STUDIES ON PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING SOLID WASTE AS CATALYST

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ABSTRACT

Production of Biodiesel from waste cooking oil is considered one of the interesting processes in recent years. In this paper, Catalyst was prepared from solid waste materials, fly ash, and used for the production of biodiesel from waste cooking oil. Physico-chemical characterization of the prepared catalyst was done using FTIR, XRD and SEM. Performance evaluation of prepared catalyst was done for the maximum yield of biodiesel by varying temperature, reactants molar ratio (methanol to WCO) and loading of catalyst were studied and analyzed. The maximum conversion of 47% WCO was obtained at 60 °C in 90 min for molar ration of 1:9 (WCO to methanol) at loading of catalyst is 1.5 % by weight of reaction mixture. The reaction was carried out till the equilibrium obtained.

KEYWORDS: Waste Cooking Oil, Flyash Catalyst, Biodiesel, FTIR, XRD, SEM, Transesterification Reaction

Received: Jun 09, 2020; **Accepted:** Jun 29, 2020; **Published:** Jul 31, 2020; **Paper Id.:** IJMPERDJUN2020549

1.0 INTRODUCTION

There are many issues associated with the application of the petroleum based fuels. Higher depletion rates of resources, increased cost for production, increased pollution problems are some of them. All these features are motivating the technologists to search for the alternative renewable fuels [1]. On the other hand, huge quantities of animal fats and waste cooking oils (WCO) are abundantly available and managing of such fats and oils is a very significant challenge due to their disposal problems. The used vegetable oil, it is other way called as waste cooking oil, is one of the best cost-effective options to harvest biodiesel. Subsequently, one of the major concerns for the manufacture of biodiesel is the cost of feedstock; use of WCO considerably increases the economic feasibility of biodiesel manufacture [2]. Transesterification with a catalyst is the reaction of oil with an alcohol (ROH , $\text{R} = \text{CH}_3$ or C_2H_5 and etc.) and a catalyst to produce esters and glycerol [3]. Methanol is basically employed due to low cost, physical and chemical advantages such as polar and smallest chain alcohol. Transesterification can happen depending on the oil at different temperatures. On the other hand, a higher temperature apparently affects the reaction rate and ester's yield. The product of the transesterification reaction contains primarily of esters, glycerol, and traces of alcohol, catalyst, triglycerides, Diglycerides, and Monoglycerides [4]. Among the methods, transesterification is the best adoptable process, which is an organic process in which an ester is transformed into the alkoxy molecule. The chemical reaction is shown in Scheme (I).

Also, the preparation of catalysts of heterogeneous from waste materials has been becoming progressively more popular from the last two decades. Some of the most interesting resources are waste biomass from agriculture such as inedible oils, animal waste and Flyash [5]. Application of waste materials is highly advantageous in view of financial or conservation costs accompanying with their discarding. The problems involved with homogeneous catalysts such as removal of costly catalysts, separation of products, longer operational time will be rightly answered by heterogeneous catalysts. Unlike to homogeneous catalysts, solid heterogeneous catalysts have the advantages of ease of separation from the reaction mixture after the reaction completed and ease of regeneration of the material for reuse [6]. The main objective of present paper is to develop the heterogeneous catalysts from solid waste materials such as flyash and to study the performance of the heterogeneous catalyst towards the biodiesel synthesis from WCO.

2.0 MATERIALS AND METHODOLOGY

The catalyst is prepared from solid waste material such as fly ash obtained from Thermal Power Plant (NTPC). The materials were collected from where they were available at low cost or zero cost. The solvents and reagents used for the preparation of solid catalysts and for reaction studies were A. R. grade (99.9%). The solvents and reagents were procured from M/S Sd Fine- Chem Limited, Mumbai, India.

