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Study of the Recent Catalysts Utilized In Biofuels Production

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Abstract
The catalyst used in transesterification process during biodiesel production plays prominent role. Utilization of suitable catalyst affects the reaction time, reaction temperature, molar ratio and the yield of methyl ester produced. Present work depicts the study of the effect of some recent catalysts such as Waste capiz (Amusiumcristatum) shell, nano-magnetic catalyst KF/CaO–Fe3O4, a modified natural zeolite as a solid catalyst, zinc hydroxide nitrate, and nanoparticles of γ-Al_2O_3 utilized in biofuels production. It has been observed that using such catalysts, the maximum yield of biodiesel maybe obtained more than 95%. Results shows that the heterogeneous catalyst zinc hydroxide nitrate and Nanoparticles of γ-Al_2O_3 are very effective catalysts and contain maximum methyl ester yield of 95 % and 97.7 ± 2.14% respectively.

Keywords: Acid Catalyst, Base Catalyst, homogenous catalyst, heterogeneous catalyst,

Introduction

The most common form of fuel being used is the fossil fuel which is formed due to the burial of organic plant and animals at extreme temperature and pressure in course of millions of years. Total energy usage by mankind annually is of the order of 1 hexajoule. The importance of fossil fuel in such circumstances is crucially noticeable. However the even bigger problem is that the fossil fuel is limited in amount and will exhausted in its amount after 2075[1]. If we assumed the energy consumption rate increasing at 8% annually. Despite the fact that the conventional energy resources will gradually die, it creates green house effect, climate change and depletion of stratospheric ozone layer resulting in increase in average temperature of earth which causes a change in rainfall pattern, rise in sea level and impact on floura and fauna. Besides this, human health issues like CO poisoning, asthma and skin related diseases are growing. Thereby for the need of alternative fuels a wide variety of optional fuels like alcohol, methanol, and biodiesels is available. A significant advancement in terms of physio chemical properties of biodiesel has been made but there is a lack of full or partial replacement of fossil fuel that need to identified. The catalytic technology plays an important role in the different conversion processes in a bio refinery for the production of liquid as well as gaseous biofuels. The development of the catalysts and catalytic processes are essential in the bio refinery with the capability and flexibility to adjust and optimize performance in response to the changes in feedstock and market demands. The development of catalysts that facilitate highly selective conversion of substrate to desired products is one of the challenges encountered by bio refinery[2-4]. The thermally stable, effective and cost effective catalysts with high selectivity towards desired products are required [5].

Transesterification can be catalyzed by both acidic-catalysts (e.g. HCl and H_2SO_4) and basic-catalysts (e.g. KOH and NaOH). Alkaline catalysts are more widely investigated because the rate of transesterification reaction by alkaline catalysts is much faster than that by acid catalysts [6].

The search of alternative catalysts as substitutes for homogenous catalysts has been conducted for some years, and scientists found that heterogeneous catalysts offer several advantages than the homogeneous ones such as reusable, easy to separate, low sensitivity towards FFA and moisture content, more environmental friendly, etc.[7-9]

The present work is primarily concerned with study of recent homogenous and heterogeneous catalyst performances for biodiesel production and thereby examining their suitability.

Materials and Methods

Homogenous Catalyst

Homogeneous the catalysts are which remains in same phase as the reactants and help in accelerating the process of chemical change. These chemicals help in attaining the equilibrium more quickly by increasing the rates of both the forward and reverse reactions to an extent. These chemicals

help in increasing the rate which is already taking place slowly and has no role in initiating the reaction. In many homogeneous catalytic processes the ligands present in the catalysts needs to be discarded or separated by some method as these are later converted into active homogeneous catalysts and finally recycled for future applications.[3,4].

Homogenous Liquid Catalyst

Hydrochloric acid

Hydrochloric acid is a clear solution of the hydrogen chloride in water and is the colourless, highly corrosive and biting. It is prepared by dissolving hydrogen chloride in water. Hydrogen chloride may be formed by the direct combination of chlorine and hydrogen gases. Use of hydrochloric acid as acid catalyst has been reported in many literature. Transesterification of complain fat with methanol has been studied for producing bio-diesel. The study has included the probe of the relationship between reaction time and reaction temperature and catalysts concentration at the time constant methanol-oil volume ratio along with determination of optimal conditions in the transesterification process and Since the presence of free fatty acids in the frying oil has not affected the catalytic activity of acids, HCL has been used as acid catalyst. The catalyst has been poured into a 1KG of preheated SFFO kept in the transesterification has been conducted at (30 or 60°C) and approximately with continuous Mixed (600 rpm).Glycerol layer down to the pot and withdrawn. While the top layer (methyl ester layer) has been draw out under vacuum. Hydrochloric acid in a study of acid-catalyzed transesterification of sunflower oil using HCL reported 95.2% of biodiesel yield with 100˚C reaction temperature and 1.85 wt% catalyst loading Cao.[10]

