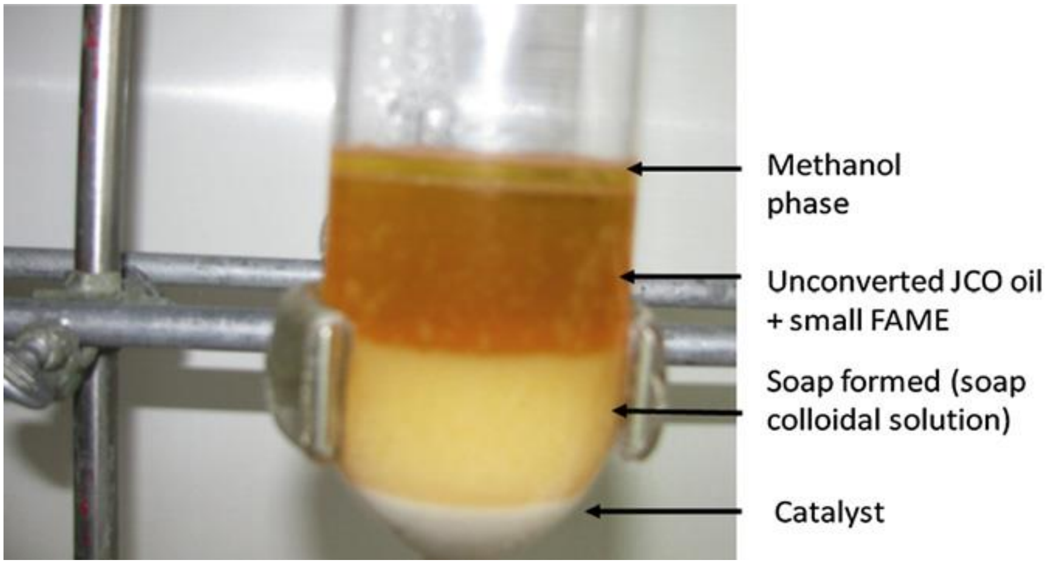


Fig 2(a) Soap Formation (A.K.Endalew et al., 2011).

The formation of soap on the surface of CaO proceeds when the FFA in the oil is supposed to neutralize the Ca^{2+} on the surface of the catalyst. Two FFA molecules are required for neutralization of a divalent Ca^{2+} and create a large molecule of soap. This inhibits the adsorption of methanol on the catalyst to proceed at a higher rate than for the transesterification reaction. The calcium soap can detach from the surface of the catalyst and create a soap colloidal solution as shown in Fig. 2(a)

2.6.3. Li-CaO catalyst

It has been reported to show a significant improvement in the transesterification of low FFA oils compared to lone CaO as a catalyst. Watkins tested Li-CaO for transesterification of glyceryl tributyrate with methanol and found a significant improvement of catalyst activity compared to the parent CaO catalyst. Li-CaO was also used in the transesterification of sunflower oil with the same method of catalyst preparation as Watkins found a higher activity than CaO. The activity of Li-CaO catalyst for transesterification of high moisture content of vegetable oil (15 wt.%) and high FFA content (6%) was tested under reaction conditions of $60^{o}C$ and 5 wt.% catalyst (based on oil) and gave a complete conversion to biodiesel in 2.5 h reaction time(Watkins et al.,2004). The Li-CaO preparation method was employed in this study but different heat-treatment and amount of doping. Mixtures of $LiNO_3$ and CaO were calcined at 550⁰ C for 3 h in air (higher than the decomposition temperature of $Ca(OH)_2$ and $LiNO_3$) and with higher loading of lithium content. Increasing the amount of Li doping on CaO decreased the surface area dramatically. In Watkins experiment, 4 wt. % Li on CaO has decreased the CaO surface area from 20 to 8 m^2/g while in Rane work doping 28.5 wt. % Li on CaO reduced the surface area from 6 m^2/g to 0.2 m2/g and in our experiment the 6.63 wt. % Li loading decreased the CaO surface area from 2 to 0.076 m^2/g. However, high pore diameter allows bulky triglycerides to diffuse easily to the catalytic sites. The reduction of surface area is due to the small ionic radius of Li^+ which fills the micro pore area of CaO. Li^+ introduced in the lattice of CaO forms a solid solution closing up the structural defects which decrease the surface area of the catalyst. Lithium doping has shown an increase in the basicity and catalytic activity of CaO. Watkins measured basicity by Hammet indicator method and obtained a 4 wt.% Li doping increased the basicity from $10 > pK_{BH+} > 8$ for CaO to $17.2 > pK_{BH+} > 15.0$, while Rane et al [2008] used the same method and reported 28.5 wt.% Li doping increased the basicity of CaO from $9.8 < pK_{BH+} < 10.1$ to $11.1 < pK_{BH+} < 15.0$. The same phenomenon was reported by Rane et al. [2008] by CO_2 adsorption basicity measurement. Though there are disparities among these studies on the surface basicity measurements of catalytic materials due to mainly concentration of Li, impregnation method, calcinations temperature and time, the presence of Li on CaO shows increased basicity than CaO alone. Higher basic strength promotes the activity of Li-CaO for transesterification. Thus, Li doping of 6.6% of CaO and calcinations temperature of 550⁰C for 3 h is sufficient to cause high basicity for the catalysts prepared by us. Li-CaO catalyst was tested for transesterification of JCO and RSO. Significant amount of soap was formed for JCO transesterification due to the high FFA content of the oil. Interestingly, the reaction products have different colors and viscosities. The sample obtained from JCO has very dark yellow color while greenish color for

RSO as shown in Fig.2(b). Fig. 2(b).a has three noticeable phases: biodiesel, soap, glycerol and catalyst from top to bottom, respectively. Both Fig.2(b).b and c didn’t produce any soap and have three noticeable phases: biodiesel, glycerol and catalyst from

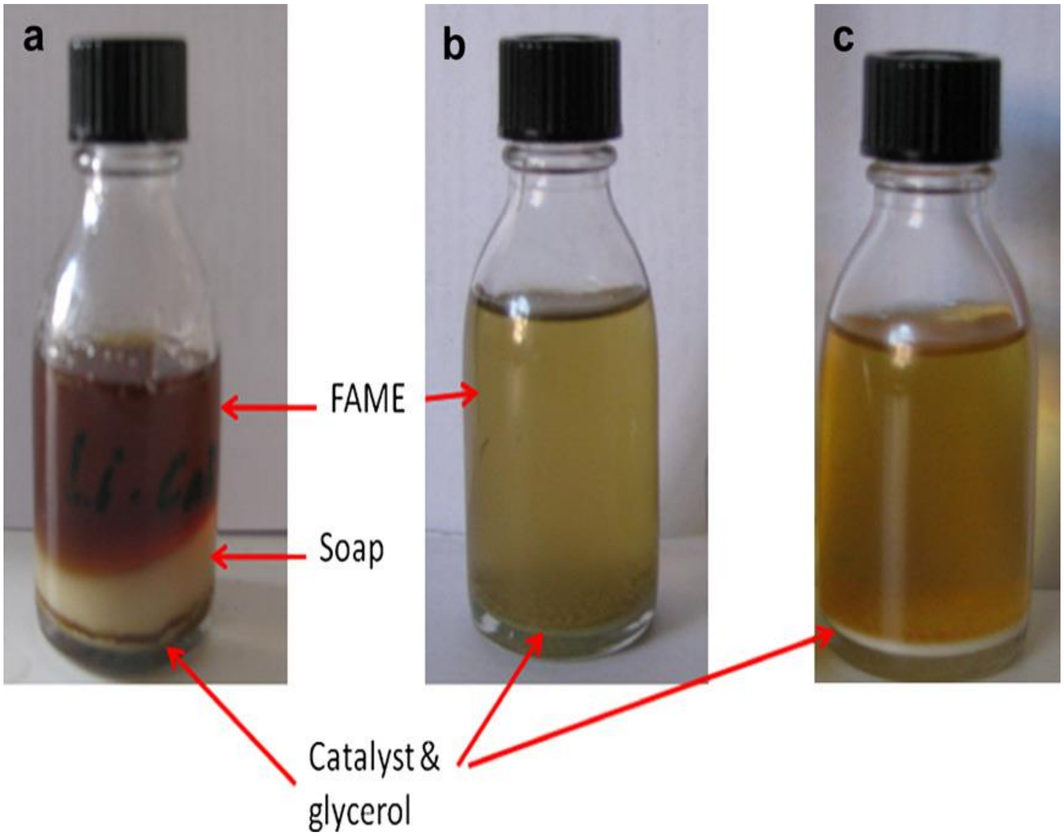


Fig. 2(b) Biodiesel from a) JCO (after centrifugation) by Li-CaO, b) RSO by Li-CaO and c) RSO by CaO catalysts (A.K.Endalew et al. , 2011).

top to down, respectively. Biodiesel obtained from RSO by Li-CaO has a greenish yellow color which is similar to commercially obtained rapeseed methyl ester (RME). Viscosity measurements showed that biodiesel of JCO by Li-CaO was found to be higher (ca. 5.8 cSt) than by CaO (ca. 4.3 cSt). The differences in color and viscosity of products from Li-CaO and CaO catalyst may be ascribed to the composition of the biodiesel and side reaction such as oxidation. A complete conversion was achieved for RSO and a conversion of 66.4% was obtained for

JCO as shown in Fig.2(c). The yield showed a better performance for Li-CaO than pure CaO catalyst during the transesterification of this high FFA containing oil.

2.6.4. La_2O_3-ZnO, La_2O_3/Al_2O_3 and La0.1Ca0.9MnO3 Transition metal oxide catalysts:

These are of interest due to their activity in simultaneous transesterification and esterification of high FFA containing vegetable oils and are found to be water tolerant, which the very active alkali and alkaline metal oxide catalyst slack.

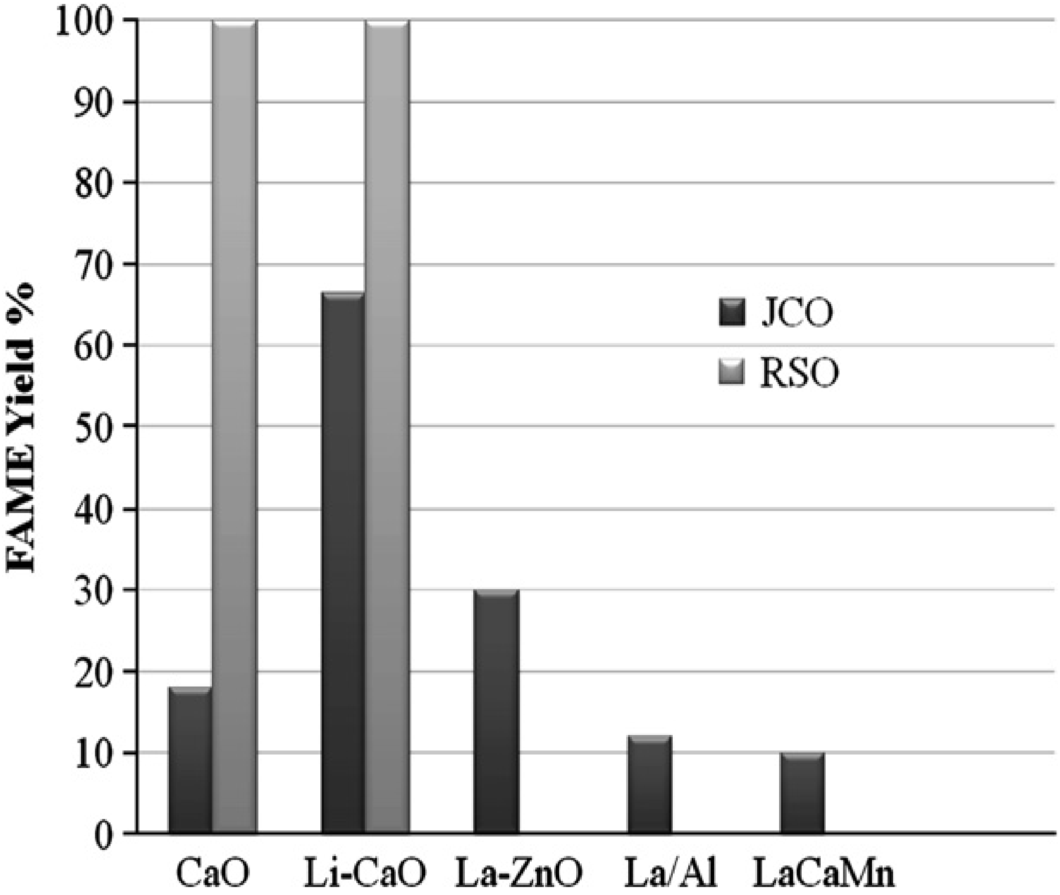


Fig. 2(c) FAME yield using catalysts of CaO, Li-CaO, La-ZnO(La_2O_3-ZnO), La-Al(La_2O_3/Al_2O_3), and LaCaMn(La0.1Ca0.9MnO_3).

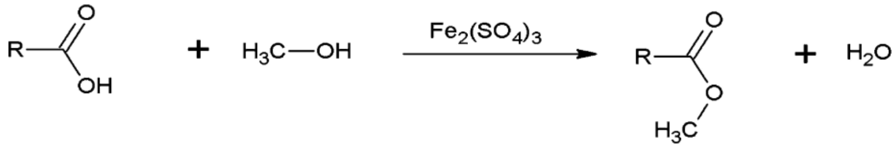
(A.K.Endalew et al., 2011).