2.1. Method of Catalyst Preparation

Fly ash is a product of coal and contains fine particles. In modern coal based power plants, fly ash is usually prevented by electrostatic precipitators (ESP) or other particle filtration equipment like bag filters after the flue gases reach the chimneys. The composition of fly ash could differ significantly depending upon the source of the coal where it burned. Mostly, the fly ash includes considerable amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminum oxide (Al_2O_3), calcium oxide (CaO) and etc. Various methods were developed to prepare catalysts using fly ash. Wet impregnation method was adopted to prepare the solid catalyst from solid waste materials. In this, for 10 gm of fly ash dry sample, 10.2 mL of 1N aqueous solution of potassium nitrate is added slowly with constant manual stirring until the homogeneous mixture is attained. Then, the excess water is driven off using the rotary evaporator. After drying at 100°C till complete removal of water, the solid mixture is calcined at a temperature of 500 °C for 5 h in an ambient air flow. The obtained dry fly ash- KNO_3 catalyst powder was characterized by XRD, SEM and FTIR technics. The prepared fly ash- KNO_3 catalyst powder was directly used for the production of biodiesel from WCO. The high temperature furnace was used to prepare fly ash- KNO_3 catalyst. The high temperature furnace was shown in Figure (2). The fly ash powder used as received condition for synthesis the catalyst and after heat treatment condition (fly ash- KNO_3 catalyst) was shown in Figure(3).

Figure 2: High temperature furnace used to prepare fly ash catalysts.

Figure 3: The fly ash used for synthesis (a) as it is received condition and (b) After heat

2.2. Characterization of Catalysts

The primary objective of catalyst characterization is to study the relationship among physical and chemical properties as well as its activity. It is important for designing and a process optimization. The characterization is required and necessary to observe the variations in chemical and physical properties of a catalyst in the course of preparation, activation and reaction steps for well understanding and control of quality. The prepared catalyst is characterized by XRD, SEM and FTIR. The prepared samples were analyzed by a Siemens 500 X-ray powder diffractometer in a flat plane geometry with a source of Cu- $K\alpha$ of wavelength, 1.5406 Å. The XRD spectra were recorded in the region of 10–80 2θ in steps of 0.001 $^\circ$ with a counting time of 1s in each step. The specifications of the instruments for the XRD analysis are given in Table 1.

Table 1: Measurement Conditions

X-Ray tube of target	Cu- $K\alpha$
Voltage	40 KV
Current	30.0 mA
slits	
Divergence slit	1.0 $^\circ$
Scatter slit	10.0 $^\circ$
Receiving slit	0.3 mm
Scanning	$\theta - 2\theta$
Scan range	10.0-80.0 $^\circ$
Scan mode	continuous scan
Scan speed	2.0 degree/min
sample pitch	0.02degree
Present time	0.6 sec

The powder XRD patterns of fly ash-KNO₃ catalyst were presented in the Figure 4. The compound exhibited the characteristic peaks of crystalline phases such as silica (SiO₂), calcium carbonate (CaCO₃), alumina (Al₂O₃) and iron oxide (Fe₂O₃). The predominant phase was quartz (SiO₂) with main peak at 23.16 $^\circ$ (2θ) and other peaks of CaCO₃, Al₂O₃ and Fe₂O₃ were identified as shown in the Figure 4. From the XRD result of fly ash-KNO₃ catalysts, it has the crystalline phases of quartz, magnetite and mullite. The hematite peak was not found due to the high concentration of magnetite.

Figure 4: XRD graph of Fly ash-KNO₃ Catalyst.

2.3. SEM Analysis

SEM is useful in obtaining morphology of the unknown components. The morphology of the fly ash-KNO₃, egg shell and sodium bentonite catalysts synthesized in the present work was examined by using a Hitachi X-650 scanning electron microscope (SEM) analyzer equipped with a CDU lead detector at 25 kV. The prepared samples were placed on aluminum pegs and coated with a gold thin film to allow them conductive. The SEM scans with a focused electron beam onto a surface to produce an image. The electrons from the beam interact with the prepared sample, generating a number of signals that can be used to attain images about the surface morphology. The SEM can produce three-dimensional images. The resolution is 0.2 nm which is 1000 times more than a light microscope. A typical SEM photograph of fly ash-KNO₃ catalyst is shown in the Figures 5 and 6. It shows the irregular morphology of fly ash-KNO₃. It provides three dimensional data on an atomic or near atomic scale for varying resolutions of 500, 100, 50 and 10 μ m.