Sulphuric Acid

Sulphuric acid is also a highly corrosive and strong mineral acid which is soluble to the water at all concentrations. This is a colourless to slightly yellow viscous liquid at room temperature and has a strong biting scent. Sulphuric acid is produced by chemical reaction carry out in three steps.In the first step, solid sulphur is burnt with oxygen to produce sulphur dioxide gas. 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.

In the third step, the sulphur trioxide is then absorbed into 97–98% pure H_2SO_4 to form fuming sulphuric acid known as oleum ($H_2S_2O_7$). The oleum is then diluted with water to get concentrated. 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.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.

Sulphuric acid the chemical formula is H_2SO_4 used in the acid-catalyzed transesterification with 0.5 wt% catalyst loading reported 92.5% biodiesel yield from Chlorella pyrenoidosa[11].

Phosphoric Acid

Phosphoric acid with the molecular formula H_3PO_4 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.

This acid is a clear colourless liquid with no biting odour. This acid has also been used as catalyst in biodiesel production. [12]

Homogeneous Solid Catalysts

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.

However, the electrolysis of potassium chloride solutions has become popular nowadays as potassium chloride is extracted from minerals such as solvate, 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.

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

Comparison of the optimum conditions of alkaline catalyzed transesterification process for biodiesel production from pure sunflower cooking oil. 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.

Most common basic catalysts is potassium hydroxide (KOH). The highest biodiesel yield produced by Calophylluminophyllum was reported at (2014) with 98.53% by using 1 wt% KOH and 9:1 methanol to oil Ratio[13].

Sodium Hydroxide

Sodium hydroxide (NaOH) has been manufactured by activating sodium carbonate with calcium hydroxide in a

metathesis reaction. The aqueous sodium hydroxide is heated to recover as a white.

This process has later been superseded by the chloroalkali 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 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 .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.

Alamu1 have used palm kernel oil to produce biodiesel through transesterification with ethanol using sodium hydroxide as a catalyst.

most common basic catalysts is sodium hydroxide (NaoH) reported 95% of biodiesel yield from soybean oil by using NaOH with 1.3 wt% catalyst loading and ethanol to oil ratio of 9:1.[14]

Heterogeneous Catalyst

The Heterogeneous catalysts are the catalyst which remains in a different phase as that of the reactants and help in accelerating the process of chemical change. As a matter of fact, heterogeneous catalysts can be separated more easily from reaction products and the reaction conditions could be less drastic than the methanol supercritical process.[15]

Heterogeneous catalysts have the advantage that separation and regeneration of the catalyst are easy and cheap. Heterogeneous basic catalysts include alkaline earth metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and hydrotalcites etc.[16]

Zinc Hydroxide Nitrate

ZHN is a recent finding in heterogeneous catalyst driven transesterification of vegetable oils. Layered compound zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2$ $2H_2O$) is effective in the transesterification of palm oil and esterification of lauric acid even when hydrated ethanol was used. ZHN is a solid catalyst whose thermal stability is investigated at 170^0C.

The transesterification process is strongly affected by the temperature, methanol, lauric acid molar ratios, catalyst concentrations (wt% in relation to the oil mass). When fixing the other parameters, temperature was varied from 100^0C to 140^0C then the ester yield was increased very largely. Then, keeping the temperature fixed at 140^0C, at constant catalyst percentage, the molar ratio was varied but the yield was not much affected this time. The variation in the percentage of the catalyst while maintaining others fixed gave the significant results providing yield up to 95.7%. The results are replicable having relative standard deviation of the content of ester only 0.93% for an average ester content of 96.8 ± 0.9 wt%.[17]

Waste Capiz

Waste Capiz shell is used as a basic material for transesterification of oils. Waste Capiz (A. cristatum) shell is obtained from fish. The Capiz cell is washed, pulverized and then it's powered form is calcined in the furnace upto 900C. During calcination, the calcium carbonate is converted to CaO which is used as a catalyst for biodiesel production from Palm oil and methanol. CaO is the acid and so takes the H+ ion from the methanol and thus making deprotonated methanol into a nucleophile followed by attacking on the carbonyl carbon of the triglycerides molecule.