Amphoteric metal oxide catalysts can be prepared by combining Lewis base metal oxides and Lewis acid metal oxides. This can lead to the prevalence of Lewis base and acid catalytic sites in a single catalyst for simultaneous esterification and transesterification reaction. The main drawback of these transition metal oxide catalysts is that they require harsh reaction conditions compared to alkali and alkaline metal oxides. Although these catalysts give better catalyst morphology, the activity towards esterification and transesterification highly depends on the basic and acid strength of the catalytic sites and the reaction conditions. Three amphoteric metal oxide catalysts were prepared and tested for transesterification of JCO at low reaction temperature. A mixture of lanthanum oxide (La_2O_3) and zinc oxide (ZnO) catalyst was prepared and tested for biodiesel production. La_2O_3-ZnO catalyst was prepared with different ratio of Zn:La and tested for simultaneous esterification and transesterification of soybean with different FFA content adjusted by adding oleic acid. A catalyst with 3:1 molar ratio of Zn: La was found to give the best FAME yield. This catalyst was proved to esterify up to 32% FFA and was tolerant to 5% water addition. Unfortunately, the reaction requires very high temperature (200ºC) and high methanol to oil ratio (36:1) which limits the applicability of the catalyst. ZnO and La_2O_3 catalyst were tested for transesterification of ethyl methyl carbonate from diethyl carbonate and methanol. ZnO was found to be more active than La_2O_3. A 26.5% conversion at 103ºC for 1:1 molar ratio of reactants was obtained by ZnO alone while La_2O_3 only yielded 12.6% conversion with the same reaction conditions. The activity of amphoteric metal oxide catalysts for esterification and transesterification depends on the morphology but is more dependent on the basic and acidic properties. Auroux and Gervasini evaluated the acidity and basicity of different metal oxides by NH_3 and SO_2 adsorption and found ZnO is more Lewis acid while La_2O_3 is more Lewis base. However, ZnO was found to have both Lewis base and acidic sites compared to the more basic La_2O_3. Shen have also measured the basicity of ZnO and La_2O_3 by CO_2 adsorption and La_2O_3 were found to have higher basic strength. Yan have measured the surface charge percentage of different ratio of

Zn: La and found that pure La_2O_3 has more oxygen ion than pure ZnO which can contribute to the higher basicity in La_2O_3 and the surface atom ratio O^{2+} : (Zn^{2+}, La^{3+}) increases as the La content increases. This supports the hypothesis that increasing the La content can increase the basicity of the surface which can enhance the activity in capturing H+ from methanol and initiate transesterification reaction. The esterification of FFA can be enhanced by the Lewis acid sites of ZnO. Catalyst surface area and porosity measurement of La_2O_3-ZnO_2 has shown an increase in pore diameter by 41.8% compared to ZnO, which may reduce the diffusion limitation of bulk triglyceride to the catalytic site and enhance the activity of the catalyst. The high content of La_2O_3 can also increase the surface basicity of the catalyst. The catalyst was tested for transesterification of JCO and a 30.1% conversion to biodiesel was obtained at low reaction temperature (60ºC) and low methanol to oil ratio (6:1). This result shows a significant enhancement of activity compared to the work reported by Yan. The disparity in the activity may emanate from the different methods of catalyst preparation and loadings increasing the surface basicity and thereby enhancing the transesterification. Unlike CaO and Li-CaO catalysts, soap formation was not noticed using this catalyst. The use of higher temperature and methanol to oil ratio may further increase the activity of the catalyst. Lanthanum oxide supported on alumina (La_2O_3/Al_2O_3) was also tested for transesterification of JCO under the same reaction conditions as the other catalysts discussed above. Al_2O_3 and MnO_3 are reported to have a weak Lewis acid site compared to ZnO. La loading reduces the strength of acidic sites in Al_2O_3 and increases the basic strength of La_2O_3. An intermediate between the acid and basic strength develops which can decrease the activity towards esterification and transesterification. 11.9% conversion was obtained employing the catalyst for transesterification of JCO. The low activity may also be due the low pore diameter of the catalyst which can create diffusion limitations. A perovskite of the type of lanthanum doped calcium manganese oxide with Mn^{4+}, Ca^{2+} and La^{3+} can create a structural defect which can increase the basicity of the catalyst. However, the activity of the catalyst for biodiesel production was found to be low, ca. 10%. Changing reaction conditions such as temperature and pressure and the active metal loading may increase the activity of the catalyst. Fig.2(c) shows the performance of the five different catalysts for biodiesel production. The activity of CaO and Li-CaO was compared with the two feedstocks, i.e. JCO and RSO. These two catalysts showed total conversion of RSO to biodiesel while their activity is greatly affected by the presence of FFA in the JCO. The other three catalysts showed very low conversion in the range of 10-30%. For this reason, the further study mainly focuses on improving the performance of CaO and Li-CaO.

2.6.5. Single-step simultaneous esterification and transesterification

CaO and Li-CaO catalysts have been found very active for the transesterification of RSO. However, these catalysts gave low FAME yield for transesterification of JCO due to the formation of much soap leading to the consumption and deactivation of the catalysts. Soap formation can be prevented using simultaneous esterification and transesterification method using solid acid and base catalysts together as mixture. $Fe_2(SO4)_3$ catalyst was tested for its activity towards esterification. Catalysts mixtures of CaO+ $Fe_2(SO4)_3$, Li-CaO + $Fe_2(SO4)_3$ and La_2O_3-ZnO + $Fe_2(SO4)_3$ were tested in a single step simultaneous esterification and transesterification of JCO under the same reaction conditions. Several organic reactions can be catalyzed by Fe^{3+} salts. Fe^{3+} acts as Lewis acid and creates an intermediate coordination with reactants. The metal salt is proved to be active catalyst for organic nucleophilic substitution and addition reactions. $Fe_2(SO4)_3$ has been tested for esterification of carboxylic acids and was found to be very effective. Esterification of stearic acid



FFA esterification reaction by $Fe_2(SO4)_3$.

with butanol using $Fe_2(SO4)_3$ catalyst was reported and a 71% conversion to butyl ester was obtained at 10:1 butanol to stearic acid ratio and at 140⁰C. $Fe_2(SO4)_3$ on supports was also tested for esterification reactions. Pipus used $Fe_2(SO4)_3/Al_2O_3$ for esterification of benzoic acid and transesterification of low FFA vegetable oil and found a complete conversion for methyl benzoate and 75% yield of methyl esters at 30:1 methanol to oil ratio and at 220⁰C. However, combination of $Fe_2(SO4)_3$ with highly active solid base catalysts such as Li-CaO and CaO for simultaneous esterification and transesterification of crude vegetable oil with high FFA in a single batch reactor system has not been reported to our knowledge so far. Combining these two types of solid catalysts without any further activation can be mixed and tested with the required proportion or ratios. This implies a cost effective system with distinctive features where two subsequent reactions take place in a single heterogeneous mold. The esterification of FFA in the oil is catalyzed by the solid $Fe_2(SO4)_3$, while transesterification reaction proceeds on the solid base acid simultaneously. The ratio of $Fe_2(SO4)_3$ to CaO and Li-CaO was adjusted to attain a complete conversion without any soap formation. A CaO:$Fe_2(SO4)_3$ weight ratio of 3:1 was tested and a FAME yield of 93.37% was obtained while Li-CaO gave a FAME yield of 96% with the same ratio as shown in Fig.2(d). The same reaction conditions as previous tests were used to achieve these yields. However, some soap formation was still observed. The $Fe_2(SO4)_3$ content was increased to a ratio of 2:1 (CaO or Li-CaO:$Fe_2(SO4)_3$) in order to avoid any soap buildup as obtained in the above experiment by increasing the esterification reaction. A complete conversion to FAME was obtained for both catalysts without any soap formation. The properties of biodiesel obtained by Li-CaO + $Fe_2(SO4)_3$ was the same as the biodiesel obtained with Li-CaO. The esterification reaction catalyzed by $Fe_2(SO4)_3$ inhibited the soap formation whereas CaO or Li-CaO catalysts enhance the transesterification reaction. A combination of La_2O_3-ZnO+ Fe_2 $(SO4)_3$ was also tested

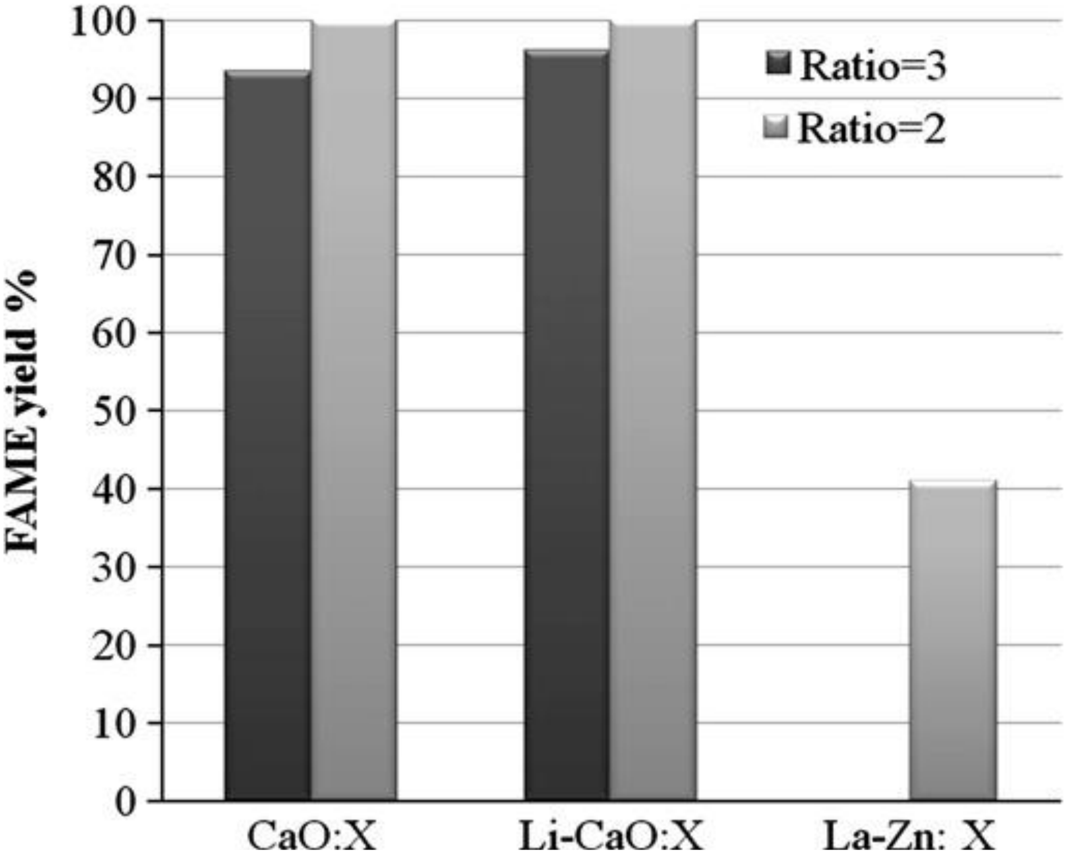


Fig.2(d) FAME yield in a single-step simultaneous esterification and transesterification of JCO by a combination of solid base and acid catalysts, where X is $Fe_2(SO4)_3$. (A.K.Endalew et al., 2011).

Table 2.4 Biodiesel yield for various catalysts with solid acid Catalysts (A.K.Endalew et al., 2011)

Catalyst type	Oil source	FFA content wt.%	Reaction conditions (value with respective sequence: temperature, alcohol to oil ratio (molar based), reaction time, catalyst amount, agitation speed)	Yield %
KSF clay and Amberlyst 15	JCO	6.5	160°C, 12:1, 6 h, 5 wt.%, 300 rpm	70
SO_4^{2-}/SnO_2-SiO_2	JCO	8.14	180°C, 15:1, 2 h, 3 wt.%, 360 rpm	97
Supported heterpoly acid	SBO	10	200°C, 27:1, 10 h, 3 wt.%, 600 rpm	93.5
12-Tungstophosphoric acid (TPA)/Nb_2O_5	WCO	8	200°C, 18:1, 20 h, 3 wt.%, 600 rpm	92
Zinc stearate/silica gel (ZS/Si)	WCO	15	200°C, 18:1, 10 h, 3 wt.%, 600 rpm	98
CaO + $Fe_2(SO4)_3$	JCO	9	60 °C, 6:1, 3 h, 5 wt.%, 300 rpm	100
Li-CaO + $Fe_2(SO4)_3$	JCO	9	60°C, 6:1, 3 h, 5 wt.%, 300 rpm	100
La_2O_3-ZnO	JCO	9	60°C, 6:1, 3 h, 5 wt.%, 300 rpm	30

WCO (waste cooking oil); SBO (soybean oil); a this study for the same reaction conditions but with 9:1 methanol to oil ratio.

The catalyst showed an increased improvement in yield compared to its counterpart which can be attributed to the cumulative effect of esterification by $Fe_2(SO4)_3$ and to the higher methanol to oil ratio. Several studies on heterogeneous catalysts for biodiesel production from vegetable oils with high FFA have been conducted by other groups. Table2.4 compares the activity of catalysts tested in our study with other previous studies on solid acid catalysts used in single-step biodiesel production from high FFA feedstock. All studies were performed in batch reactors. However, solid acid catalysts have a major drawback that they entail harsh reaction conditions to achieve high biodiesel conversion. As shown in Table2.4, the requirement to obtain 70-98% conversions to FAME, the temperature should be at the range of 160-200 ^{0}C with very high alcohol to oil ratio and lengthy time. Thus, our study shows that a mixture of active solid acid and base catalysts leads to a significant improvement in the yield by applying mild reaction conditions.

2.6.6. Catalyst reuse

The performance of reused catalysts was tested using three catalyst recovery methods. CaO and Li-CaO are very sensitive to ambient air where the catalyst can be deactivated due to the reaction of atmospheric CO_2 with CaO and the presence of moisture. The first recovery method was recycling the catalyst with the glycerol from the previous reaction. Almost all the glycerol produced in the previous reaction was used to cover the catalyst so as to avoid air contact with the catalyst. The second method tested was drying the catalyst at 250^{0}C in oven so as to burn the biodiesel and keep the glycerol below the boiling point.

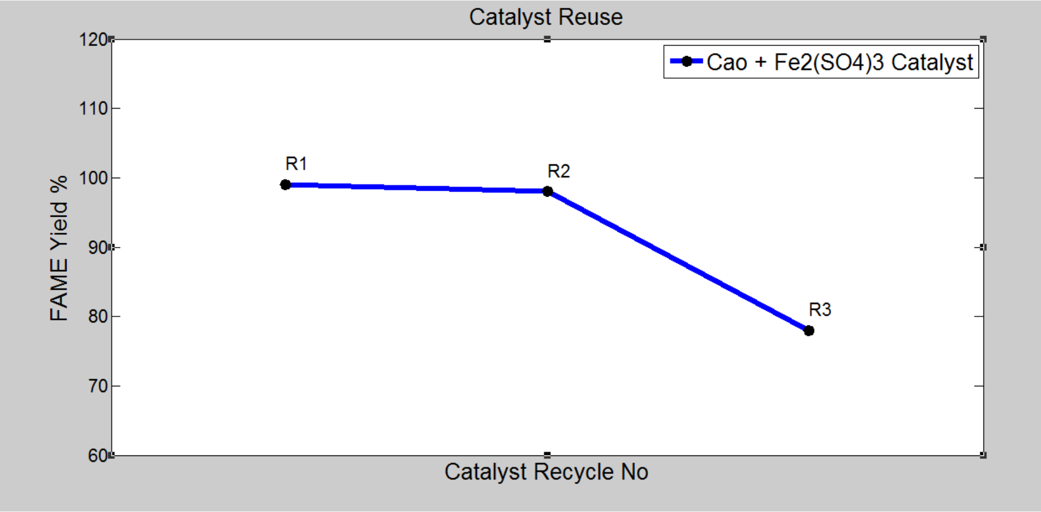


Fig.2(e) Reuse performance of CaO + $Fe_2(SO4)_3$ catalyst, R is recycle number (A.K.Endalew et al., 2011).