Figure 5: SEM photographs of fly ash-KNO₃ catalyst with 500 and 100 μ m resolutions.

Figure 6: SEM photographs of fly ash-KNO₃ catalyst with 50 and 10 μ m resolutions.

2.4. Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR was used to study the changes in a material and also give data about the functional of a sample. It requires practically sample preparation with potassium bromide as a pellet. However, around 15 mg of the prepared catalysts sample is employed in the attenuated total reflectance (ATR) sample holder of a Perkin Elmer Spectrum 100 FT-IR spectrometer. The samples were recorded in the range of 4000-400 cm^{-1} , baseline was corrected and the spectra were smoothened. The FTIR bands from 900 to 1200 cm^{-1} were recognized as various types of Si-O and Si-O-Si stretching vibrations. The other bands between 450 and 900 cm^{-1} in the spectra of fly ash-KNO₃ were gave the typical Si-O and Si-

O–Al bending modes. The FTIR patterns of fly ash-KNO₃ catalyst is shown in Figure 7.

Figure 7: FT-IR patterns of fly ash-KNO₃ catalyst.

3.0 EXPERIMENTAL

The prepared heterogeneous catalyst is used for the production of biodiesel from WCO. It has a series of three sequential reversible reactions where triglycerides (TGs) are converted to diglycerides (DGs) and DGs are converted to monoglycerides (MGs) and MGs are converted to glycerol. In each step an ester is formed and thus three ester molecules are generated from one molecule of TG. At the initial stage of the reaction, there is a need of vigorous mixing of oil. So, the oil and the methanol get uniformly mixed. However, as the process results the formation of the product, slight mixing is required to facilitate the settling down of glycerol, so that reactions can continue in the upper layer of methanol and oil. The stoichiometry of transesterification of triglyceride (WCO) with methanol was shown in Scheme (I). The stoichiometric relation between the oil and the increase there suitable to The transesterification reaction is accelerated by a catalyst. Various types of catalysts including homogeneous (such as HCl, H₂SO₄) [7] or heterogeneous catalysts (metal based catalysts like Zeolite supported alumina) are employed for the process. The advantages of heterogeneous catalysts like ease of separation of products attracting the researchers to go with heterogeneous catalysis. As the reaction is reversible in nature excess alcohol is used to shift the reaction towards the products. Flyash catalytic performance is studied in synthesis of biodiesel from WCO. All the experiments were performed at atmospheric pressure and the effect of several variables were studied on the conversion of WCO to biodiesel. The different parameters and their range used in the experiments were given in Table 2.

Table 2: List of Different Parameters and Their Range in the Experiments

Parameters	Range
Temperature	40, 50 and 60 °C
Mole Ratio (Alcohol to WCO)	6:1, 9:1 and 12:1
Catalyst Loading (% of reaction mixture weight)	0.5, 1.0 and 1.5
Rotational Speed	800 rpm

3.1. Experimental Setup

A magnetic stirrer assembled with heating mantle (make REMI) was used to carry out the reaction. A one liter three necked round bottom flask was used as reactor which was equipped with a reflux condenser of water-cooling at the center neck. One neck of the flask was used as thermo well for a thermometer and the other neck is closed with a dummy cap through which reactants to be fed and mid reaction samples were collected for analysis. The entire apparatus was placed in an oil bath to maintain the reaction temperatures with ± 2 °C accuracy. The experimental system was shown in Figure 8.

In a usual run, certain amount of WCO and calculated amounts of catalyst taken into the RB flask. The whole contents were heated up to required temperature gradually. Room temperature water supply was arranged across the reflux

condenser to arrest the escaping of vapors which were formed during the reaction. Then, after attaining the pre specified temperature, specified amount of methanol was introduced to the flask and the instant was read as zero time. The entire process was carried out at ambient pressure. For every 15 min of time interval, the stirrer was switched off and the mixture were permitted to settle for 2-3 min. After settling the reaction mixture, around 5 mL of reaction mixture from top layer was collected carefully using a pipette so that neither bottom layer nor catalyst particles are present in the sample. The sample was transferred to an ice cold chamber and for that sample 5 mL of isopropyl alcohol was added and analysis was carried out immediately. The process was continued for 90 min and every 15 min sample was collected and analyzed immediately. The composition of WCO was given in Table 3.

