Biodiesel Production by using $CaO\text{-}Al_2O_3$ Nano Catalyst

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Abstract— *Because of biodegradability and non-toxicity biodiesel has become more attractive as alternative fuel. Biodiesel is produced mainly from vegetable oils by transesterification of triacylglycerols. From economic and social reasons, edible oils should be replaced by lower-cost and reliable feed stocks for biodiesel production such as non-edible plant oils. Biodiesel is considered an alternate and renewable substitute for petro-diesel. Pure vegetable oils and animal fats are being widely used for biodiesel production which is resulting in increased food cost and thus causing economic imbalance. In this research, inedible oils e.g. Jatropha oil is investigated for biodiesel production through transesterification process by using $CaO\text{-}Al_2O_3$ nanocatalyst, synthesized via top down technique. The synthesized nanoparticles were then characterized by XRD. The average crystallite size determined by XRD analysis was 29.9nm.It was calculated by using the Scherrer equation. These nanoparticles were tested to be used as a nanocatalyst for the production of biodiesel from Jatropha curcas oil. The fatty acid content of the oil and the biodiesel was analyzed using Gas Chromatography-Mass Spectroscopy (GC-MS). Propanoic acid ($C_5H_{10}O_3$) was observed to be the most abundant compound present in methyl esters. Methanol to oil molar ratio of 3:1 and 5:1 were investigated for optimization process. The optimization results for production of biodiesel from the transesterification of Jatropha curcas oil catalyzed by $CaO\text{-}Al_2O_3$ nanoparticles showed maximum yield i.e. 82.3% at 5:1 methanol to oil molar ratio.*

Keywords— ***Jatropha curcas oil, CaO Nanoparticles, Al_2O_3 Nanoparticles, biodiesel, Transesterification.***

I. INTRODUCTION

Energy is considered to be the most vital element for the growth and development of an economy. The demand of energy is significantly increasing with globalization. Fossil fuels are widely used as a natural source of energy but because of their rapid depletion and high CO_2 emissions, the need to find an alternative and renewable source of energy is becoming increasingly important.

Biodiesel is one such alternative renewable source of energy which has the potential to substitute and replace fossil fuels. It can be defined as a biofuel comprising of mono-alkyl esters of long chain fatty acids, produced from renewable biolipids via transesterification process. It is a clean burning (Chew, & Bhatia, 2008), eco-friendly alternative fuel, produced majorly from plant oils and animal fats. Of these feed stocks, jatropha, karanja, mahua and castor oils are the most often used in biodiesel (Ivana, et al., 2012) synthesis. Various oils extracted from seeds or kernels of non-edible crops are potential feed stocks for biodiesel production. The important non-edible oil plant is Jatropha (Ivana, et al., 2012). Biodiesel can be produced from edible oils e.g. soybean, sunflower, rapeseed, palm etc. as well as non-edible oils e.g. jatropha, jojoba, tallow, Pongamia etc. From socioeconomic reasons, edible oils should be substituted by reliable and low cost inedible sources for biodiesel production. Among the sources of non-edible oils, *Jatropha curcas* oil is gaining worldwide attention because of its high oil content (Sujatha, 2006) and the superior quality of the biodiesel it produces (Raja *et al*., 2011). For example, the main toxic compounds injatropha plants are protein curcin and purgative agents, protein ricim in castor (Ivana, et al., 2012).

Jatropha curcas is a perennial, drought resistant and poisonous shrub or small tree belonging to the family *Euphorbiaceae* (Chew, & Bhatia, 2008), which is native to Central and South America (Martinez-Herrera *et al.*, 2006). It can grow on barren land, requires minimum care, produces low cost seed, and contains high oil content with short growth period. Its seeds have a high potential for beneficial utilization and contains 25-40% oil by weight (Heller, 1996).The Jatropha seed also consists of highly toxic agents, majorly phorphol esters and curcin (Tanya *et al*., 2011) which renders the seed as inedible and poisonous to humans and animals. The Jatropha seedcake can be used as an organic fertilizer (Makkar *et al*., 1998) and after detoxification process it can also be used as an animal feed (Gaur *et al*., 2011). *J. curcas* oil is widely considered as a potential substitute to fossil fuel and has a high flash point which makes it very safe to handle (Raja *et al*., 2011).

