Homogeneous Catalysts used in Biodiesel Production: A Review

R. Mohandass\textsuperscript{a,**}, K. Ashok\textsuperscript{a}, A. Selvaraju\textsuperscript{a}, S. Rajagopan\textsuperscript{b}
\textsuperscript{a}Department of Mechanical Engineering, Pondicherry Engineering College, Pondicherry 605 014, India
\textsuperscript{b}Department of Chemistry, Pondicherry Engineering College, Pondicherry 605 014, India

Abstract - Catalysts play vital role in the conversion of FFA or feed stocks to respective esters at faster rate and in minimum reaction temperature. Different research groups have produced biodiesel through transesterification using methanol or ethanol along with catalysts of different kinds. These catalysts have been identified as homogenous and heterogeneous catalysts. Among these catalysts, homogeneous catalysts have been preferred by many researchers for the reason that more biodiesel can be produced relatively at faster rate. These homogeneous catalysts are available both in liquid and solid form at ambient conditions. On the basis of their physical and chemical properties and their ability to reactivity, the catalyst in liquid or solid phase is selected for either esterification or transesterification. This paper provides information on the homogeneous catalysts and their properties. Use of homogeneous catalysts by different research groups has also been reviewed.

Keywords: Catalyst; Transesterification; Biodiesel

1. INTRODUCTION

The forecast on depletion of fossil fuels in near future has made world community to look for alternate sources for liquid fuels to internal combustion engines. Crude oil extracted at different parts of the globe is found to be the liquid matter that has the origin of thick vegetation, biomass and other organic matters buried under earth’s crest several million years ago. With this knowledge that petroleum is the extract of organic matters, now-a-days edible and non-edible oils from plants and seeds are directly used to produce bio-fuels to meet the requirement in industrial and domestic sectors. Bio-diesel is a well-known substitute for diesel fuel and is produced from vegetable oils through different chemical processes. A chemical process requires always a catalyst to bring down reaction time and to increase quantity of product. Several research works have been carried out by researchers to identify both liquid and solid catalysts on the basis of physical properties of reactants and the nature of reactions. This paper gives an over view of both liquid and solid catalysts that are widely used in bio-diesel production.

2. BIO-DIESEL PRODUCTION

Vegetable oils that derived from seeds of different plants cannot be used as bio-diesel due to deviation of their physical, thermo-physical and thermodynamic properties when compared with that of diesel. The bio-diesel from any feedstock is produced using the well-known chemical technology, transesterification preceded by esterification, a chemical process that is chosen on the basis of the content of free fatty acids (FFA) in vegetable oils. The transesterification process which is also known as alcoholsysis converts the feedstock into fatty acid alkyl esters (FAAE). When methanol is used in transesterification, the yield is called as fatty acid methyl esters (FAME) that can be directly fed to the diesel engine or used after mixing with petro-diesel fuel in different ratios. Literature [1-25] reveal that there are many catalysts identified by different research group for production of biodiesel at faster rates. These catalysts are enlisted as acidic catalysts, alkaline catalysts and enzymatic catalysts. The following sections provide an insight on different homogeneous catalysts used for production of bio-diesel in laboratory-scale or large scale.

3. HOMOGENEOUS LIQUID CATALYSTS

3.1 Hydrochloric acid

Hydrochloric acid with a molecular formula, HCL is a clear solution of hydrogen chloride in water and is colorless, highly corrosive and pungent. It is prepared by dissolving hydrogen chloride in water. Hydrogen chloride may be formed by the direct combination of chlorine (Cl\textsubscript{2}) and hydrogen (H\textsubscript{2}) gases. Use of hydrochloric acid as acid catalyst has been reported in many literature.

Transesterification of beef tallow with methanol has been studied by Ehiri et al. [1] for producing bio-diesel. Hydrochloric acid has been used as acid catalyst. The study has included the investigation of relationship between reaction time, reaction temperature and catalyst concentration at constant methanol - oil volume ratio along with determination of optimal conditions in the transesterification process and the associated maximum biodiesel yield.