In the last method the catalyst was recovered from the first cycle by through filtration of the liquid (glycerol and biodiesel) from the solid catalyst combination. From the three methods, the first method was found effective in recovering the catalyst without deactivation by CO_2 from air. CaO + $Fe_2(SO4)_3$ was recycled three times as shown in Fig.2(e). Significant amount of soap has been formed in the second recycle of Li-CaO + $Fe_2(SO4)_3$ catalysts. Soap formation was found to be the major problem while recycling the catalyst, which can be due to the deactivation of both the catalysts for transesterification and esterification. The catalyst was probably deactivated by the presence of CO_2 as the reactor was not sealed from ambient air. Water from the esterification reaction can also be a source of deactivation, though CaO is said to be more water tolerant. Moreover, though both CaO and $Fe_2(SO4)_3$ with or without the reaction conditions under the agitation speeds were found to show high performances during the recycling of the catalyst mixtures in the reaction medium, CaO has been reported to be leaching in small amounts into the liquid products. This phenomenon of CaO dissolution has therefore to be corroborated in our further studies in order to assess the long-term stability of these catalysts for biodiesel production.

2.7. Conclusions

Biodiesel production from JCO requires both esterification and transesterification processes due to its high FFA content. Single step simultaneous esterification and transesterification method using heterogeneous catalysts can simplify the biodiesel production process and decreases the cost of production. Base and acid solid catalysts were tested for transesterification of jatropha oil. Mixtures of solid base and acid catalysts were also tested for simultaneous esterification and transesterification. CaO catalyst was found to have low yield due to high soap formation. Li-CaO catalyst was found to have better activity compared to the parent catalyst (CaO). Soap formation was found to be the main problem which reduced the activity of these two catalysts. La_2O_3-ZnO, La_2O_3/Al_2O_3 and $La_{0.1}Ca_{0.9}MnO_3$ catalysts were found to have low activity towards transesterification due to the low base or acid strength. Due to increased La content of La_2O_3-ZnO, its activity was found higher than the studies reported earlier in the literature. High temperature and pressure, longer reaction time and/or high reactant ratios can promote the activity of these catalysts. Mixture of active solid base and $Fe_2 (SO4)_3$ solid acid catalysts was found to be effective for simultaneous esterification and transesterification in a single-step reactor. CaO + $Fe_2 (SO4)_3$ and Li-CaO + $Fe_2 (SO4)_3$ catalysts have shown significant activity for biodiesel production. Due their high basic surfaces, CaO and Li-CaO catalysts were deactivated by the presence of atmospheric CO_2. Avoidance of atmospheric contact may increase the life of these very active base catalysts together with the solid acid catalysts.

2.8. Research Objective

The literature review is addressed to the application of various heterogeneous catalysts for biodiesel production. Heterogeneous catalysts are environmentally benign, non-corrosive, easily separated from the liquid products; give higher activity, selectivity and longer catalyst lifetime. However a high molar ratio of alcohol to oil, large amount of catalyst and high temperature and pressure are required while utilizing heterogeneous catalysts to produce biodiesel.Transesterification using CaO as solid catalyst and other basic alkaline earth metal compounds like calcium methoxide and barium hydroxide with different edible and non-edible oils has been studied.

Transesterification is basically a sequential reaction. 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 diglycerides and form more free fatty acids. These are undesirable reactions which reduce the yield of the biodiesel product. Therefore, after refining the raw materials, the acidic feedstocks should be pretreated to inhibit the saponification reaction. There are three primary approaches for reducing the amount of free fatty acids: esterification of free fatty acids with methanol, in the presence of acidic catalysts; using iodine as a catalyst; adding glycerol into the acidic feedstock with a catalyst like zinc chloride and heated to a high temperature. The first approach can eliminate the separation, corrosion, toxicity, and environmental problems, but the reaction rate is slower while the advantage of the last approach is that no alcohol is needed and the water (formed from the reaction) can be immediately vaporized and vented from the mixture.

The objective of this project was to study the effect of various catalyst types on the yield of biodiesel, which is made from neem oil having high free fatty acid (20%), and to optimize the various parameters affecting the yield of biodiesel by using Taguchi Method and ANOVA.