Catalyst plays a major role in the production of biodiesel as it enhances the reaction rate of transesterification process and also aids in producing high yields of biodiesel. Conventional homogeneous and heterogeneous catalysts such as KOH, NaOH, Zeolite etc. are most commonly used in the industrial process to generate biodiesel. However, the transesterification process by these conventional catalysts leads to saponification reaction and low yield of biodiesel (Aracil *et al*., 2006), hence; it requires additional downstream process which reflects the high cost of production. Therefore, the focus on the development of new approaches is greatly increasing to achieve an efficient process for biodiesel production.

Recently, nano catalysts have gained special attention for biodiesel production, because of their high catalytic efficiency, large surface area, high resistance to saponification and good rigidity (Hu e*t al*., 2011). The study for the production of biodiesel using nanoparticles as catalyst is very limited. The present study attempts to investigate the behaviour of CaO-Al_2O_3 as a nano catalyst for the transesterification reaction of Jatropha oil.

II. MATERIALS AND METHODS

All the experiments were conducted in Nano Sciences & Technology Labs of National Centre for Physics, Quaid-i-Azam University, Islamabad, Pakistan. *Jatropha curcas* oil was used as a raw material for the biodiesel production. Chemicals used in the laboratory i.e. methanol (99% pure) and chloroform were provided by NS &TD of NCP Labs. Calcium Hydroxide (chuna) was purchased from the local market of Islamabad. Aluminum Oxide was purchased from local market of Islamabad

2.1 CaO-Al_2O_3 Nano– Catalyst Preparation

Nanoparticles of CaO and Al_2O_3 were prepared in the laboratory by the Ball milling process. Calcium Hydroxide (1.0 g) and Aluminum Oxide (1.0 g) were accurately weighed and then converted to nanoparticles by using Ball Milling Technique at 200 rpm for 2 hours at room temperature. In the ball milling process the CaO and Al_2O_3 powder was placed in the ball mill separately and subjected to high-energy collision from the balls. After obtaining the desired nanosize, the two chemicals were then mixed in equal proportions and calcined at 500^0Cfor 3 hours in the Wisetherm furnace to investigate their efficiency as a mixture of Calcium Oxide and Alumina nanoparticles.

2.1.1 Characterization of CaO-Al_2O_3 Nanoparticles

The synthesized nanoparticles were then characterized using X-ray diffraction (XRD) for the determination of crystallite size and shape from diffraction peak characteristics. An XRD analysis was conducted on a diffractometer with a Cu radiation source at voltage of 40 kV and current of 35 mA. Samples were analyzed with a locked couple scan type.

FIGURE 1: WISETHERM FURNACE

2.2 Jatropha Oil Analysis

Jatropha oil was analyzed for its composition by GC-MS test which was conducted in NC & TD of NCP. The composition of oil was analyzed by Gas Chromatography. Sample solution for GC-MS was prepared by dissolving 01-mL of the oil in 05-mL chloroform and stirred for 3-5 minutes with a magnetic stirrer on the hot plate for GC-MS analysis. 01-mL of this sample

was then injected for analysis. The fatty acids in Jatropha oil were identified and quantified by comparing their retention times and peak areas to those of standard fatty acids.

2.3 Transesterification Process

All glassware was oven-dried and cooled to room temperature. Methanol to Oil ratio was varied for optimization process. Other parameters including Temperature, Reaction Time, Stirring Speed, amount of oil and pH were kept constant throughout the experiment. The experiments were conducted in a 1000 ml round bottom flask equipped with a condensing, heating and stirring facility. A thermometer was fixed by the use of a retort stand for verifying and controlling the temperature of the heating plate.

Firstly, 0.1 gm of prepared nano catalyst was poured into a 1000 ml round bottom flask containing a measured amount of methanol i.e. 300 ml of methanol for 3:1 and 500 ml for 5:1 and allowed to mix for a while at room temperature. The mixture was then refluxed at 100^0C for 1 hour at 600 rpm. After 1 hr, the reflux was stopped by cooling the flask with ice. After cooling, 100 ml oil was then added and this mixture was again refluxed at 100^0C for 3 hours at 600 rpm. To prevent methanol loss during the reaction, a water-cooled condenser was used.

After the completion of reaction, the mixture was cooled to room temperature. The product formed was then allowed to settle overnight to enhance separation. Two distinct liquid phases were formed during separation such that crude ester phase at the top and glycerol phase at the bottom. The yield of methyl esters (biodiesel) produced was calculated using the following formula:

$$\text{Percentage Yield} = \frac{\text{Volume (ml) of Biodiesel x 100}}{\text{Volume (ml) of Reactants}}$$

FIGURE 2: TRANSESTERIFICATION SETUP

2.4 Product Purification

The bottom glycerol phase was removed and the crude methyl ester layer at the top was separated and purified through filtration process. The remained water and unreacted methanol in the methyl esters were then removed by heating the product to 110^oC and maintained for a while until the bubbles disappeared. This biodiesel was then collected and stored in an air-tight bottle at room temperature.

