Synthesis and characterization of Nano-Catalyst for the production of Biodiesel from Pongamia pinnata oil

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Abstract: Biodiesel production from *Pongamia pinnata* oil provides an alternative energy source for various uses. Fe3O4 was prepared by the co-precipitation method at 60°C and 400 rpm until it reached a thick consistency and dried in a hot air oven for 6 hours, maintaining the temperature at 150°C. The CaO was prepared from the mussel shells by the calcination method at 300°C to 800°C in a muffle furnace for 4 hours. The Nano catalyst ZrO_2/CaO-Fe3O4 was prepared by doping. The prepared catalyst was characterized by FTIR, SEM, XRD and Particle size analysis to study its catalytic activity. It was transesterified using the ZrO2/CaO-Fe3O4 catalyst at various experimental conditions: 5% (w/w) catalyst concentration, 12:1% methanol to oil molar ratio, 65°C reaction temperature and 50 min of reaction time, at which a maximum biodiesel yield of 98.11 wt% was obtained. The fuel properties were analyzed using the ASTM D6751 standard. The prepared nanocatalyst seems to be highly active in terms of quality and efficiency.

Keywords: Pongamia pinnata oil; Co-precipitation; Nano catalyst; Transesterification; Doping.

INTRODUCTION

Crude oil is a most essential commodity because of the increase in demand in the economy. Nowadays the consumption of energy is increased for use in industries, transportation, and electricity. Due to this condition, the need for fossil fuels increased, such as diesel, petroleum, coal, and natural gas. Fossil fuels are made from decomposing plants and animals. These fuels are found in the Earth's crust and contain carbon and hydrogen, which can be burned for energy.[4]

Some of the alternative sources of renewable energy like biogas, ethanol and biodiesel, which are mainly used in transportation. Commonly biodiesel is prepared from vegetable oil or animal fats. Soya bean oil, grape seed oil, and cocoa butter are examples of seed oils, or fats from seeds. Olive oil, palm oil, and rice bran oil are examples of fats from other parts of fruits. In common usage, vegetable oil may refer exclusively to vegetable fats which are liquid at room temperature. Animal fats and oils are lipids derived from animals: oils are liquid at room temperature, and fats are solid. Chemically, both fats and oils are composed of triglycerides. Although many animal parts and secretions may yield oil, in commercial practice, oil is extracted primarily from rendered tissue fats from feedstock of animals like pigs, chickens and cows.[4]

Vegetable oils are usually edible. Some of the preparations have been undergone to produce biodiesel from non-edible oils like Castor oil, Karanja oil, Mahua oil, Jatropha, etc. Which is widely used for the production of biodiesel because of its availability, high yield with short reaction time, low temperature and pressure.[7]

The Millettia pinnata tree (Pongamia pinnata) belongs to the Fabaceae family. It is a legume tree that grows to about 15-25 m in height with a large canopy that spreads equally wide. It may be deciduous for short periods. It is native to eastern and tropical Asia, Australia, and Pacific islands. It has a straight or cooked trunk, 50-80 cm in diameter with gray-brown bark, which is smooth or vertically fissured. Its wood is white colored. Flowering generally starts after 3-4 years with small clusters of white, purple, and pink flowers blossoming throughout the year. The seeds are about 1.5-2.5 cm long with a brittle, oily coat, and are unpalatable in natural form to herbivores. It requires a temperature slightly below 0° C and up to about 50°C and annual rainfall of 500-2,500 mm.[12]

Croppings of indehiscent pods can occur for 4–6 years. The brown seed pods appear immediately after flowering and mature in 10 to 11 months. Millettia pinnata seeds generally contain oil (27-39%), protein (17-37%), starch (6-7%), crude fiber (5-7%), moisture (15-

20%) and ash content (2-3%). Nearly half of the oil content of M. pinnata seeds is oleic acid. Oil made from the seeds, known as pongamia oil, has been used as lamp oil, in soap making, and as a lubricant. Pongamia can produce 9 to 90 kg of seeds annually per adult tree in India, equivalent to a potential yield of between 900 kg and 9,000 kg per hectare. The blend of Pongamia pinnata oil biodiesel with conventional diesel has been found to result in lower CO, hydrocarbon, and smoke emissions as compared to pure conventional diesel.[4] The prepared Karanja oil exemplified the composition of 9.75% linolenic, 6.24% linoleic acid, 60.25% oleic and 23.76% saturated acyl groups.