3. EXPERIMENTATION:

Fig.3(a) Neem Tree With Fruits

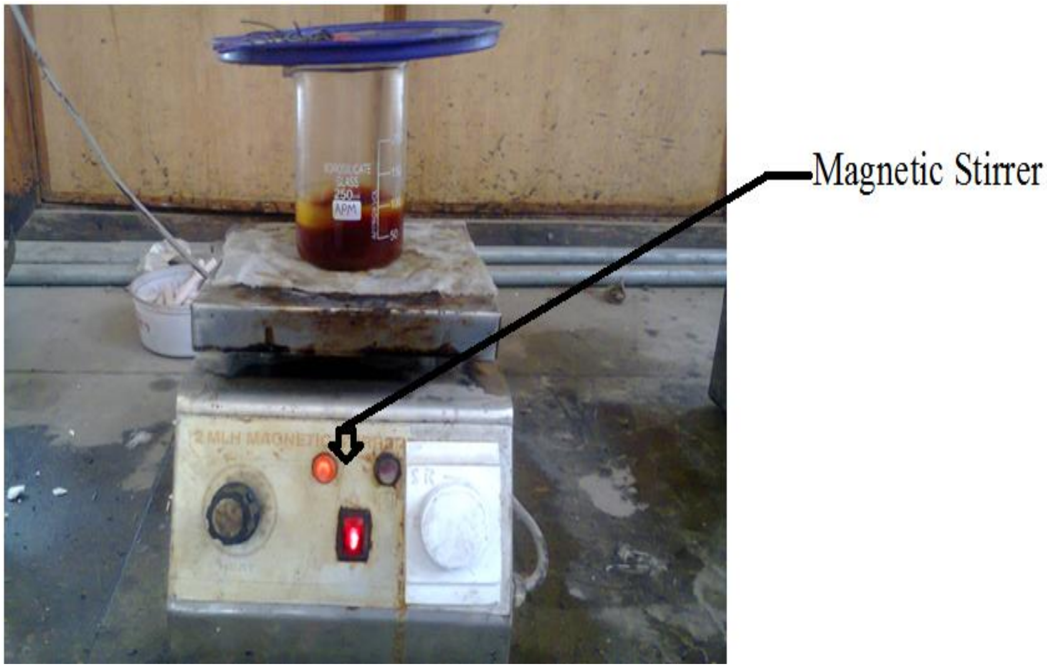


Fig.3(b) Magnetic Stirrer

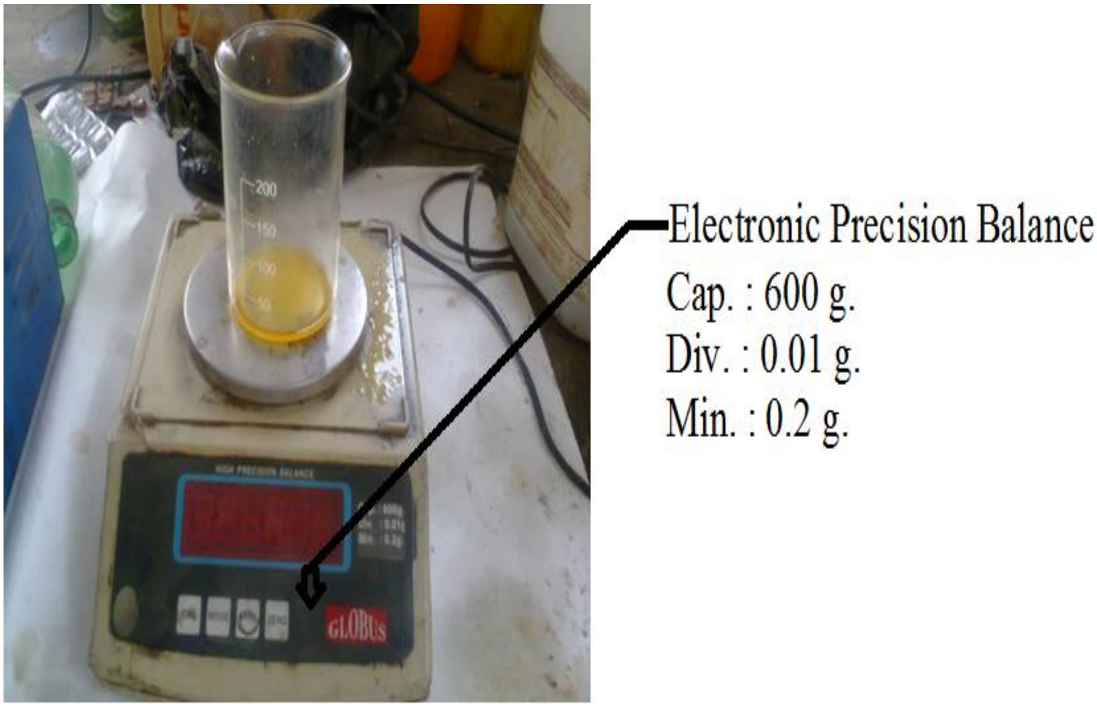


Fig.3(c) Electronic Precision Balance

Fig.3(d) Magnetic Stir Bar

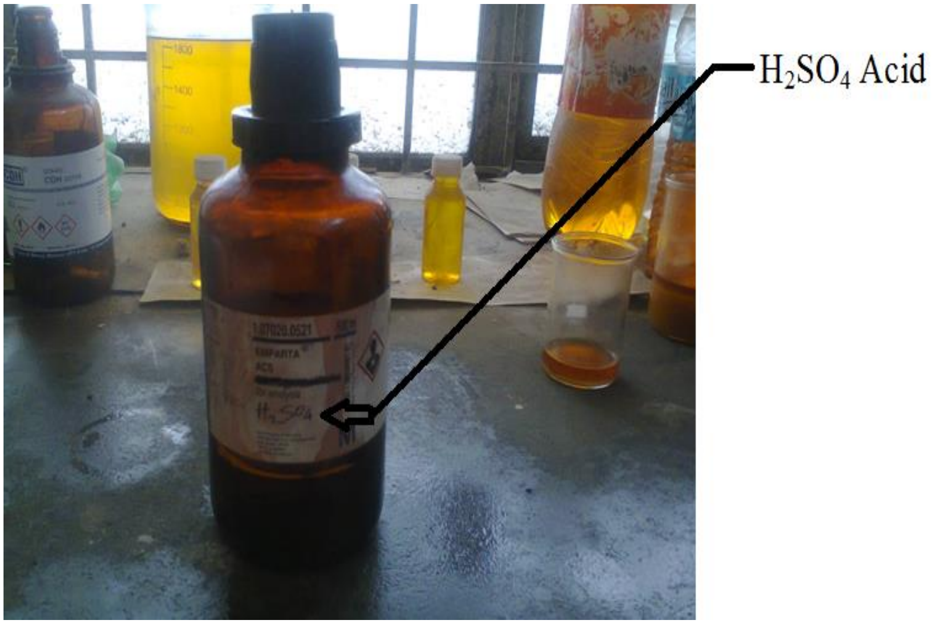


Fig.3(e) H_2SO_4 Acid

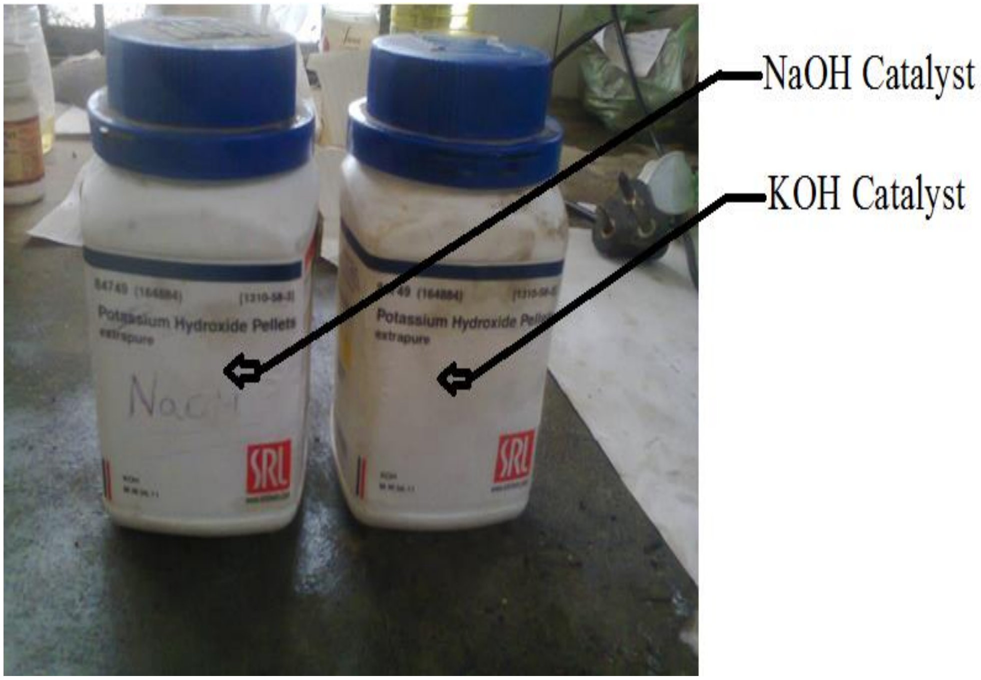


Fig.3(f) NaOH and KOH Catalyst

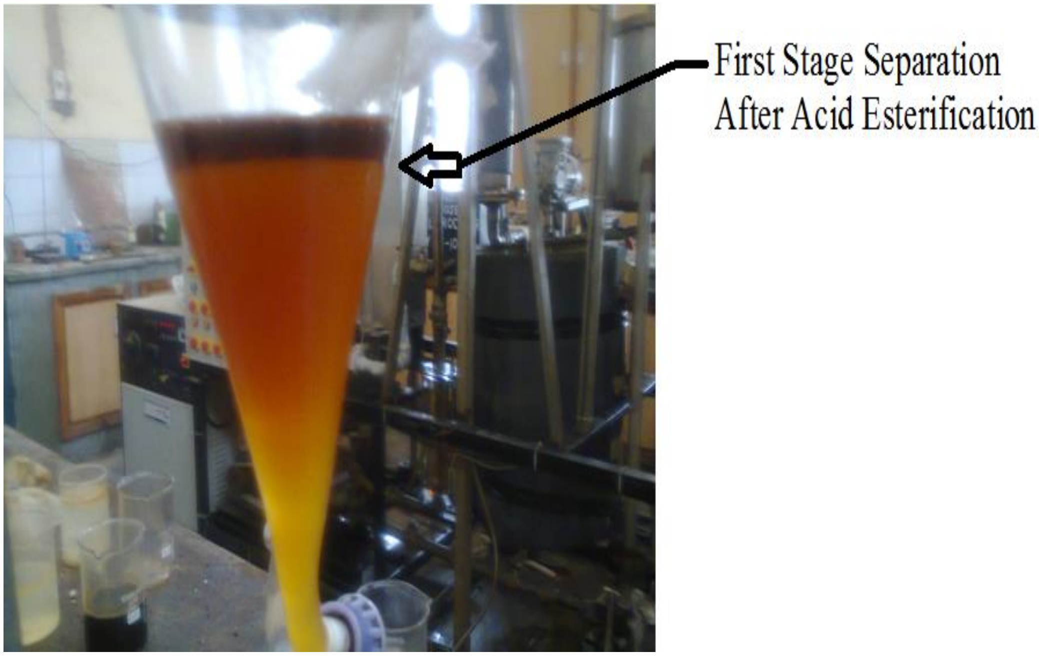


Fig.3(g) First Stage Separation After Acid Esterification

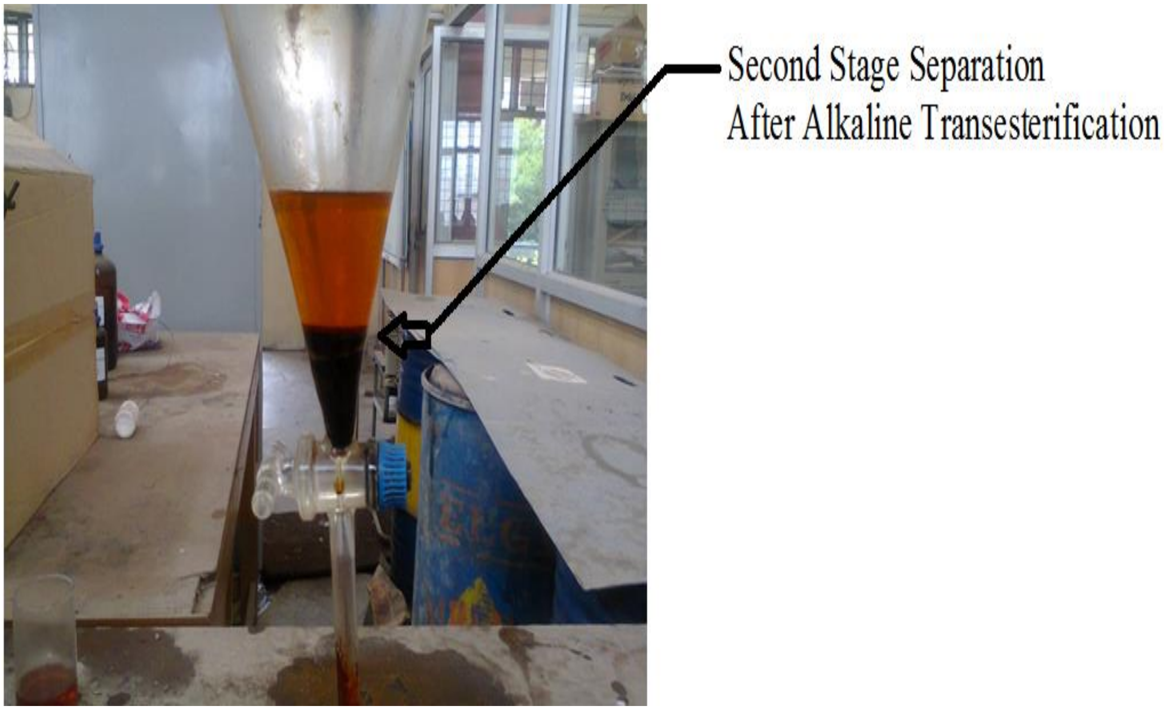


Fig.3(h) Second Stage Separation After Alkaline Transesterification

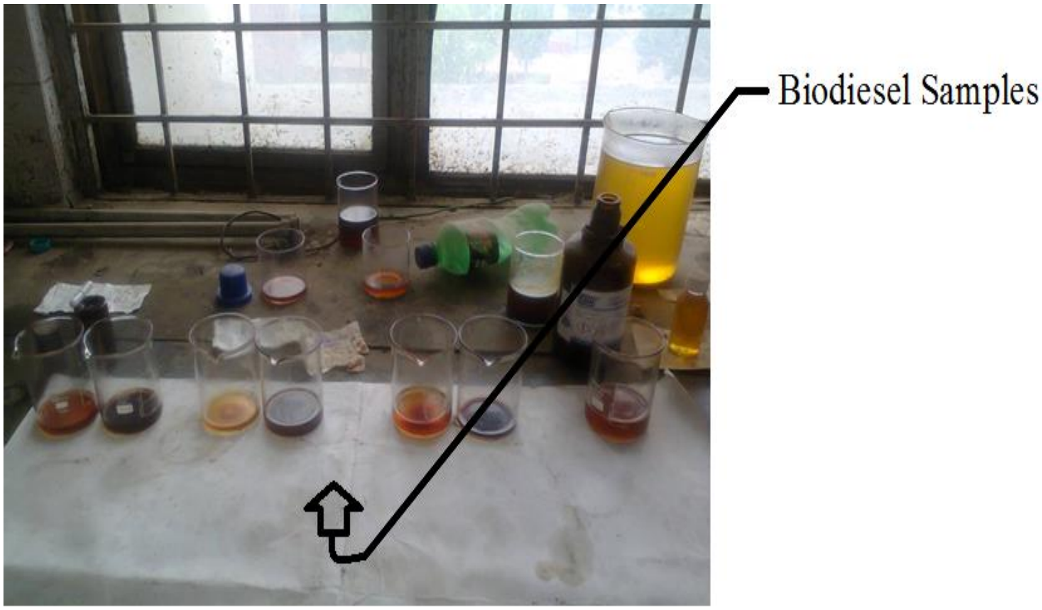


Fig.3(i) Biodiesel Samples

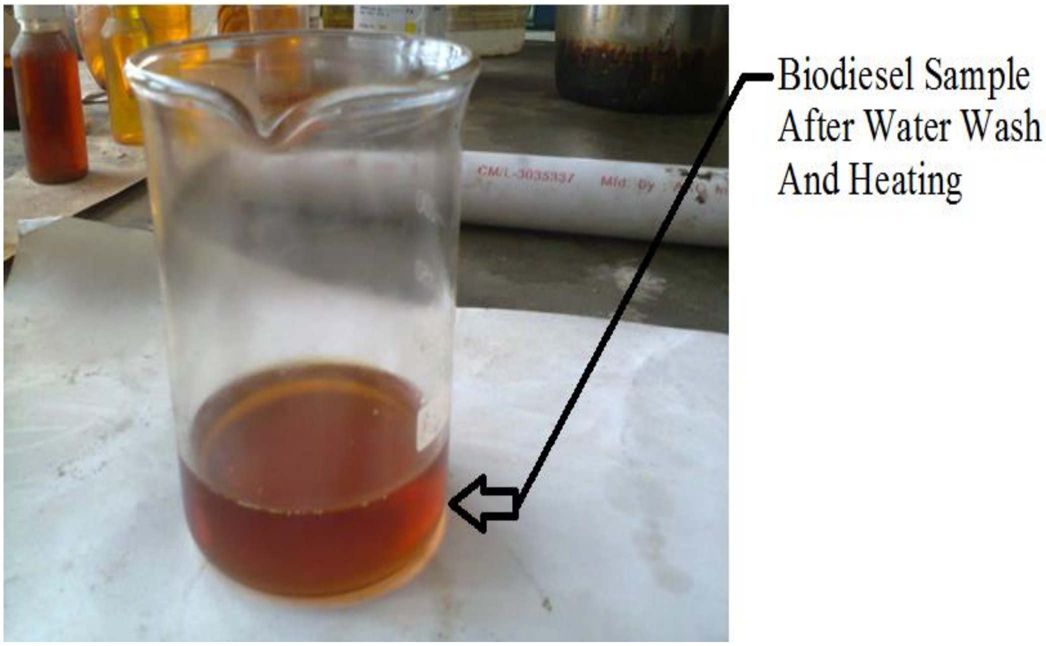


Fig.3(j) Biodiesel Sample After Water Wash and Heating

3.1. Biodiesel production from neem oil using two step transesterification

Currently, most of the biodiesel is produced from the edible/refined type oil using methanol and alkaline catalyst. However, large amount of non-edible type oils and fats are available in our country. In this study, crude neem oil is used as alternative fuel for biodiesel production. The difficulty with alkaline transesterification of these oils has contained large amounts of free fatty acids (FFA). These free fatty acids quickly react with the alkaline catalyst to produce soaps that inhibit the separation of the ester and glycerin (M.Agarwal et al., 2012). A two-step transesterification process is developed to convert the high FFA oils to its mono-esters. Using 50gm. of oil, the optimum combination of parameters for pretreatment were found to be 0.45 v/v methanol-oil-ratio,0.5% v/v H_2SO_4 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, 75min 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%.

Physicochemical analysis of neem oil biodiesel

The properties of the biodiesel were shown in Table 3.1(a). It is compared with the American standard (ASTMD6751) and European specification (EN14214). The density, flash point, iodine number, cetane number, pour point, moisture content, and the calorific value conform to the approved international standards. The viscosity also conformed to the American standard. The amount and type of the fatty acid content in the biodiesel are the major factors that determine the viscosity of biodiesel. In addition, the neem oil and neem oil biodiesel compared with vegetable oil from other sources.

Table 3.1(a) Physicochemical analysis of neem oil biodiesel compared with standards (Awolu and Layokun, 2013)

Properties	Values	ASTM specification	EN 14214
Physical state at 25°C	Liquid	-	-
Percent moisture content	0.05	0.05 max	-
Specific gravity at 25°C	0.900	0.87 to 0.90	0.86 to 0.90
Kinematic viscosity (mm2/s)	5.5	1.9 to 6.0	3.5 to 5.0
Saponification value (mg KOH/g)	207	-	-
Iodine value (g I2/100 g)	70.5	-	120 max
Cetane number	55.31	40 min	51 min
Calorific value (MJ/kg)	39.89	-	-
Pour point (°C)	4	-15 to 10	-
Cloud point (°C)	8	-3 to 12	-
Flash point (°C)	110	100 min	120 min

ASTM American society for testing materials, EN European standard for biodiesel, max maximum, min minimum

Gas chromatography analysis of neem oil biodiesel

The result of the chromatography analysis of neem oil biodiesel was shown in Table 3.1(b). The percentage of unsaturated fatty acid is 80.02%, while the percentage of saturated fatty acid is 19.97%. It has been shown that biodiesel fuel with more unsaturated fatty acid composition has more density but has less viscosity, lower cetane number, and heating value (Gaikwad. et al., 2014). It also has lower thermal efficiency compared to high saturated fatty acid composition. It emits lower HC and CO, and less smoke compared to highly saturated biodiesel fuel.

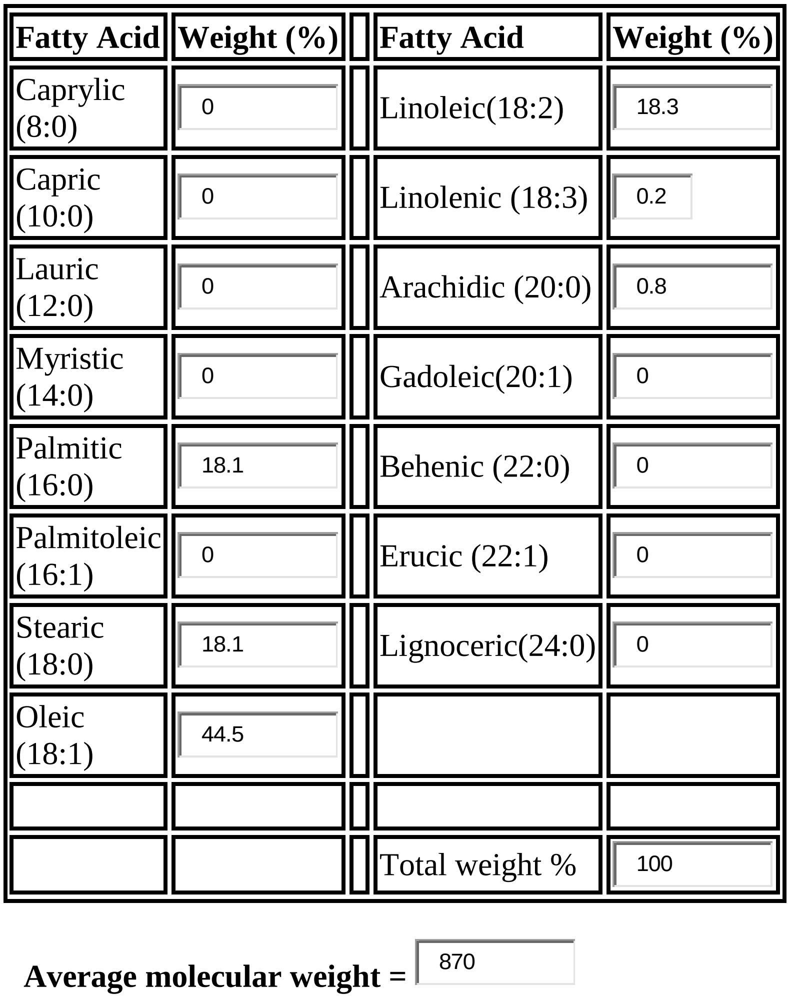
Table 3.1(b) Fatty acid composition of Neem Oil (Martin et al.,2010).