Transesterification of frying oil has been carried out by Daniyan et al. [2]. Since the presence of free fatty acids in the frying oil has not affected the catalytic activity of acids, hydrochloric acid has been used as acid catalyst. The frying oil has been pre-heated to a temperature of 120 °C, in order to remove trapped water molecules in the oil and then allowed to cool to 60 °C. Hydrochloric acid at a concentration of 0.8-1.8% of the weight of oil, has been mixed with methanol and the mixture has been carefully poured into the frying oil in the molar ratio of 8:1 and stirred at 200 rpm for 8 hours. It has then been poured into a separating funnel and allowed to settle for 24 hours after which the lighter biodiesel formed at the top layer has been recovered.
Fadhil et al. [3] has reported the transesterification of spent fish frying oil (SFFO) that has been carried out in a laboratory-scale setup. The catalytic solution (1% hydrochloric acid by weight of oil dissolved in methanol at a molar ratio of 6:1 of oil) has been poured into a 1000 g of preheated SFFO kept in a three necks round bottomed flask that has been provided with a mechanical stirrer, thermometer and a condenser. The transesterification has been conducted at (32 or 60°C) for 1h with continuous stirring (600 rpm). After the reaction was over, the mixture has been left to cool down after which it has been transferred into a separating funnel and left overnight to obtain two layers. Glycerol layer (lower layer) has been withdrawn while the top layer (methyl ester layer) has been extracted under vacuum.

3.2 Sulphuric acid
Sulphuric acid with the molecular formula H₂SO₄ is also a highly corrosive and strong mineral acid which is soluble in water at all concentrations. It is a colorless to slightly yellow viscous liquid at room temperature and has a strong pungent odour. Sulphuric acid is produced by chemical reaction executed in three steps.

In the first step, solid sulphur is burnt with oxygen to produce sulphur dioxide gas.

\[
S + O_2 \rightarrow SO_2
\]

In the second step, this sulphur dioxide is oxidized to get sulphur trioxide gas by using oxygen in the presence of a vanadium oxide as catalyst.

\[
2 SO_2 + O_2 \rightleftharpoons 2 SO_3
\]

In the third step, the sulphur trioxide is then absorbed into 97–98% pure H₂SO₄ to form fuming sulphuric acid known as oleum (H₂SO₄). The oleum is then diluted with water to get concentrated sulphuric acid.

\[
\begin{align*}
H_2SO_4 + SO_3 & \rightarrow H_2SO_4 \text{ (as a catalyst)} \\
H_2SO_7 + H_2O & \rightarrow 2 H_2SO_4
\end{align*}
\]

Sulphuric acid is found to be a leading candidate particularly for esterification of vegetable oils with high FFA contents. Freedman et al.[4] have employed different catalysts to carry out kinetic studies on production of biodiesel from soybean oil. Butanol has been mixed with soybean oil in the molar ratio 30:1. Trans esterification has been carried out with 1 % sulphuric acid as a catalyst and reaction conditions including rate constants and kinetic order have been analyzed at temperatures (°C), 77, 87, 97, 107 and 117.

Alcoholysis of soybean oil using sulphuric, hydrochloric, formic, acetic, and nitric acids has been evaluated by Goff et al. [5] at 0.1 and 1 wt% loadings at temperatures of 100 and 120°C in sealed ampoules. It has been reported that only sulphuric acid has proved more effective in conversion of free fatty acid to esters.

Prateepchaikul et al. [6] have prepared methyl esters from mixed crude palm oil containing a high free fatty acid content by using a two-stage process. Sulphuric acid has been used as the catalyst in an esterification reaction. Subsequently, a transesterification reaction has been carried out using sodium hydroxide as the catalyst.