MATERIALS AND METHODS

In this study, Pongamia pinnata was used as feedstock to produce biodiesel by transesterification reaction. Brown mussel shell (Perna Perna) collected from the seashore near Nagapattinam was used to prepare CaO. Iron oxide (Fe_3O_4) is prepared using Ferrous Sulfate ($FeSO_4$), Ferric chloride ($FeCl_3$), Sodium Hydroxide (NaOH) and C-TAB (Cetyl-Trimethyl Ammonium Bromide). The magnetic nano-catalyst was doped with Fe_3SO_4, ZrO_2 and CaO by co-precipitation method. Methanol (99.5% pure) was used as a solvent for the transesterification reaction. The chemicals and reagents used in this study were of analytical grade and purchased from Sisco Research Laboratories, Mumbai, India.

CATALYST PREPARATION

Preparation of CaO from mussel shells:

Calcium oxide can be produced by thermal decomposition of materials like limestone or seashells that contain calcium carbonate in a lime kiln. The process that is used to prepare burnt lime is known as calcination. The mussel shells were cleaned and washed thoroughly with warm water several times. Then the cleaned and dried mussel shells are peeled and cut in half. The cleaned and washed mussel shells were calcined at 700°C with a heating rate of 7°C/min for 4 hrs in the muffle furnace. Then the calcinated mussel shells are cooled at room temperature for an hour. After the calcination process, the brown mussels shell was decomposed to CaO. The solid powder was crushed and sieved to pass 100 mesh screens. All calcined samples were kept in a closed ve ssel to avoid the reaction with carbon dioxide (CO_2) and humidity in the air before being used. This resulting solid which is as known as a non-impregnated catalyst.

Preparation of Fe_3O_4:

The co-precipitation technique is probably the simplest and most efficient chemical pathway to obtain magnetic iron oxide nanoparticles. 27.8 g of FeSO4 was completely dissolved in 100 ml of distilled water to prepare aqueous solution A. Then, 16.2 g of FeCl3 was completely dissolved in 100 ml of distilled water to prepare aqueous solution B. Further, 4 g NaOH was completely dissolved in 100 ml distilled water to prepare aqueous solution C. 0.3 g of C-TAB (Cetyl-Trimethyl Ammonium Bromide) was measured. A 1000 ml beaker was placed on the magnetic hot plate with a magnetic pellet inside the beaker. Solution A (FeSO4) and solution B (FeCl3) were poured into a 1000 ml beaker. Load the 100 ml dissolved NaOH solution into the burette and place it on the top of the 1000 ml beaker with the help of the holder. When the magnetic hot plate is on the pellet starts stirring and heat produces from the plate. The heat was maintained at 60°C and the rpm is maintained under 400. After 5 minutes the measured C-TAB is added to the solution and the stirring continues. Then the loaded NaOH solution leaves the drop by drop to the solution. The stirring continues for 8 hours. After that, the solution gets concentrated. The concentrated solution is kept in the hot air oven under 150°C. The dried solution is crushed and stored in a zip cover.

Doping of ZrO_2/CaO-Fe_3O_4:

The magnetic core was prepared by a convenient co-precipitation method based on literature with some modifications. Briefly, 27.8 g of FeSO4 7H2O, 16.2 g of FeCl3, 12.3 g of ZrO2, 5.6 g of CaO, 4 g of NaOH and 0.3 g of C-TAB were completely dissolved in 100 ml distilled water to prepare aqueous solution. The final pH value of the aqueous solution was maintained at about 12. The nano-magnetic solid base catalyst was prepared by a co-precipitation method. A 1000 ml beaker was placed on the magnetic hot plate with a magnetic pellet inside the beaker. 27.8 g of FeSO4 7H2O, 16.2 g of FeCl3, 12.3 g of ZrO2 and 5.6 g of CaO were completely poured into the 1000ml beaker. Load the 100 ml dissolved NaOH solution into the burette and place it on the top of the 1000 ml beaker with the help of the holder. When the magnetic hot plate is on the pellet starts stirring and heat produces from the plate. The heat was maintained at 600C and the rpm is maintained under 400. After 5 minutes the measured C-TAB is added to the solution and the stirring continues. Then the loaded NaOH solution leaves drop by drop to the solution after 20 minutes. The stirring continues for 8 hours. After that, the solution gets concentrated. The concentrated solution is kept in the hot air oven under 1500C. The dried solution is crushed and the final catalyst was stored in desiccators.