2.5 Biodiesel Analysis

Biodiesel was also analyzed by the above GC-MS method for fatty acid content described in section 2.2 under similar conditions. 1-mL of the prepared biodiesel was dissolved in 5-mL chloroform and stirred for 3-5 minutes with a magnetic stirrer on the hot plate for GC-MS analysis. 1-mL of this sample was then injected for analysis. Identification of methyl ester peaks was done by comparing the retention times between the samples and the standard compounds. Methyl esters (biodiesel) were quantified by comparing the peak areas between the samples and the standard compounds.

2.6 Optimization of Biodiesel Production from *J. curcas* oil

The described method in section 2.3 was done using different methanol to oil ratio for the aim of investigating the maximum yield at different ratios. The methanol to ratio was investigated at 3:1 and 5:1 for optimization of transesterification reaction for biodiesel production. The optimal value was determined by keeping all other parameters constant.

III. RESULTS AND DISCUSSION

3.1 Catalyst Screening

$CaO\text{-}Al_2O_3$ nano catalyst was investigated as a substitute for the homogenous and heterogonous catalysts used in conventional transesterification process. Furthermore, the amount of catalyst used and soap formation reaction was carefully observed.

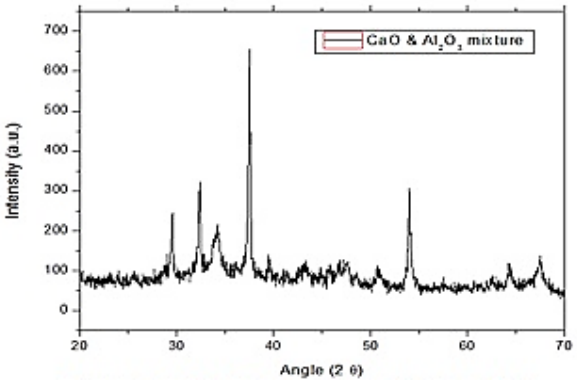

FIGURE 3: XRD SPECTRA OF NANOCATALYST

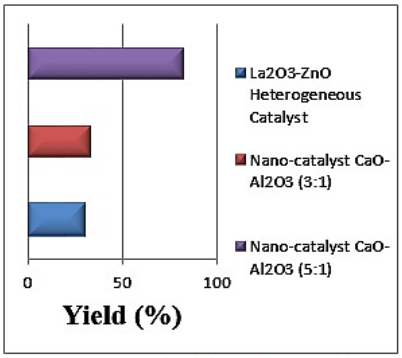

FIGURE 4: COMPOSITION OF CATALYST

3.1.1 XRD Results

Table 3.1 shows XRD data for synthesized nanoparticles of $CaO\text{-}Al_2O_3$. Diffraction peaks at different angles i.e. 20.1, 20.4, 20.5, 20.6, 20.7, 20.8, 21.0, 21.1., 21.4, 21.5, 21.8, 21.9, 22.2, 29.5, 32.3, 34.1, 37.5 and 54.1 degrees were observed in the spectrum of the XRD pattern of $CaO\text{-}Al_2O_3$ nanoparticles. XRD pattern of $CaO\text{-}Al_2O_3$ suggests that the nano catalyst has a BCC structure.XRD data was also used to determine particle size using the Scherrer equation. The particle size of $CaO\text{-}Al_2O_3$ nanoparticles calculated from the above mentioned equation was found out to be 29.9 nm.

3.1.2 Comparison of Conventional Heterogeneous Catalyst with Nano catalyst for Jatropha Oil Transesterification

Yield of biodiesel from Jatropha oil by conventional heterogeneous catalyst and nano catalyst is compared. La_2O_3-ZnO was used as a solid heterogeneous catalyst at 6:1 methanol to oil molar ratio, 300 rpm stirring speed, 60°C temperature for 3 hours (Chew, and Bhatia, 2008). In this experiment $CaO\text{-}Al_2O_3$ was used as a nano catalyst at 3:1 and 5:1 methanol to oil molar ratio, 600 rpm stirring speed, 100°C temperature for 3 hours.