Bermchans and Hirata [7] has employed two-step process for production of biodiesel from Jatropha curcas seed oil. The first step has related to acid esterification to convert FFA in the oil to esters, which is mainly a pretreatment process. During esterification, 0.60 w/w methanol-to-oil ratio in the presence of 1% w/w H₂SO₄ as an acid catalyst has been processed for 1 hour reaction at 50 °C. After this reaction, the mixture was allowed to settle for 2 hours and the methanol–water mixture separated at the top layer was removed. The second step of transesterification has been subsequently carried out to yield biodiesel.

Yingying et al. [8] have reported a similar method for producing biodiesel from Jatropha curcas L. oil. The mixture of sulphuric acid and methanol is added to Jatropha curcas L. oil to convert FFA to esters. A sealed 340-ml stainless steel autoclave equipped with a magnetic stirrer and an automated heating system has been used to carry out the esterification process.

Patil et al. [9] have produced biodiesel from waste cooking oil using sulphuric acid as a acid-catalyst in two-step process, namely, esterification (first step) and transesterification (second step).

Arora et al. [10] have carried out esterification of free fatty acids (FFA) in rice bran oil with methanol in the presence of sulphuric acid as a homogeneous catalyst. The effects of catalyst concentration (0.15 to 1.0 wt%), reaction temperature (318 K to 333 K), and molar ratio of oil to methanol (1:5 to 1:30) on the conversion of FFA have been studied.

3.3 Phosphoric acid
Phosphoric acid with the molecular formula H₃PO₄ is not a very strong acid. It is a stronger acid than acetic acid, but weaker than sulphuric acid and hydrochloric acid. It is prepared by adding sulphuric acid to phosphate rock with water as shown below.

\[
3 H_2SO_4 + Ca_3(PO_4)_2 + 6 H_2O ~\rightarrow~ 2 H_3PO_4 + 3 CaSO_4 \cdot 2H_2O
\]

This acid is a clear colorless liquid with no pungent odour. This acid has also been used as a catalyst in biodiesel production.

Dholakiya [11] has developed a scheme to produce the biodiesel from low cost feed stock such as cotton seed oil by using super phosphoric acid as a catalyst. The biodiesel synthesis has been carried out in a three neck 1000 ml round bottom flask equipped with stirrer, thermometer, water condenser and heating system. Investigation on the effect of varying oil : alcohol molar ratios of 1:40, 1:30, 1:20, 1:10 and 1:5 with the catalyst amounting to 5 % of the weight of the oil has been made. It has been reported that the yield from transesterification is found to be more at the molar ratio 1:10. It has further been concluded that as this catalyst has not formed the soap, esterification and transesterification of free fatty acid and oil could simultaneously be conducted to produce biodiesel.
Anand and Kaushik [12] have studied the esterification of palm fatty acid distillate using super phosphoric acid as an acid-catalyst. Investigation has been made at different oil to alcohol ratios ranging from 1:6 to 1:12 and amount of catalyst varying between 5 to 9% by mass. The effects of different physico-chemical parameters such as temperature, palm fatty acid distillate to methanol molar ratio and amount of catalyst on the conversion of biodiesel have been investigated. It has been reported that a maximum conversion feed stock to biodiesel has been obtained at the reaction temperature of 70°C with 9% of catalyst concentration and 1:12 molar ratio.

4. HOMOGENEOUS SOLID CATALYSTS

4.1 Potassium hydroxide

Potassium hydroxide which is commonly called as caustic potash is a white solid with the chemical formula, KOH and is corrosive to metals and tissue. KOH has been manufactured in large scale till last century by adding potassium carbonate (potash) to a strong solution of calcium hydroxide (slaked lime). This reaction causes calcium carbonate to precipitate, leaving potassium hydroxide in solution which is heated further to get solid KOH.

\[
\text{Ca(OH)}_2 + \text{K}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\ \text{KOH}
\]

However, the electrolysis of potassium chloride solutions has become popular nowadays as potassium chloride is extracted from minerals such as sylvinite, carnallite and potash available at different parts of the earth. Potassium chloride is also extracted from salt water and can be manufactured by crystallization from solution. This method as illustrated in the following chemical reaction yields KOH along with chlorine and hydrogen that have many industrial uses.

\[
2\ \text{KCl} + 2\ \text{H}_2\text{O} \rightarrow 2\ \text{KOH} + \text{Cl}_2 + \text{H}_2
\]

KOH has found an important role in the production of biodiesel as a solid catalyst through transesterification.