For understanding the effect of the percentage of catalyst on the rate of reaction, a mechanism step is required. After the transesterification reaction, the glycerol is produced which reacted with the catalyst CaO forming glyceroxide and this reacting with the methanol forms $CH_3OeCaeO(OH)_2C_3H_5$.

With the increase in the percentage of the CaO above 3%, the amount of $CH_3OeCaeO(OH)_2C_3H_5$ also increased which is less reactive in nature than the CaO. Therefore the rate of reaction decreases and the amount of biodiesel produced is less.

If we increase the reaction time, there is a better contact probability is attained and thus increasing the biodiesel yield. But further increase in the reaction time gives no significant effect on yield.

The main property of heterogeneous catalyst is the reusability. The maximum yield obtained is almost 92.8% when the catalyst is used first time. After this, the CaO catalyst is washed with methanol and recalcined and then further used. But the disadvantage is that the yield is further reduced and the yield is reduced to half when waste capiz catalyst is used for the third time as compared to that of the first time.[18]

Zeolite

These catalysts are crystalline 3-d structure of Al and Si.

They have high thermal stability, near about 1000 ^{o}C and surface area. It also has acidic shape selectivity which helps to influence reactions. It has more effect on mono glyceride yield.

Zeolite has Lewis acid and Bronsted acid sites. Micro porous walls are due to Lewis acid and Bronsted acid site are present on both internal and external surfaces.

Zeolite is used for removal of FFA fats in waste oils. One Bronsted acid site is produced when Al^{3+} substitute one Si^{4+}. This cation is neutralized by Na^+. The bi products like Ca^{2+},

Mg^{2+} and Li^{3+} are the hydroxyl groups that strengthen those acid sites. The introduction of protons with dilute hydrochloric acid also helps in adjusting the acidity of zeolite. Large pore zeolite such as Y(gama) and mordenite has higher activity (biodiesel yield 92%) than medium pore ZSM-5 and Al containing mesoporous MCM-41 (biodiesel yield <30%). Zeolite with large pore favors reaction by rendering the active sites.

But this has some drawbacks also. It does not exhibit high activity in transesterification. Transesterification of Pongamia oil gives low yield (~59%) over a long time reaction (24 hours).

Introduction of Li^+ ion into zeolite with $La(NO_3)_3$ resulted into higher conversion with higher stability than zeolite due to presence of more external Bronsted acid sites available for reaction. So it's the new alternative for natural zeolite.[19]

Al_2O_3

This catalyst is generally used in solid gel phase while in reaction. Gelation temperature was obtained at 70 ºC. To get maximum biodiesel yield, reaction time of 4 hour and molar ratio of 12:1 is the optimum condition.

Catalyst and methanol were thoroughly mixed in room temperature. The solution is then added to the bottom of the batch reactor. Then the vegetable oil is mixed at 85% g/g ratio. The temperature is then kept between 293k to 333k. The reaction allowed to take place for 1 hour. The withdrawn samples are then distilled to separate it from the Al_2O_3. The extracted catalyst can be reused. The surface of Na supported samples monotonically decreased as Na loading increases.

Liquid phase Na loaded Al_2O_3has ability to yield ~90% biodiesel. The catalyst can be separated from the biodiesel produced by sampling filtering process.

313k was found to be the optimum temperature for the transesterification reaction to proceed. It gave same 90% yield only in 2 hour reaction. But by raising temperature to 333k, yield reduced to 73 %

So the drawback it has is that there should be optimum amount of temperature, i.e. 313k and Na loading, i.e. 20% in g/g ratio.

Moreover, homogeneous mixture gives far better result than heterogeneous Na loaded Al_2O_3.[20]

Conclusions

Based on exhausted investigation of different types of catalyst, following conclusions may be drawn:

- Homogeneous catalysts is the (basic or acid) possess high catalytic activity in the shorter time, and operating temperature ranging from 40 to 65 °C at atmospheric pressure.
- There are two-step process of biodiesel production, these catalysts have proved capable in simultaneous advancing of the esterification along with transesterification in solution is allowed to settle.
- The ZHN catalysed transesterification reaction gives a very high yield up to 95.7%. The catalyst percentage is having larger effect on yield rather than the molar ratio.
- The only problem while using ethanol in place of the methanol was that using this, the results showed a drastic decrease in the yield. The difference in the reactivity was largely due to higher hygroscopic character of the former and the lower density of the latter. But the difference was lesser at higher temperature.
- For increasing the yield of the biodiesel, the amount of catalyst can not be extended after a certain extent of 3%. While using the parameter of reaction time to increase the yield, there is also an existing optimum limit after which no significant rise in yield is present.
- The catalyst is reusable having effectiveness half in the third use as compared to first one.

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