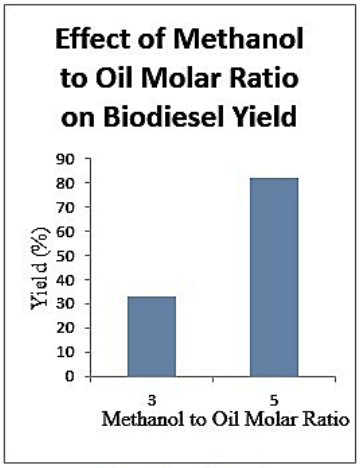

FIGURE 5: EFFECT OF METHANOL ON BIO-DIESEL YIELD

3.2 Effect of Methanol to Oil Molar Ratio

Methanol amount based on oil weight was varied as 3:1 and 5:1. It was observed that during 3:1 ratio, a very low yield i.e. 33 % was obtained. While in the 5:1 ratio experiment, a yield of 82.3 % was obtained. This sets 5:1 ratio as the optimum ratio for this reaction. As methanol to oil ratio was increased, the unreacted oil settled at the bottom was significantly decreased.

3.3 GC-MS Analysis

In order to properly analyze the content of the Jatropha oil biomass, the appropriate lipid and FAME standards were calibrated. The characteristic biomass lipid and FAME chromatograms produced via the appropriate analyses can be found below in Figure 6, 7, and 8. Gas chromatography was also used to determine the FAME content, which is the derived product of the triglycerides present in the biomass through transesterification using methanol.

3.3.1 Jatropha Oil Chromatogram

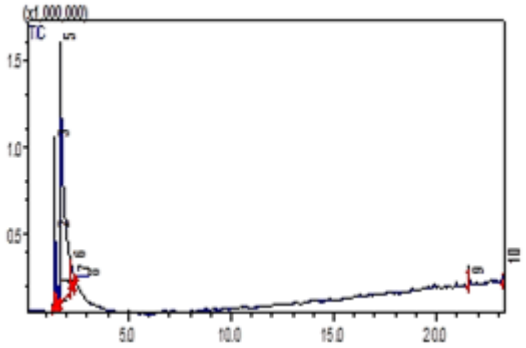

FIGURE 6: JATROPHA OIL GC-MS ANALYSIS

3.3.2 FAME Chromatogram

3.3.2.1 FAME Produced from 3:1 Methanol to Oil Ratio

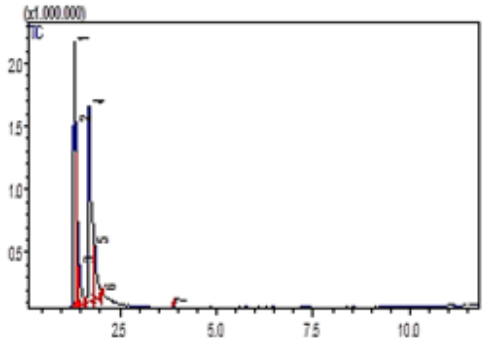

FIGURE 7: FAME PRODUCED FROM 3:1 RATIO

3.3.2.2 FAME Produced from 5:1 Methanol to Oil Ratio

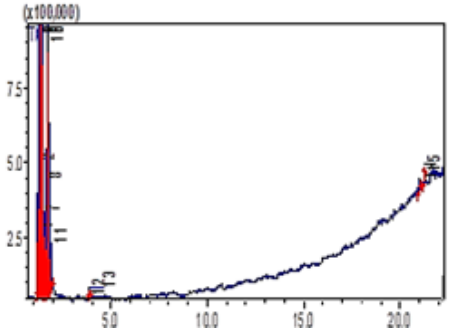

FIGURE 8: FAME PRODUCED FROM 5:1

Advantages of Jatropha oil are lower PM emission, higher compression ratio associated with higher injection pressure, higher diffusion combustion (Ivana, et al., 2012).

According to Table 1 the acid value of Jatropha oil varies from 0.92 mg catalyst/gto 28 mg catalyst /g (Ivana, et al., 2012). Further detail is also given in Table 1.