Conversion of feed stock to biodiesel has been achieved through transesterification in the presence of mixture of methanol and KOH. The reaction temperature has been maintained to 50°C, 60°C and 70°C besides regular stirring of the mixture for 1.5 h. At length, the product mix has been allowed to settle down in a separating funnel for 8 hour after which the biodiesel has been extracted.

Jamil and Muslim [15] have investigated transesterification of Jatropha curcas oil using KOH as a catalyst. The performance of KOH catalyst has been verified by conducting the kinetics experiments at the atmospheric pressure with molar ratio of 1:12, 1:14 and 1:16 of the oil to methanol, the reaction temperature in the range of 30 – 60°C, and with the catalyst in the range of 0.75 – 1.5% (by weight). It has been reported that the optimum oil (methyl ester) yield could be achieved for the molar ratio of 1:16, with the catalyst concentration of 1.5%.

Kawentar and Budiman [16] have synthesized biodiesel from second-used cooking oil. Only a single step method, namely, transesterification has been used for the production of biodiesel. The feedstock is mixed with methanol as a reactant and KOH as a base catalyst. The optimum condition (the ester content 92.76 %) of biodiesel production has been achieved at the reaction temperature of 66.5°C, molar ratio of methanol to oil 18:1, and 1 wt.% KOH.

Buendía-Tamariz et al. [17] have studied the production of biodiesel from chicken fat and pennycress oil through esterification and transesterification processes. In the first step, esterification has been carried out using H₂SO₄ as the acid catalyst and the subsequent transesterification has been done using KOH as the basic catalyst. The study has quantified the effects of the concentration of basic catalyst on the percent of fat conversion and the yield of biodiesel. The biodiesel has been evaluated for its properties as a fuel and has been compared with the standards of the American Society for Testing and Materials.

Chicken fat as a feedstock for the production of biodiesel in a two-step transesterification has been employed by Nuhu and Kovo [18]. The esterification, which is the first step and precursor to the transesterification has been done using 20 wt % of hydrogen tetroxosulphate as a acid catalyst along with methanol chicken fat molar ratio of 40:1 at a reaction temperature of 60 C and a reaction time of 80 minutes. The transesterification as the second step has been carried out using potassium hydroxide as catalyst with methanol. It is reported that the highest Chicken Fat Methyl Ester (CFME) yield of 93.4% has been obtained from 50g of chicken fat at reaction temperature of 60°C and a reaction time of 120 minutes corresponding to 1:6 molar ratio of oil-to-methanol with 1 wt% catalyst concentration.

4.2 SODIUM HYDROXIDE

Sodium hydroxide (NaOH) has been manufactured by activating sodium carbonate with calcium hydroxide in a metathesis reaction. Calcium carbonate which is not soluble in solution is allowed to settle down and

Published by: http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 05, May-2016

IJERTV5IS050381

(This work is licensed under a Creative Commons Attribution 4.0 International License.)
Separated. The aqueous sodium hydroxide is heated to recover as a white solid substance.

\[ \text{Ca(OH)}_2(aq) + \text{Na}_2\text{CO}_3(s) \rightarrow \text{CaCO}_3(s) + 2\text{NaOH(aq)} \]

This process has later been superseded by the chloralkali process which is an electrolytic process using sodium chloride as the reactant material. Nowadays, sodium hydroxide is industrially produced by this chloralkali process using brine solution available in abundance. The overall reaction for the electrolysis of brine is thus:

\[ 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2(g) + \text{H}_2(g) + 2\text{NaOH} \]

Similar to the by-products of potassium hydroxide manufacturing, chlorine and hydrogen gases are produced in the above process. Solid sodium hydroxide is obtained from this solution by the evaporation of water.