Fatty acid	Formula	Systemic name	Structure	Wt (%)
Palmitic	C16H32O2	Hexadecanoic	16:0	18.1
Stearic	C18H36O2	Octadecanoic	18:0	18.1
Oleic	C18H34O2	cis-9-Octadecenoic	18:1	44.5
Linoleic	C18H32O2	cis-9,cis-12-Octadecedianoic	18:2	18.3
Linolenic	C18H30O2	cis-6,cis-9,cis-12 Octadecatrienoic	18:3	0.2
Arachidic	C20H40O2	Eicosanoic	20:0	0.8
Total Saturated Fatty Acid		37%		
Total Mono – unsaturated Fatty Acid		44.50%		
Total Poly – unsaturated Fatty Acid		18.5		

Table 3.1(c) Comparative study of NOME (Biodiesel) [Aransiola et al., 2012]

Sl. No.	Fuel Property	Diesel	Biodiesel	NOME (Biodiesel)	Neem Oil
1	Kinematic viscosity, mm2/s (at 40 °C)	1.3 – 4.1	1.9 – 6.0	5.53	35.83
2	Specific gravity (at 15°C)	0.85	0.86– 0.90	0.8762	0.92
3	Boiling point, °C	188-343	182 – 338	–	–
4	Flash point, °C	60 – 80	100 – 170	150	–
5	Cloud point, °C	-15 to 5	-3 to 12	6	19
6	Pour point, °C	-35to15	-15 to 10	3	10
7	Cetane number (ignition quality)	40 – 55	48 – 65	–	–
8	Stoichiometric air/fuel ratio (AFR)	15	13.8	–	–

Table 3.2(a) Triglyceride (Neem Oil) Molecular weight calculation



Fatty Acid	Weight (%)		Fatty Acid	Weight (%)
Caprylic (8:0)	0		Linoleic(18:2)	18.3
Capric (10:0)	0		Linolenic (18:3)	0.2
Lauric (12:0)	0		Arachidic (20:0)	0.8
Myristic (14:0)	0		Gadoleic(20:1)	0
Palmitic (16:0)	18.1		Behenic (22:0)	0
Palmitoleic (16:1)	0		Erucic (22:1)	0
Stearic (18:0)	18.1		Lignoceric(24:0)	0
Oleic (18:1)	44.5			
			Total weight %	100

Average molecular weight = 870

The molecular weight of a particular fat or oil depends on its fatty acid profile. Fatty acid profile is the relative proportion of different fatty acids in an oil or fat. In order to determine the fatty acid profile, the oil is usually converted into alcohol esters of fatty acid and then their proportionate weight is measured using gas chromatography. The relative proportions of the esters are then converted back to corresponding amounts of fatty acids. The fatty acids of animal and plant origin are all straight carbon chains differing mainly in chain length and the number of double bonds (saturation). A saturated fatty acid chain with ‘n’ number of carbons will have a chemical structure of CH_3- $(CH_2)_{n-2}$-COOH. Once the fatty acid profile of the oil is known, it is easy to calculate the average molecular weight of the oil. The molecular weight of a single fatty acid ‘i’ can be calculated as:

$MW_i = 14.027C-2.016d+31.9988$

Where ‘*C*’ is the number of carbons and‘d’ is the number of double bonds. The average molecular weight of fatty acid mixture can be calculated by dividing the sum of all reported fatty acid weights by total moles in the mixture. Numerically,

Average molecular weight of fatty acids = $\sum f_i / \sum (f_i/MW_i)$

Where, f_i are the weight fraction of a reported fatty acid. The molecular weight of the triglyceride (oil molecule) containing three fatty acids can be calculated as:

MW=3*Average molecular weight of fatty acids+38.049

38.049 is the weight of glycerol backbone

Table 3.2(b) Fatty acid composition:

Fatty acid	Formula	Structure	Molecular Wt	Wt (%)
Palmitic	$C_{16}H_{32}O_2$	16:0	256	18.1
Stearic	$C_{18}H_{36}O_2$	18:0	284	18.1
Oleic	$C_{18}H_{34}O_2$	18:1	282	44.5
Linoleic	$C_{18}H_{32}O_2$	18:2	280	18.3
Linolenic	$C_{18}H_{30}O_2$	18:3	278	0.2
Arachidic	$C_{20}H_{40}O_2$	20:0	312	0.8

$$Average\ Molecular\ Wt\ of\ Fatty\ Acids$$

$$= \frac{18.1*256+18.1*284+44.5*282+18.3*280+0.2*278+0.8*312}{100}$$
$$= 277.522$$

Molecular Wt of Triglyceride (Neem Oil) =3*Average molecular weight of fatty acids+38.049

Where 38.049 is the weight of glycerol backbone

So, Molecular Wt of Triglyceride (Neem Oil) = 3*277.522 + 38.049

= 870.615

≈ 870

Table 3.2(c) Catalyst weight Calculation:

Molar Ratio(Alcohol/Oil)	Qty. of Neem Oil(g)	Methanol(g)	Catalyst % [wt/wt of Oil]		
			1.0%	1.25%	1.50%
4.5:1	50	8.28	0.50	0.625	0.75
6:1	50	11	0.50	0.625	0.75
7.5:1	50	13.79	0.50	0.625	0.75

Molecular Wt of 1 gm mole of Triglyceride (Neem Oil) = 870 gm.

Molecular Wt of 1 gm mole of Methanol= 32 gm.

1 gm mole of Triglyceride (Neem Oil) reacts with 3 gm mole of Methanol Stoichiometrically.

<u>For molar ratio (Methanol/Oil) = 4.5:1</u>

50 gm of Oil will react with = (32/870)*50*4.5 = 8.28 gm of Methanol.

<u>For molar ratio (Methanol/Oil) = 6:1</u>

50 gm of Oil will react with = (32/870)*50*6 = 11 gm of Methanol.

<u>For molar ratio (Methanol/Oil) = 7.5:1</u>

50 gm of Oil will react with = (32/870)*50*7.5 = 13.79 gm of Methanol.

3.2. MATERIALS AND METHODOLOGY:

3.2(i) 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).

3.2(ii) 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.

3.2(iii) 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.

3.2(iii)(a) 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.

3.2(iii)(b) 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 refined neem oil to less than 1% of FFA.Viscosity reduction increases with increase in methanol-to-oil ratio.

3.2(iii)(c) 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.

4. RESULTS AND DISCUSSION:

4.1(i) Acid esterification:

4.1(i)(a) 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 as shown in Tab.4(a).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.4(a) 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.

Table 4(a) Effect of methanol-to-oil ratio

Methanol to Oil Ratio(v/v)	0.35:1	0.40:1	0.45:1	0.50:1	0.55:1
Conversion Efficiency (%)	77	84	95	90	87

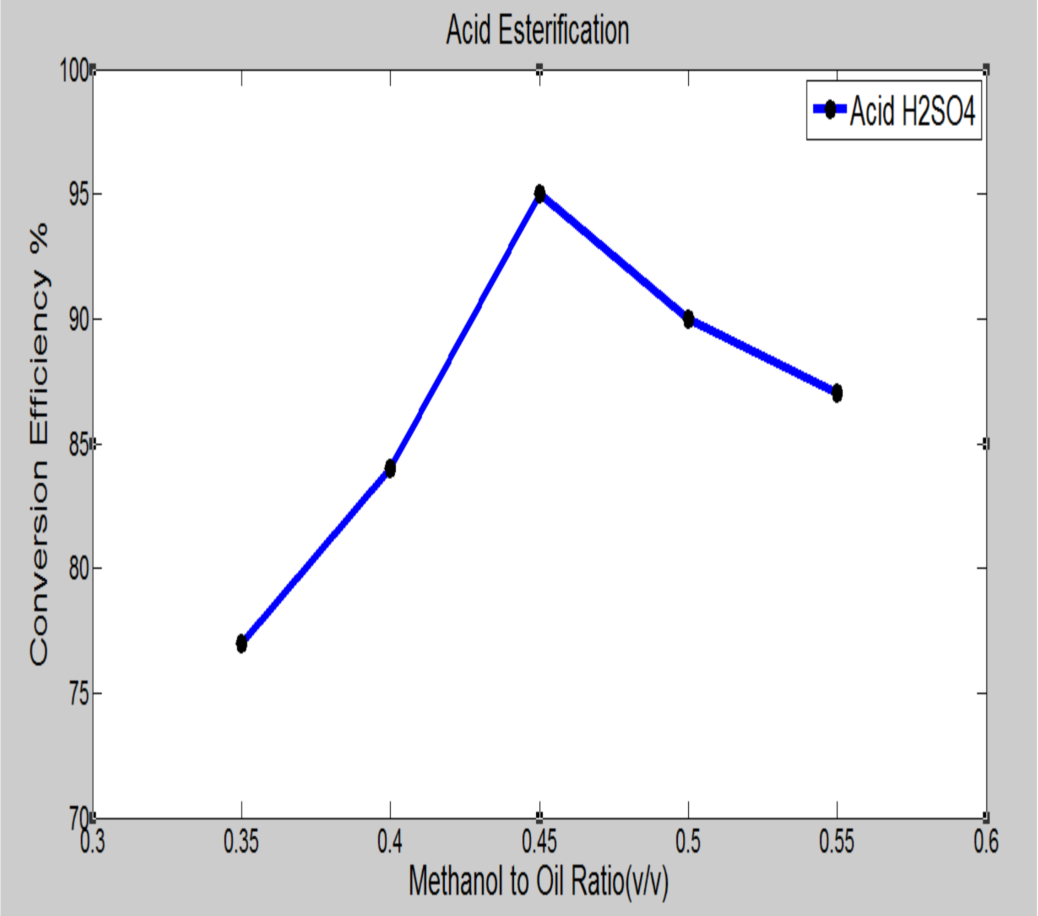


Fig. 4(a) Effect of Methanol-to-oil ratio on conversion efficiency

4.1(i)(b) 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 H_2SO_4 as shown in Tab.4(b). Effect of acid catalyst variation is shown in Fig.4(b) from the figure more than 0.5% v/v H_2SO_4, the product color is become black. Lower amount of sulphuric acid addition affects the final product yield.

Table 4(b) Effect of acid catalyst amount

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

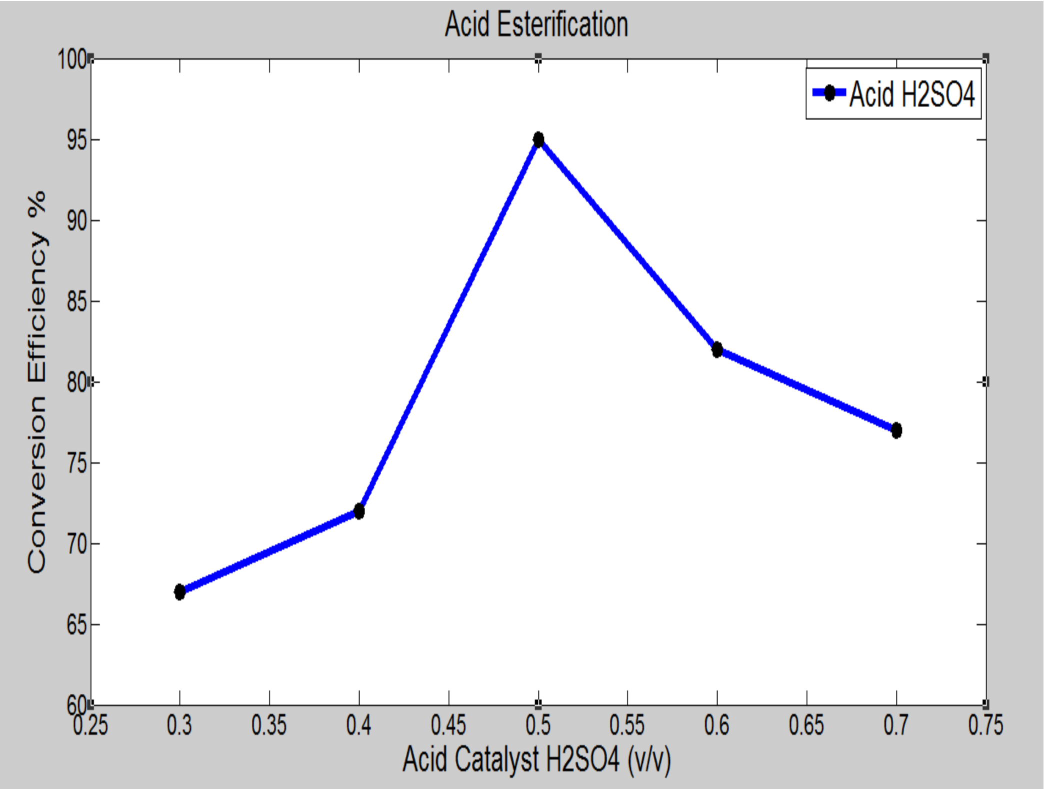


Fig.4(b) Effect of acid catalyst amount on conversion efficiency

4.1(i) (c) 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.

4.1 (ii) Alkaline transesterification:

4.1(ii) (a) 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. 4(c) 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 as shown in Tab.4(c). With further increase in methanol-to oil molar ratio the conversion efficiency is decreases.

Table 4(c) Effect of methanol-to-oil ratio

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

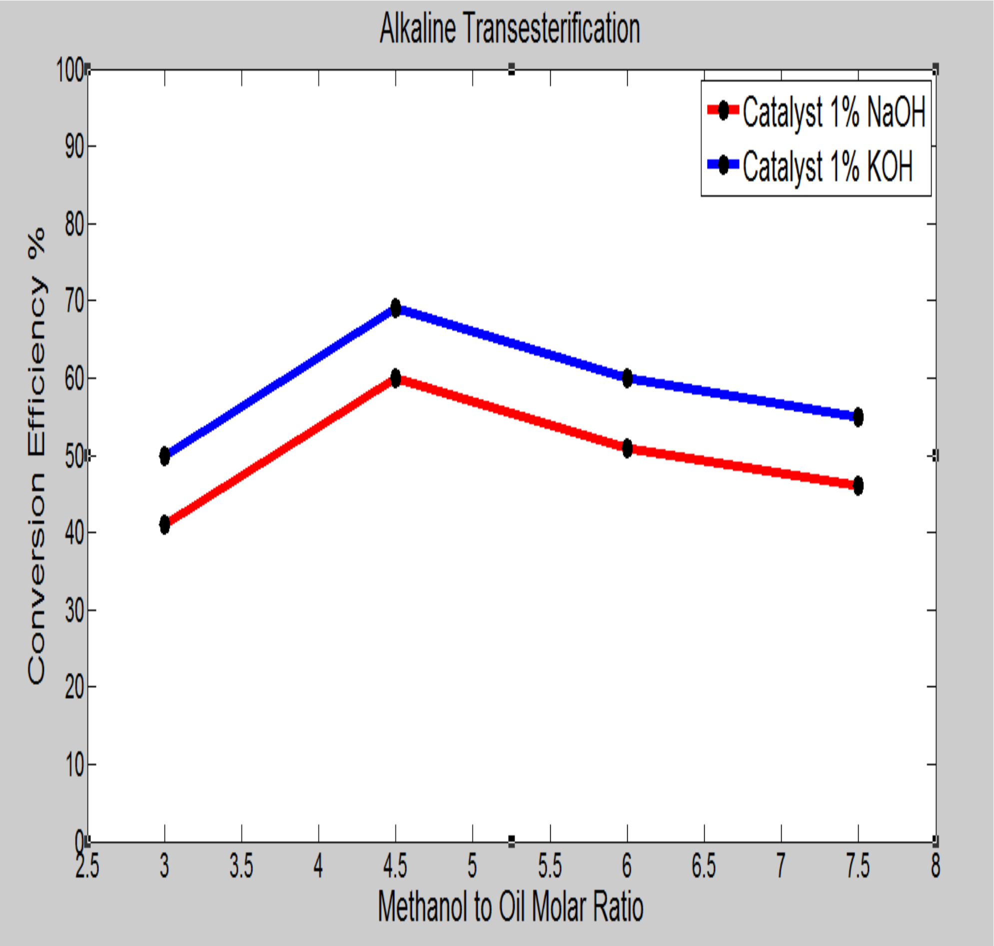


Fig.4(c) Effect of methanol on conversion efficiency

4.1(ii) (b) 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.4(d) 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 as shown in Tab.4(d).