Preparation of Biodiesel:

The four ways to convert oils and fats into biodiesel are transesterification, blending, micro-emulsion and pyrolysis-transesterification. Transesterification is the process in which fat or oil reacts with an alcohol to form esters and glycerol. A catalyst is used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. Transesterification is a commonly used multi-step chemical reaction. The main factor which affects transesterification is the amount of alcohol and catalyst; reaction temperature, pressure and time. Transesterification or alcoholysis is defined as the process in which non-edible oil is allowed to chemically react with alcohol. In this reaction, methanol and ethanol are the most commonly used alcohols because of their low cost and availability. This reaction has been widely used to reduce the viscosity of non-edible oil and for the conversion of triglycerides into ester. Transesterification can be carried out in two ways: catalytic transesterification and noncatalytic transesterification. It is widely known that catalytic transesterification faces two problems. The main problem is the processes are relatively time-consuming and need the separation of the oil, alcohol, catalyst, and saponified impurities mixture from the biodiesel. Purification of biodiesel is much easier as no catalyst is required during the supercritical transesterification process, thus preventing soap formation or saponification from occurring. However, the drawbacks of the supercritical alcohol transesterification process are the high temperature and pressure that result in the high cost of the apparatus. The Pongamia pinnata oil is measured and taken into the transesterification setup. The methanol and nanocatalyst were measured and mixed. The mixed solution was added to the oil after 10 min of heating. The temperature was maintained at 60°C and the rpm is maintained at 450. After 60 min. of reaction the oil and methanol mixed with nano catalyst is set to settle in the extraction funnel. Then after extraction the oil was tested using GC-MS.

RESULTS AND DISCUSSION

Characterization of ZrO_2/CaO-Fe_3O_4 Nano Catalyst:

XRD analysis

The x-ray diffraction of ZrO2/CaO.Fe3O catalyst in Figure-1. The formation of peaks may be due to the interaction of the catalyst with water molecules formed as a byproduct during synthesis and moisture absorbed when exposed to atmospheric air.

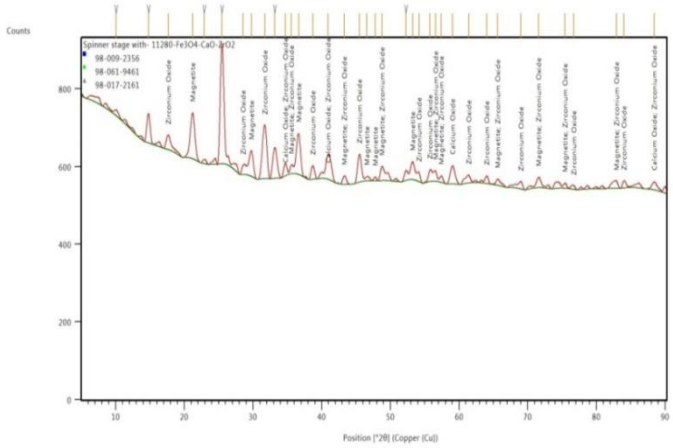

Figure:1- XRD pattern of ZrO_2/CaO-Fe3O4 catalyst

SEM analysis:

The SEM analysis was conducted to investigate the morphology of the catalyst. The surface properties of the ZrO2/CaO-Fe3O4 were influenced by the incorporation of the dopant. The synthesized ZrO2/CaO-Fe3O4 nanocatalyst was found to be clustered in the form. The ZrO2/CaO-Fe3O4 nanocatalyst was found spherical in shape -Figure-2. Heterogeneous catalyst with a different size was observed from this analysis.

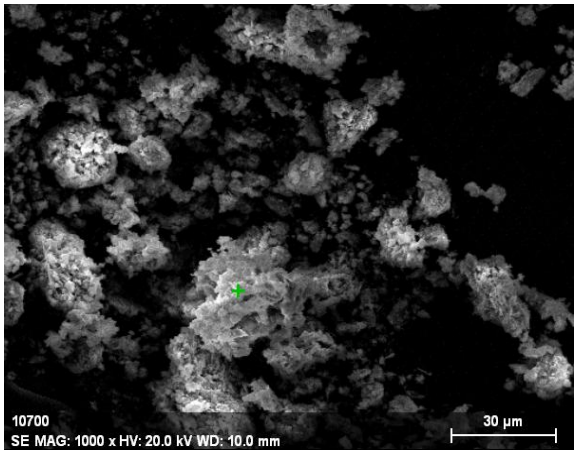

Figure:2- SEM of ZrO_2-CaO-Fe_3O_4 catalyst

FTIR analysis:

Characteristics of ZrO2/CaO-Fe3O4 were analyzed using FTIR analysis. The FTIR spectra represent the functional groups in ZrO2/CaO-Fe3O4 –Figure-3. This technique allows the identification of structural changes in the molecular binding between microorganisms and metal atoms, which can provide information about the nature of their interactions.