TABLE 1
COMPARISON OF JATROPHA OIL AND PETRO-DIESELS

S.No	Parameters	Petrodiesel	Jatropha Oil
1	Local Name	Diesel	Jatropha ratanjyo
2	Oil Colour	Yellow	Pale Yellow
3	Calorific Values **(KJ/Kg)**	43.35	39.77
4	Density **(Kg/m^3)**	815	880 – 918
5	Flash Point **(°C)**	45-60	137 – 240
6	Pour Point **(°C)**	– 6.70	–
7	Kinematic Viscosity at **(27°C)**	4.30	49.90
8	Carbon Residues **(%, W/W)**	0.03 – 0.1	0.20 – 0.44
9	Cetane Number	47.00	45 – 52.31
10	Botanical Name	–	*Jatropha curcas*
11	Oil Content of Jatropha	–	Seed wt% (20 – 60), Kernel Wt % (40 – 60)
12	Jatropha Kinematic viscosity at **40°C(mm^2/s)**	–	4.80
13	Jatropha Oil Cloud Point	–	2.7
14	Jatropha Oil as Food	–	Non–Edible
15	Jatropha Oil Oxidation Stability at **110°C,h**	–	2.3
16	Best Ratio of Alcoholysis	–	5:1 (Alcohol:Oil)
17	Reaction Temperature	–	(80 – 100) **°C**
18	Catalyst	–	Al_2O_3:CaO
19	Size of Nanocatalyst	–	29 nm

Jatropha plant is one of the most promising potential oil sources for biodiesel production in South-East Asia, Central and South America, India and Africa. Today, it is the major feedstock for production of biodiesel in developing countries like India, where the annual production is about 15,000 t (Ivana, et al., 2012). It can grow almost anywhere, on waste, sandy and saline soils, under different climatic conditions as well as under low or high rainfall and frost. Its cultivation is easy, without intensive care and minimal effort. Its healthy life cycle of 30–50 years eliminates the yearly replantation. Jatropha oil content varies depending on the types of species, but it is about40–60% in the seeds and 46–58% in the kernels. Jatropha has comparable properties to diesel, such as calorific value and Cetane number. It has a great potential as an alternative fuel since it does not require any modification of the engine (Jain, and Sharma, 2010). The serious problem with Jatropha oil is its toxicity to people and animals (Ivana, et al., 2012).

Also, in the methanolysis reactionof jatropha and tobacco oils (the molar ratio 5.6:1 and 10:1, respectively) a high ester yield of 98% was obtained in 1.5 h and 5 min (Ivana, et al., 2012).

Crude and refined, deodorized Jatropha oils containing the FFA15% and 1%, respectively, illustrate the significance of the type of feedstock for biodiesel production. The FFA content of the former oil is far beyond the acceptable limit of base catalyzed Transesterification (Ivana, et al., 2012).

A biodiesel synthesis by using heterogeneous (solid) catalysts is environmentally friendly because of a simple product separation and purification, which reduces the waste water amount. The additional benefit of the heterogeneous catalyst use is the possibility of their easy regeneration and reuse that make the biodiesel synthesis process cost-effective (Dossin, et al., 2006). However, a major disadvantage of using heterogeneous catalysts is a low reaction rate caused by diffusion limitations in the three-phase (oil–alcohol–catalyst) reaction mixture, as well as the complex catalyst preparation followed by a significant contribution to the environmental impact in some cases. Recent researches have been focused towards low cost and eco-friendly heterogeneous catalysts with a high catalytic activity. Generally, the preparation of this type catalyst involves washing, drying, crushing/powdering and calcinating at high temperatures (Ivana, et al., 2012).

The type of a heterogeneous catalyst for the biodiesel production from non-edible vegetable oils depends on the FFA content in the feedstock. The most often used non-edible oil in previous investigations of heterogeneously catalyzed alcoholysis is Jatropha oil (Table 1).

The alkyl esters yield obtained in heterogeneously catalyzed alcoholysis is also influenced by the applied reaction conditions. Compared to homogeneously catalyzed reaction, the initial methanol : oil ratio, the catalyst loading and the reaction temperature are higher and the reaction time is much longer in order to achieve comparable esters yields. Generally, the optimal reaction conditions providing the highest alkyl esters yield must be experimentally determined.

However, in most cases, the heterogeneous catalysts are recycled up to three times after which a significant decrease in the FAME yield is observed. Catalyst deactivation can be caused by three main reasons: product and by-product adsorption on the catalyst surface, the active sites leaching into the solution and the catalyst structure collapse (Deng, et al., 2011). In order to avoid the catalyst active sites blocking with organic residues or poisoning with atmospheric CO_2, researchers use different regeneration methods: washing with methanol and drying, washing with methanol and hexane followed by drying and calcinations at a desired temperature, drying and calcination (Vyas, et al., 2009) and recycling the catalyst with glycerol (Endalew, et al,. 2011).

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