Sonawane et al. [19] have produced methyl ester of Karanja from Karanja oil through transesterification. This process has involved methanol as an alcohol and NaOH as a catalyst. Experiments have been performed to identify optimum conditions obtained using process parameters such as reaction temperature, % of catalyst, quantity of methanol used for the preparation of ester.

Alamul et al. [20] have used palm kernel oil to produce biodiesel through transesterification with ethanol using sodium hydroxide as a catalyst. It has been observed that 100 g palm kernel oil, 20.0% ethanol (wt% palm kernel oil), 1.0% sodium hydroxide, 60°C reaction temperature and 90 min reaction time has yielded an average of 95.8% biodiesel.

Anastopoulos et al. [21] have studied transesterification reactions of four different vegetable oils (sunflower, rapeseed, olive oil and used frying oil) with ethanol, using sodium hydroxide as catalyst. The effects of the mass ratio of catalyst to oil (0.25 – 1.5%), the molar ratio of ethanol to oil (6:1 – 12:1), and the reaction temperature (35 – 90 °C) have been observed for the conversion of sunflower oil. It is reported that the maximum yield of ethyl esters reached 97.14% at an optimize condition.

Lomsahaka and Hamza [22] have converted refined African mahogany oil into biodiesel using NaOH as a solid catalyst in transesterification process. A solution of 0.1648 g of sodium hydroxide pellets in 42 cm³ of methanol has been added to a 250 cm³ of this mahogany oil and heated at 60 °C. The reaction mixture has been stirred at this temperature for 30 minutes and then cooled to room temperature. The formed mahogany biodiesel has been then separated from glycerine. The biodiesel was washed with deionised water and dried.

An experimental study for the production of biodiesel using karanja (Pongamia pinnata) seeds as a raw material has been made by Imran et al. [23] through one-step transesterification with oil to methanol molar ratio (1:6 to 1:12), variation of Catalyst (NaOH) concentration (0.5% to 1.6% wt of oil). It has been reported that the maximum yield of biodiesel up to 85% with methanol to oil ratio 9:1 and for 1.5 hr reaction at 65 °C.

Folaranmi [24] has adopted a two-step process to produce biodiesel from jatropha oil. In the first step, a mixture of concentrated H₂SO₄ (1% w/w) with methanol (30% v/v) was heated separately at (50 °C) and then added to the heated oil in the flask. The mixture was stirred for 1 hour and allowed to settle for 2 hours. In the second step, transesterification has been done by adding the mixture of sodium hydroxide and methanol and heated to 60 °C. This mixture has been stirred for 45 minutes using a magnetic stirrer and then left to settle for 24 hours to remove glycerin as a by-product. The biodiesel thus produced has been thoroughly washed to make it free from excess methanol and soap.

Siddiqua et al. [25] have used palm oil as a source to produce biodiesel through transesterification. It has been reported that methanol was more effective variable than alkali concentration and temperature. It has been observed further that 12.5 ml methanol / 50 ml oil and 0.4 gm NaOH / 50 ml oil with a reaction temperature of 55°C has given a maximum yield with the calorific value of palm biodiesel being 38899.51 kJ/kg.

5. CONCLUSIONS

Homogeneous catalysts (basic or acid) possess high catalytic activity in shorter time, and mild operating temperatures ranging from 40 to 65 °C at atmospheric pressure. In two-step process of biodiesel production, these catalysts have proved capable in simultaneous advancing of the esterification along with transesterification.

**Abbreviation**

- FFA   Free Fatty Acid
- HCL   Hydrochloric acid
- H₂SO₄ Sulphuric acid
- H₃PO₄ Phosphoric acid
- KOH   Potassium Hydroxide
- NaOH  Sodium Hydroxide
- PSCO  Pure sunflower cooking oil
- WSCO  Waste sunflower cooking oil
- FAAA  Fatty acid alkali esters
- FAME  Fatty acid methyl esters
- SFFO  Spent fish frying oil
- CFME  Chicken fat methyl ester

**REFERENCES**