Table 4(d) Effect of alkaline catalyst

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

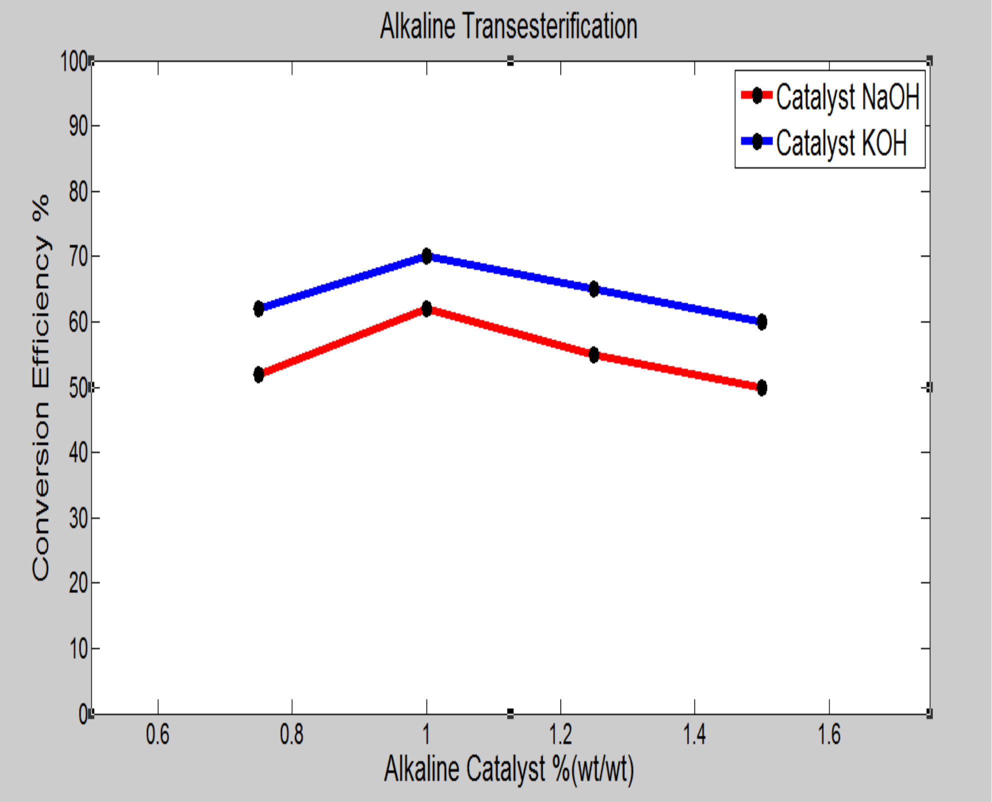


Fig.4(d) Effect of alkaline catalyst amount on conversion efficiency

4.1(ii)(c) 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.4 (e). By varying temperature in four different levels such as 45, 50, 55 and 60˚C among these 50˚C gave maximum methyl ester yield as shown in Tab.4(e). If greater than 50˚C, chance for loss the methanol. The maximum ester efficiency 72% is achieved at 50˚C.

Table 4(e) Effect of reaction temperature

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

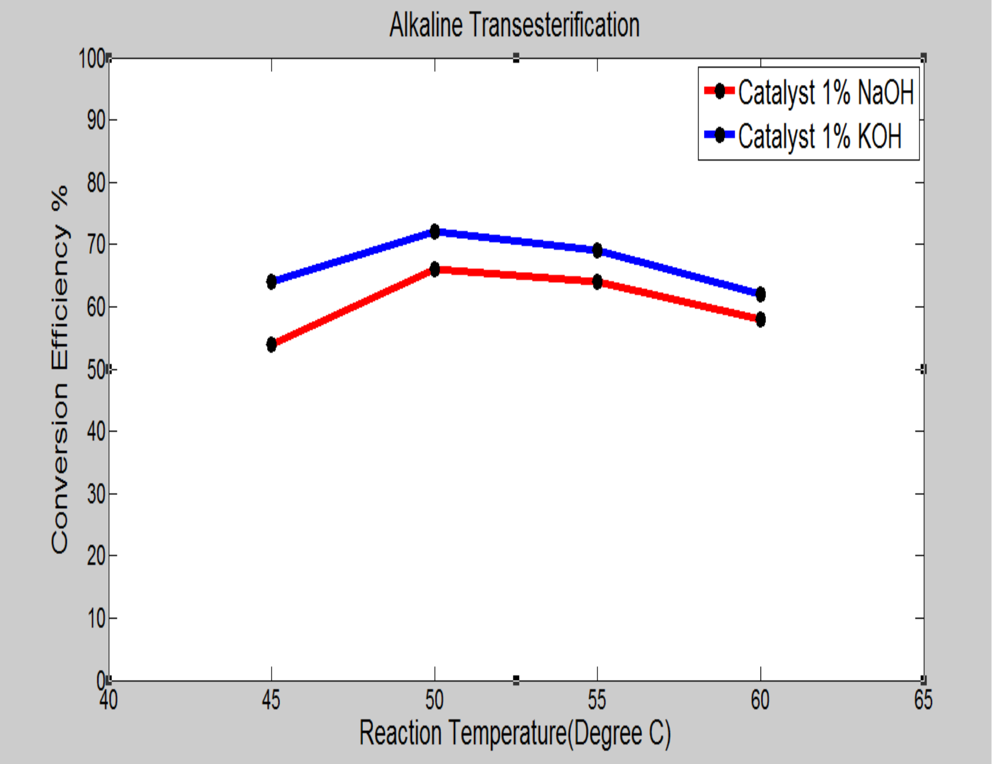


Fig.4 (e) Effect of reaction temperature on conversion efficiency

4.1(ii)(d) 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.4(f) 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 as shown in Tab.4(f). From these experiments the optimum yield is obtained at 75min reaction.

Table 4(f) Effect of reaction time

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

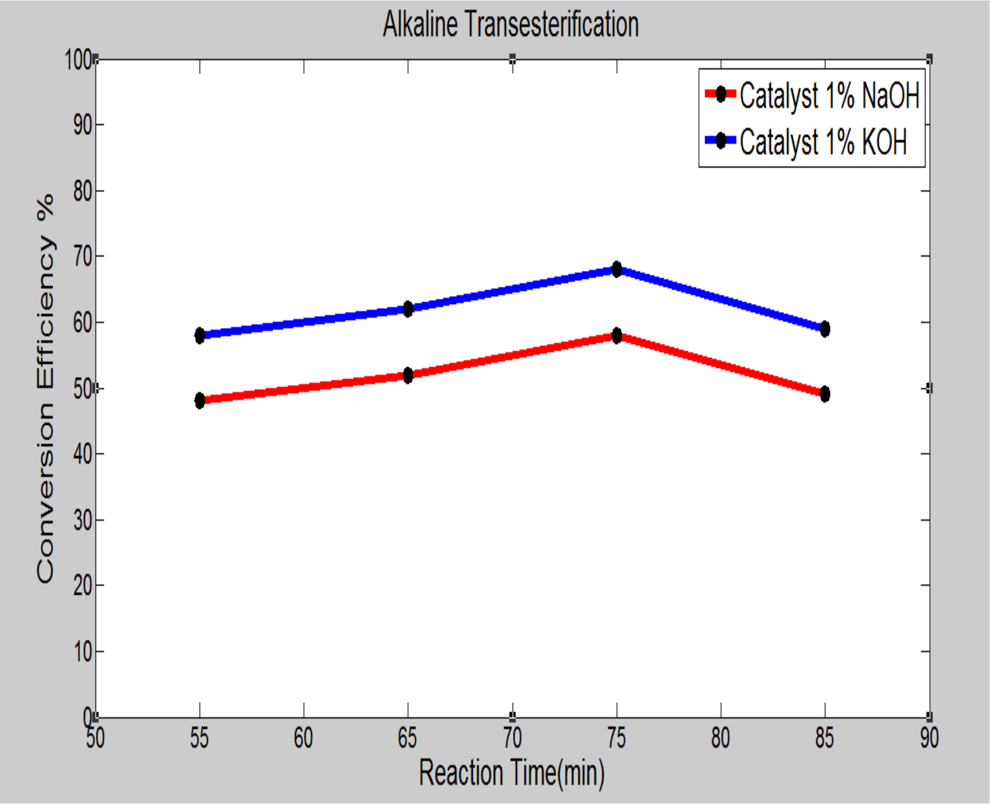


Fig.4(f) Effect of reaction time on conversion efficiency

4.2. 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. Taguchi Method to Optimize the Process Parameters:

Taguchi method is based on performing evaluation or experiments to test the sensitivity of a set of response variables to a set of control parameters (or independent variables) by considering experiments in “orthogonal array” with an aim to attain the optimum setting of the control parameters. Orthogonal arrays provide a best set of well balanced (minimum) experiments. Table 5(a) Shows eighteen standard orthogonal arrays along with the number of columns at different levels for these arrays. An array name indicates the number of rows and columns it has, and also the number of levels in each of the columns. For example array L4 (23) has four rows and three “2 level” columns. Similarly the array L18 (2137) has 18 rows; one “2 level” column; and seven “3 level” columns. Thus, there are eight columns in the array L18. The number of rows of an orthogonal array represents the requisite number of experiments. The number of rows must be at least equal to the degrees of the freedom associated with the factors i.e. the control variables. In general, the number of degrees of freedom associated with a factor (control variable) is equal to the number of levels for that factor minus one. For example, a case study has one factor (A) with “2 levels” (A), and five factors (B, C, D, E, F) each with “3 level”. Table 5(b) depicts the degrees of freedom calculated for this case. The number of columns of an array represents the maximum number of factors that can be studied using that array.

Table 5(a) Standard orthogonal arrays

Orthogonal array	Number of rows	Maximum number of factors	Maximum number of columns at these levels			
			2	**3**	**4**	**5**
L_4	4	3	3	-	-	-
L_8	8	7	7	-	-	-
L_9	9	4	-	4	-	-
L_{12}	12	11	11	-	-	-
L_{16}	16	15	15	-	-	-
L_{16}'	16	5	-	-	5	-
L_{18}	18	8	1	7	-	-
L_{25}	25	6	-	-	-	6
L_{27}	27	13	-	13	-	-
L_{32}	32	31	31	-	-	-
L_{32}'	32	10	1	-	9	-
L_{36}	36	23	11	12	-	-
L_{36}'	36	16	3	13	-	-
L_{50}	50	12	1	-	-	11
L_{54}	54	26	1	25	-	-
L_{64}	64	63	63	-	-	-
L_{64}'	64	21	-	-	21	-
L_{81}	81	40	-	40	-	-

The signal to noise ratios (S/N), which are log functions of desired output, serve as the objective functions for optimization, help in data analysis and the prediction of the optimum results. The Taguchi method treats the optimization problems in two categories: static problems and dynamic problems. For simplicity, the detailed explanation of only the static problems is given in the following text. Next, the complete procedure followed to optimize a typical process using Taguchi method is explained with an example.

Table 5(b) The degrees of freedom for one factor (A) in "2 levels" and five factors (B, C, D, E, F) in "3 levels"

Factors	**Degrees of freedom**
Overall mean	1
A	2-1 = 1
B, C, D, E, F	5 × (3-1) = 10
Total	12

Static problems

Generally, a process to be optimized has several control factors (process parameters) which directly decide the target or desired value of the output. The optimization then involves determining the best levels of the control factor so that the output is at the target value. Such a problem is called as a "STATIC PROBLEM". This can be best explained using a P-Diagram (Figure 5(a)) which is shown below ("P" stands for Process or Product). The noise is shown to be present in the process but should have no effect on the output. This is the primary aim of the Taguchi experiments - to minimize the variations in output even though noise is present in the process. The process is then said to have become ROBUST.

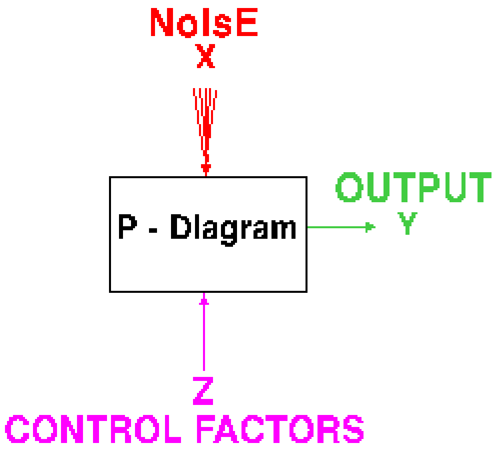


Figure 5(a) P- Diagram for static problems.

Signal to Noise (S/N) Ratio:

There are three forms of signal to noise (S/N) ratio that are of common interest for optimization of static problems.