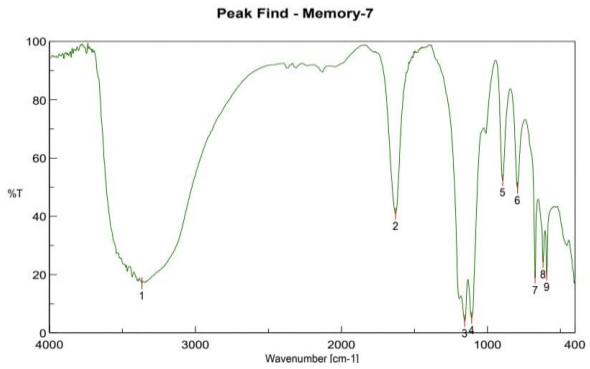

Figure:3-FTIR spectrum of ZrO_2/CaO-Fe3O4 catalyst

Transesterification

The important parameters optimized to get maximum yield of biodiesel are effect of calcinations temperature, effect of methanol to oil ratio, effect of catalyst concentration, effect of reaction time and effect of reaction temperature.

Effect of methanol to oil molar ratio:

The molar ratio of alcohol to triglyceride is the most important variable affecting the biodiesel yield. However, due to the reversible nature of the reaction, excess alcohol is usually used in transesterification to shift the reaction to the product side. The higher mass ratio of reactant increases the contact between the methanol and oil molecules so the methyl ester concentration increases with the increase in mass ratio of methanol to oil. The temperature, reaction time and catalyst concentration were fixed at 65°C, 50 min and 5% respectively. As the molar ratio of methanol to oil increased from 3:1 to 18:1, the production yield also increased. A further increase in the ratio resulted in lower biodiesel. The optimum molar ratio of oil to methanol was determined as 12:1 for maximum yield (87.25 wt%) of biodiesel fuel from Pongamia pinnata oil using ZrO2/CaO-Fe3O4 catalysts as shown in fig-4.

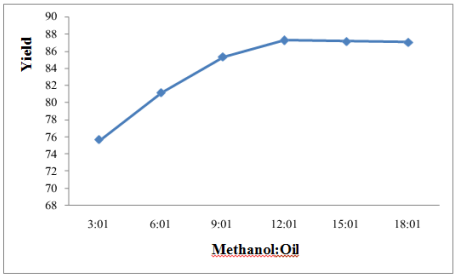

Figure:4- Effect of methanol to oil molar ratio

Effect of catalyst concentration:

Biodiesel production can be affected by the amount of catalyst used. The catalyst functions to accelerate the reaction rates, catalyst concentration is the important factor that affects the transesterification reaction. The nanocatalyst concentration was varied in the range of 2 to 7% (w/w) to examine the effect of different concentrations. The maximum biodiesel yield of 91.26 wt% was obtained with a 5 % nanocatalyst concentration as shown in figure-5, indicates that the biodiesel yields beyond 7% due to poor diffusion between oil and methanol, where the biodiesel gets absorbed on the surface of the catalyst when the catalyst concentration increases. An increasing amount of heterogeneous catalysts caused the slurry too viscous giving rise to the problem of mixing and a demand for high power consumption for adequate stirring.

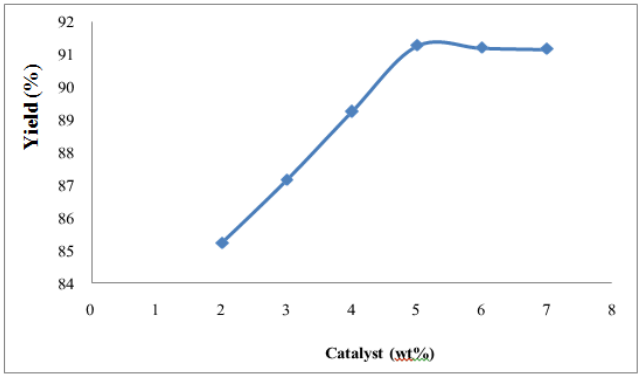

Figure:5- Effect of Catalyst concentration

Effect of reaction time

Reaction times have a direct effect on the yield of methyl esters. Reaction time is important in catalytic activity where the increasing methyl esters yield is directly proportional to the time. An increase in time increases the fatty acid esters conversion, whereas the fall over the yield is due to the long exposure of the catalyst and the methanol. The conversion increases with reaction time. Besides, a longer reaction time does not increase the yield of biodiesel. The effect of reaction time on the conversion was conducted in optimized conditions of a 12:1 molar ratio of methanol to oil with 5% nanocatalyst for varying reaction times 20-70 min. The biodiesel yield was increased to 94.6 wt% as the reaction time was increased to 50 min.