[1] Smaller-the-better

This is expressed as

$$n = -10 \, \mathrm{Log}_{10} \, [\text{mean of sum of squares of measured data}]$$

This is usually the chosen S/N ratio for all the undesirable characteristics like “defects” for which the ideal value is zero. When an ideal value is finite and its maximum or minimum value is defined (like the maximum purity is 100% or the maximum temperature is 92 K or the minimum time for making a telephone connection is 1 sec) then the difference between the measured data and the ideal value is expected to be as small as possible. Thus, the generic form of S/N ratio becomes,

$$n = -10 \, \mathrm{Log}_{10} \, [\text{mean of sum of squares of } \{\text{measured} - \text{ideal}\}]$$

[2] Larger-the-better

This is expressed as

$n = -10\ \mathrm{Log}_{10}$ [mean of sum of squares of reciprocal of measured data]

This is often converted to smaller-the-better by taking the reciprocal of the measured data and next, taking the S/N ratio as in the smaller-the-better case.

[3] Nominal-the-best

This is expressed as

$$n = -10 Log_{10} [\frac{square\ of\ mean}{variance}]$$

This case arises when a specified value is the most desired, meaning that neither a smaller nor a larger value is desired

Application of Taguchi Method:

Determine the effect of four process parameters: Reaction temp (A), Catalyst Concentration (wt %) (B), Molar ratio (Methanol/Oil) (C) and Reaction time (D) on the yield of Neem Oil Methyl Ester (NOME). Also estimate the optimum setting of the above process parameters for maximum yield. Table 5(c) depicts the factors and their levels.

Table 5(c) Factors and their levels

Factor		**Levels**		
		1	**2**	**3**
A	**Reaction Temp (°C)**	50	55	60
B	**Catalyst Concentration (wt %)**	1.0	1.25	1.50
C	**Molar Ratio (Methanol/Oil)**	4.5	6.0	7.5
D	**Reaction Time(min)**	55	65	75

5.1. Selection of the design matrix and performing the experiments

The present experiment is associated with four factors with each at three levels. Table 5(a) indicates that the best suitable orthogonal array is L9. Table 5(d) shows the design matrix for L9. Next conduct all the nine experiments and observe % yield of neem oil methyl ester (NOME). The summary statistic, ηi, for an experiment, i, is given by

$$n_i = -10Log_{10}\, C_i$$

where Ci refers to mean squared deviation for experiment i and the mean square refers to the average of the squares of the nine observations in the experiment i. Table 5(d) also depicts the observed value of ηi for all the nine experiments. This summary statistic ηi is called the signal to noise (S/N) ratio.

Table 5(d) L_9 array matrix experiment table.

Expt No	Column number and factor assigned				η (%)
	1 Reaction Temp (°C) (A)	2 Catalyst Concentration (wt %) (B)	3 Molar Ratio (Methanol/Oil) (C)	4 Reaction Time (min) (D)	
1	1	1	1	1	37.14
2	1	2	2	2	36.85
3	1	3	3	3	36.81
4	2	1	2	3	36.68
5	2	2	3	1	36.22
6	2	3	1	2	36.42
7	3	1	3	2	35.71
8	3	2	1	3	35.83
9	3	3	2	1	35.55

Table 5(e) Yield of Neem Oil Methyl Ester and S/N ratio (η)

Exp. No	% Yield of Neem Oil Methyl Ester(NOME)				S/N ratio (η)
	Sample 1	Sample 2	Sample 3	Mean	
1	70.8	73.9	71.3	72.0	37.14
2	65.2	70.4	74.1	69.9	36.85
3	68.9	70.2	68.8	69.3	36.81
4	66.6	69.2	69.1	68.3	36.68
5	61.8	68.5	64.4	64.9	36.22
6	65.8	67.9	65.2	66.3	36.42
7	58.2	63.5	61.9	61.2	35.71
8	57.3	66.6	63.0	62.3	35.83
9	58.2	61.4	60.4	60.0	35.55
			Mean	**66.0**	**36.35**

According to the analysis for the case of larger the better the mean squared deviations (MSD) of each experiment were evaluated using the following equation

$$MSD = \frac{1}{n}\sum_{i=1}^{n}(\frac{1}{y_i})^2$$

Where n is the number of repetitions of each experiment and yi the yield of Neem Oil methyl ester.

Then the S/N ratio was evaluated using the equation

S/N ratio = -10 Log (MSD)

The effect of parameter level is defined as the deviation it causes from the overall mean. Hence as a first step , calculating the overall mean value of S/N ratio for the experimental region defined by the factor levels in Table 5(f).

5.2. Calculation of factor effects

The effect of a factor level is defined as the deviation it causes from the overall mean. Hence as a first step, calculate the overall mean value of η for the experimental region defined by the factor levels in Table 5(d) as

$$m = \frac{1}{9}\sum_{i=1}^{9} n_i \ = \frac{1}{9}(n_1 + \ n_2 \ + \ n_3 \ + \cdots + n_9 \ ) = 36.35$$

The effect of the temperature at level A1 (at experiments 1, 2 and 3) is calculated as the difference of the average S/N ratio for these experiments (mA1) and the overall mean. The same is given as

The effect of temperature at level

$$A_1 = m_{A1} - m = \frac{1}{3}(n_1 + n_2 + n_3) - m$$

Similarly,

The effect of temperature at level

$$A_2 = m_{A2} - m = \frac{1}{3}(n_4 + n_5 + n_6) - m$$

The effect of temperature at level

$$A_3 = m_{A3} - m = \frac{1}{3}(n_7 + n_8 + n_9) - m$$

Using the S/N ratio data available in Table 5(d). The average of each level of the four factors is calculated and listed in Table 5(f). These average values are shown in Figure 5(b) they are separate effect of each factor and are commonly called main effects.

Table 5(f) Average η for different factor levels

Factor		Levels		
		1	2	3
A	Reaction Temp (^{0}C)	36.93*	36.44	35.69
B	Catalyst Concentration (wt %)	36.51*	36.30	36.26
C	Molar ratio(Methanol/Oil)	36.46*	36.36	36.24
D	Reaction Time(min)	36.30	36.32	36.44*

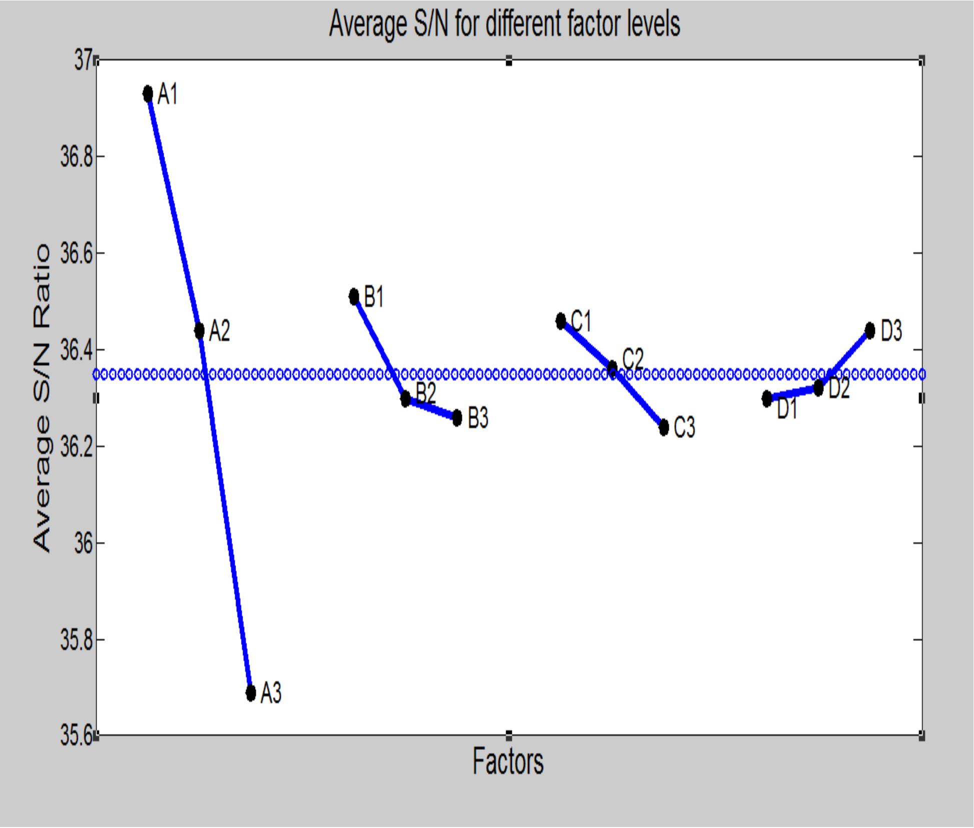


Figure 5(b) Plots of factor effects

5.3. Selecting optimum factor levels

Our goal in this experiment is to maximize the yield of Fatty Acid Methyl Ester (FAME). Since –log depicts a monotonic decreasing function, we have to maximize η. Hence the optimum level for a factor is the level that gives the highest value of η in the experimental region. From Figure 5(b) and the Table 5(f), it is observed that the optimum settings of reaction temp, catalyst concentration (wt %), molar ratio (methanol/oil) and reaction time are A1, B1, C1 and D3. Hence we can conclude that the setting A1B1C1D3 can give the highest η for Neem Oil Methyl Ester.

5.4. Developing the additive model for factor effects

The relation between η and the process parameters A, B, C and D can be approximated adequately by the following additive model:

$$n\left(A_i + B_j + C_k + D_l\right) = m + a_i + b_j + c_k + d_l + e$$

Where the term m refers to the overall mean (that is the mean of η for the experimental region). The terms ai, bj, ck and dl refer to the deviations from μ caused by the setting Ai, Bj, Ck, and Dl of factors A, B, C and D, respectively. The term e stands for the error. In additive model the cross- product terms involving two or more factors are not allowed. The above equation is utilized in predicting the S/N ratio at optimum factor levels.

5.5. Analysis of Variance (ANOVA)

Different factors affect the yield of NOME to a different degree. The relative magnitude of the factor effects are listed in Table 5(f). A better feel for the relative effect of the different factors is obtained by the decomposition of variance, which is commonly called as analysis of variance (ANOVA). This is obtained first by computing the sum of squares.

$$Total\ Sum\ of\ Squares = \sum_{i=1}^{9} n_i^2 = ((37.14)^2 + (36.85)^2 + \cdots \ldots + (35.55)^2) = 11898.80$$

$$Sum\ of\ Squares\ Due\ to\ Mean = (Number\ of\ Exp.)\ X\ m^2 = 9\ X\ (36.35)^2 = 11891.90$$

$$Total\ Sum\ of\ Squares(Sum\ of\ Squares\ of\ all\ 9\ Experiments) = \sum_{i=1}^{9} (n_i - m)^2 = 2.54$$

$$Sum\ of\ Squares\ due\ to\ factor\ A = \left[(Number\ of\ Experiments\ at\ level\ A1) \times (m_{A1} - m)^2\right] + \left[(Number\ of\ Experiments\ at\ level\ A2) \times (m_{A2} - m)^2\right] + \left[(Number\ of\ Experiments\ at\ level\ A3) \times (m_{A3} - m)^2\right] = [3 \times (36.93 - 36.35)^2] + [3 \times (36.44 - 36.35)^2] + [3 \times (35.69 - 36.35)^2] = 2.34$$

$$Sum\ of\ Squares\ due\ to\ factor\ B = \left[(Number\ of\ Experiments\ at\ level\ B1) \times (m_{B1} - m)^2\right] + \left[(Number\ of\ Experiments\ at\ level\ B2) \times (m_{B2} - m)^2\right] + \left[(Number\ of\ Experiments\ at\ level\ B3) \times (m_{B3} - m)^2\right] = [3 \times (36.51 - 36.35)^2] + [3 \times (36.30 - 36.35)^2] + [3 \times (36.26 - 36.35)^2] = 0.11$$

$$Sum\ of\ Squares\ due\ to\ factor\ C = \left[(Number\ of\ Experiments\ at\ level\ C1) \times (m_{C1} - m)^2\right] + \left[(Number\ of\ Experiments\ at\ level\ C2) \times (m_{C2} - m)^2\right] + \left[(Number\ of\ Experiments\ at\ level\ C3) \times (m_{C3} - m)^2\right] = [3 \times (36.46 - 36.35)^2] + [3 \times (36.36 - 36.35)^2] + [3 \times (36.24 - 36.35)^2] = 0.07$$

$$\text{Sum of Squares due to factor } D = \left[(\text{Number of Experiments at level } D1) \times (m_{D1} - m)^2\right] + \left[(\text{Number of Experiments at level } D2) \times (m_{D2} - m)^2\right] + \left[(\text{Number of Experiments at level } D3) \times (m_{D3} - m)^2\right] = [3 \times (36.30 - 36.35)^2] + [3 \times (36.32 - 36.35)^2] + [3 \times (36.44 - 36.35)^2] = 0.03$$

So the sum of squares due to factor A, B, C and D computed as 2.34, 0.11, 0.07 and 0.03, respectively. Now all these sum of squares are tabulated in Table 5(g) this is called as the ANOVA table.

Table 5(g) ANOVA table for η (S/N Ratio)

Factor		Degree of freedom	Sum of squares	Mean square =Sum of squares/ Degree of freedom	F	Contri-bution (%)
A	**Reaction Temp (^oC)**	2	2.34	1.170	46.8	92.12
B	**Catalyst Concentration (wt %)**	2	0.11	0.055	2.2	4.33
C	**Molar Ratio (Methanol/Oil)**	2	0.07	0.035	1.4	2.76
D	**Reaction Time (min)**	2	0.03	0.015	0.6	0.79
Error		0	0			
Total		8	2.54			
(Error)		(4)	0.10	0.025		

In the present study, the degrees of freedom for the error will be zero. Hence an approximate estimate of the error sum of squares is obtained by pooling the sum of squares corresponding to the factors having the lowest mean square. The parameters C and D are used to estimate the error sum of squares. They account for four degrees of freedom and their sum of squares is 0.10. Referring to the sum of squares in table, the parameter A makes the largest contribution 92.12% to the total sum of squares. The factors B, C and D make 4.33 %, 2.76% and 0.79% each. The larger the contribution of a particular parameter to the total sum of squares, the larger the ability is of that factor to influence S/N ratio. Moreover, the larger F-value, the larger will be the factor effect in comparison to the error mean square.

Degrees of freedom

The degrees of freedom associated with the grand total sum of squares are equal to the number of rows in the design matrix.

The degree of freedom associated with the sum of squares due to mean is one.

The degrees of freedom associated with the total sum of squares will be equal to the number of rows in the design matrix minus one.

The degrees of freedom associated with the factor will be equal to the number of levels minus one.

The degrees of freedom for the error will be equal to the degrees of freedom for the total sum of squares minus the sum of the degrees of freedom for the various factors.

In the present experiment, the degrees of freedom for the error will be zero. Hence an approximate estimate of the error sum of squares is obtained by pooling the sum of squares corresponding to the factors having the lowest mean square. As a rule of thumb, the sum of squares corresponding to the bottom half of the factors (as defined by lower mean square) are used to estimate the error sum of squares. In the present experiment, the factors C and D are used to estimate the error sum of squares. Together they account for four degrees of freedom and their sum of squares is 0.10.

5.6. Interpretation of ANOVA table

The major inferences from the ANOVA table are given in this section. Referring to the sum of squares in Table 5(g) the factor A makes the largest contribution to the total sum of squares [(2.34/2.54) x 100 = 92.12%]. The factor B makes the next largest contribution (4.33%) to the total sum of squares, whereas the factors C and D make only 2.76% and 0.79% contribution respectively. The larger the contribution of a particular factor to the total sum of squares, the larger the ability is of that factor to influence η. Moreover, the larger the F-value, the larger will be the factor effect in comparison to the error mean square or the error variance.

5.7. Prediction of η under optimum conditions

In the present experiment, the identified optimum condition or the optimum level of factors is A1B1C1D3. The value of η under the optimum condition is predicted using the additive model as

$$\begin{aligned} n_{opt} &= m + (m_{A1} - m) + (m_{B1} - m) + (m_{C1} - m) + (m_{D3} - m) + e \\ &= 36.35 + (36.93 - 36.35) + (36.51 - 36.35) + (36.46 - 36.35) \\ &\quad + (36.44 - 36.35) + 0 = 37.29 \end{aligned}$$

Table 5(h) Main effects plot of the control parameters

Reaction Temp (^{0}C)	50	55	60		**Catalyst Con. (Wt %)**	1	1.25	1.50
S/N ratio (η)	36.93	36.44	35.69		**S/N ratio (η)**	36.51	36.30	36.26
Molar Ratio (Methanol/ Oil)	4.5	6.0	7.5		**Reaction Time (min)**	55	65	75
S/N ratio (η)	36.46	36.36	36.24		**S/N ratio (η)**	36.30	36.32	36.44

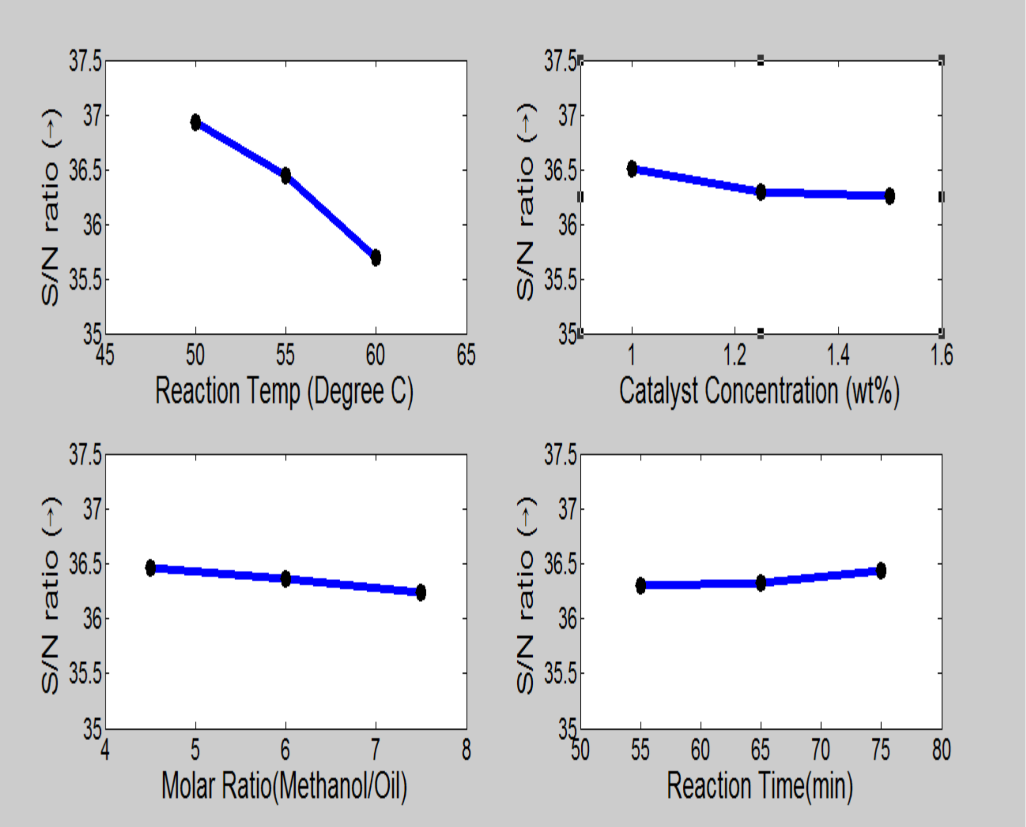


Fig.5(c) Main effects plot of the control parameters

5.8 CONCLUSION:

Result of the Proposed Optimized Experimental Condition

The optimum conditions to achieve effective performance for the production of neem oil methyl ester and the contributions of each parameter to the S/N ratio under the optimal conditions are shown in Table 5(i)

Table 5(i) Optimum conditions for settling the control parameters and their contributions:

Parameters		Level	Level description	Contribution
A	Reaction Temperature	1	50°C	0.58
B	Catalyst Concentration	1	1.0 wt %	0.16
C	Methanol to Oil Molar Ratio	1	4.5:1	0.11
D	Reaction Time	3	75 min	0.09
Total contribution from all parameters				0.94
Current grand average of performance				36.35
Expected result under optimum conditions				37.29

The calculated S/N ratio corresponding to nine set of experiments given in Table 5(d). The average S/N ratios of parameter at each level for neem oil methyl ester are shown in Table 5(f). Also the main effect plot for S/N ratio is shown in Fig 5(c). The average S/N ratio for maximum percentage yield of neem oil methyl ester is obtained at level 1 (Reaction Temperature 50°C), level 2 (Catalyst conc. 1.0%by wt), level 3 (Methanol to oil molar ratio 4.5:1) and level 4 (reaction time 75min). i.e., the optimum parameter setting for high percentage yield of neem oil methyl ester is A1B1C1D3. The results of ANOVA for S/N ratios are given in

Table5(g). The percentage of yield of neem oil methyl ester has been significantly improved using Taguchi Method.

The Taguchi method, which uses a set of orthogonal arrays for performing the fewest experiments, was employed to design experimental trials, with an ANOVA performed to more systematically analyze the relative importance of each experimental parameter on the production of neem oil methyl ester.

The reaction temperature, catalyst concentration and methanol to oil molar ratio were found to be significant parameters affecting the production of neem oil methyl ester. The contribution of the reaction temperature on the production process was larger than that of any other parameter. The yield of neem oil methyl ester obtained with the optimal experimental parameters was greater than that obtained from experiment no.1, which gave the highest yield from the experimental trials, and the theoretically expected value.

The experiments conducted under the optimized conditions showed a meaningful enhanced process performance. The Taguchi method provided a systematic and efficient mathematical approach to evaluate and optimize the process for the production of neem oil methyl ester, using only a few well-defined experimental sets for the optimization of the parameters.

5.9. Cost Analysis (Md. Hasan Ali et al., 2013 and V. Manieniyan et al. ,2010):

Table 5(j) Cost of the components of biodiesel production

Sl.No.	Component	Cost (Rs.)
1	Sodium Hydroxide (Catalyst)	230/kg
2	Potassium hydroxide (Catalyst)	360/kg
3	Neem oil (Feedstock)	115/ litre
4	Methanol (Alcohol)	45/ litre
5	Glycerin (By product of Biodiesel)	150/ litre

Table 5(k) Calculation of biodiesel production cost

Sl. No.	Component	Cost (Rs.)
1	Neem Oil – 100 ml	11.50
2	Two step transesterification Cost - 65 ml (45 ml + 20 ml) of Methanol [4.5 Methanol/Oil Molar Ratio]	2.925
3	Catalyst KOH 1.0 gm	0.36
4	Recovery (Glycerin 50 ml)	7.50
5	Total Cost (1 + 2 + 3 – 4)	14.785 – 7.50 = 7.285

Cost of biodiesel from 100 ml neem oil has come 7.285 Rs. with the help of Tab.5 (j) and Tab.5 (k).

Biodiesel production from 1 litre Neem Oil=0.70 Litre

So Cost of Biodiesel per litre = [(7.285 /100)*1000] / 0.70 = 104.07 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.

6. INFERENCE & RECOMMENDATIONS:

➢ INFERENCE

From all the experimentation performed above, it can be clearly observed that Neem Oil Methyl Ester (NOME) can be obtained by two step transesterification process only as the FFA content of neem oil is large. By using single step transesterification, the yield will be very less and in some case NOME cannot be obtained.

Taking together all these results, the optimized biodiesel yield of 74.30% was produced at reaction time of 75 min, catalyst amount of 0.50 g, temperature of 50°C, and methanol/oil molar ratio of 4.5.

ANOVA analysis showed that the temperature had the highest effect on the biodiesel yield followed by catalyst amount, methanol to oil molar ratio and reaction time

The result of this work showed that the maximum yields were obtained at lowest factor values. This will definitely have economic advantage on neem oil biodiesel production as low energy cost, low catalyst amount, low methanol/oil molar ratio, and low temperature are able to produce high biodiesel yield.

This was in agreement with the works of Awolu and Layokun, Meher et al., Jeong et al. and Marchetti and Errazu.

➢ RECOMMENDATIONS

Preliminary investigation has been done with the KOH and NaOH catalysts for the production of neem oil methyl ester (biodiesel) and it is found that KOH catalyst is better than NaOH catalyst in terms of % yield of biodiesel.So optimization of only KOH catalyst has been done in this study.

In the optimization of parameters, KOH catalyst has been used with different concentration (1.0%, 1.25% and 1.5%) with the other parameters like methanol to oil molar ratio, reaction temperature and reaction time.

So, we can further do the optimization by using different catalyst types (NaOH, KOH and $NaOCH_3$), catalyst concentration, reaction temperature and methanol to oil ratio with three levels.

So Four Parameters and Three Level

No of experiment required = 3*3*3*3 =81.

But by using Taguchi Method of optimization

No of experiment required = 9 only.

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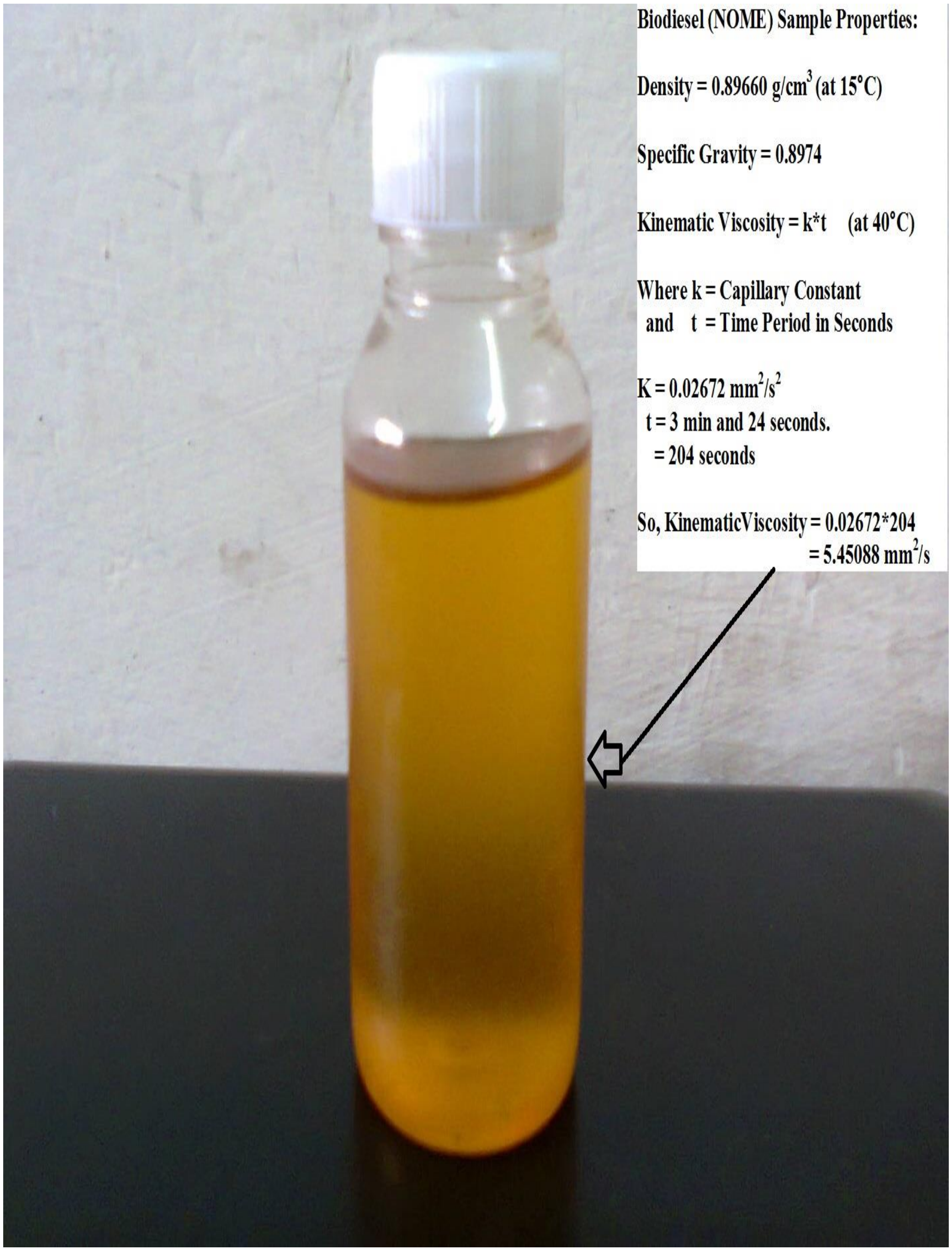

Biodiesel (NOME) Sample Properties:

Density = 0.89660 g/cm^3 (at 15°C)

Specific Gravity = 0.8974

Kinematic Viscosity = k*t (at 40°C)

Where k = Capillary Constant
and t = Time Period in Seconds

K = 0.02672 mm^2/s^2
t = 3 min and 24 seconds.
= 204 seconds

So, KinematicViscosity = 0.02672*204
= 5.45088 mm^2/s

Fig.6:Biodiesel(NOME) sample properties:

Density : 0.89660 gm/cm^3 (at 15^{0}C)

Specific Gravity : 0.8974

Kinematic Viscosity : 5.45088 mm^2/s (at 40^{0}C)