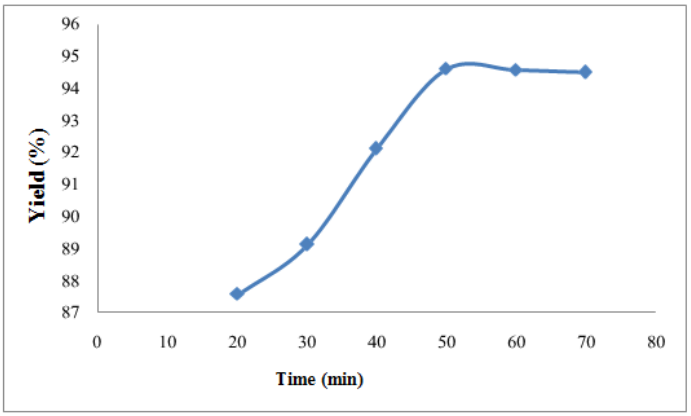

Figure:6- Effect of reaction time

Effect of reaction temperature:

The reaction temperature is another important factor that affects biodiesel yield. Other conditions were maintained at 65 min with 5% catalyst and 12:1 methanol to oil molar ratio. The reaction temperature varied from 52 to 77°C. An increase in temperature increases the solubility of solvent with an enhanced diffusion rate and also increases the biodiesel yield. The reaction temperature must be less than the boiling point of alcohol to ensure that the alcohol will not leak out through vaporization. A higher reaction temperature can decrease the viscosities of the oil and result in an increased reaction rate, and a shortened reaction time. The result indicates that the biodiesel conversion was low at lower temperatures and increased sharply and reached 98.11wt% at 60°C. The decrease in yield is due to the methanol vaporization, making the methanol availability insufficient. The other reason that adds to the decrease in the yield on increasing the temperature is the polarity of methanol, which reduce at higher temperature.

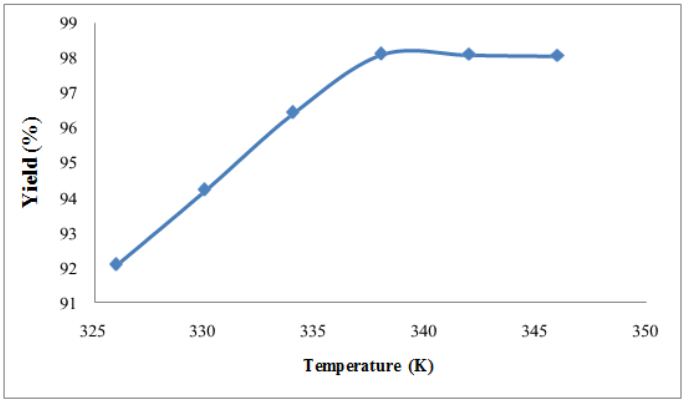

Figure:7- Effect of reaction temperature

Optimized Process Parameters for biodiesel production

Methanol to oil molar ratio: 12: 1, catalyst concentration: 5wt%, reaction time: 50 min and reaction temperature: 338 K to give a maximum biodiesel yield of 98.11%.

Characterization of Biodiesel

Characterization of biodiesel was done to make sure that it can be used in automobiles. As per the ASTM D6751 standard test methods, the properties of Pongamia pinnata biodiesel were determined.

CONCLUSION

The ZrO2/CaO-Fe3O4 Heterogeneous nanocatalyst has shown effective catalytic activity for the conversion of Pongamia pinnate oil into biodiesel. The synthesized nanocatalyst exhibited a spherical shape with a size of 24.18 nm and a hexagonal structure. The ZrO2/CaO-Fe3O4 nanoparticles calcined at 600°C have shown maximum catalytic activity. The optimal process conditions for maximum biodiesel yield of 98.11 wt% were catalyst concentration 5% (w/v), methanol to oil ratio 12:1% (v/v), temperature (65°C) and time (50 min). The fuel properties of *Pongamia pinnata* biodiesel were determined as per the ASTM D6751 standard. Thus, it is concluded that both Pongamia oil and ZrO2/CaO-Fe3O4 Nano catalyst are suitable for large-scale production of biodiesel.

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