Figure 8: Experimental setup for biodiesel synthesis from WCO

Figure 9: (a) Waste cooking oil, (b) Formation of two layers of the reaction mixture in the biodiesel production process

Figure 10: Samples of the reaction mixture collected at different time intervals. (15- 90 min)

Figure 8: Experimental setup for biodiesel synthesis from WCO Figure 9: (a) Waste cooking oil, (b) Formation of two layers of the reaction mixture in the biodiesel production process Figure 10: Samples of the reaction mixture collected at different time intervals. (15- 90 min)

Table 3: Composition of waste cooking oil

Name of the fatty acid	Molecular formula	(%) Composition
Stearic	C ₁₈ H ₃₆ O ₂	04.5
Oelic	C ₁₈ H ₃₄ O ₂	21.1
Linoleic	C ₁₈ H ₃₂ O ₂	66.2
Eicosanioc	C ₂₀ H ₄₀ O ₂	00.3
Others		07.9

After completion of the reaction, the reaction mixture was shifted to a separating funnel and permitted to separate in to the two layers. The top layer (biodiesel layer) was recovered and analyzed. The remaining methanol was removed by using rotary evaporation system. Data was collected to determine the conversion of WCO. The experiments were performed to study the effect of various parameters for example temperature, molar ratio and loading of a catalyst. Formation of two layers of the reaction mixture in the biodiesel production process was shown in Figure 9. The reaction mixture samples were collected at different time intervals was shown in Figure 10.

4.0 RESULTS AND DISCUSSIONS

Number of experiments was conducted for the reaction system of biodiesel production from WCO. The effect of the various parameters such as temperature, molar ratio of the reactants and catalyst loading were studied and were presented

in the following sections. The effect of the various parameters over the progress of reaction/conversion were studied, data collected and the results were analyzed.

4.1. Effect of Temperature

As the reaction rate constant is a function of a temperature, it is significant to study the effect of temperature on the formation of biodiesel from the WCO. In order to find the best temperature, the reaction was carried out at various molar ratios of methanol to oil at different temperatures, using three different catalysts. The temperature effect was studied at catalyst loading of 1.0 % and molar ratio of WCO to methanol is 1:9. As shown in Figure 13, the reaction rate was slow at lower temperatures and with increase in temperature from 40 to 60 °C, a resultant increase in the conversion of the WCO was observed. But at the temperatures of 70 °C and above, there is fractional decrease in the conversion of WCO. It may be due to the fact that the boiling point of methanol is around 65 °C and reaction above this temperature might cause the methanol to vaporize into gas phase leading to low conversion of WCO. In addition, higher temperatures would increase the risk of saponification. Thus, the highest reaction temperature was limited to 60 °C for the transesterification of WCO and methanol. The effect of temperature at molar ratio of WCO to methanol is 1:9, catalyst loading is 1.0 % based on weight percent of the solution mixture was shown in Figures 10 and 12.

Figure 11: Effect of temperature for the conversion of WCO with the catalyst fly ash-KNO₃ for mole ration= 9 catalyst loading=1 %

Figure 12: Comparative plot of maximum conversions of WCO with the temperature For the 1.5% fly ash-KNO₃ catalyst.

4.2. Effect of Molar Ratio of WCO to Methanol

One of the most significant factors that alter the yield of product is the molar ratio of methanol to WCO. This parameter is imperative for showing the catalyst performance. While the stoichiometric molar ratio of methanol to triglycerides for transesterification is 3:1, excess molar ratios are employed to increase the solubility and to improve the contact among the triglyceride and alcohol particles. Precisely, it has furthermore been evidenced that the use of excess alcohol is a good selection in increasing the reaction rate of the transesterification where heterogeneous catalysts are regarded.

The effect of the molar ratio of methanol to WCO, on the conversion of WCO was studied with the three catalysts and varying loading of a catalyst. Figures 13 to 15 represent the change in the percentage conversions of WCO at 0.5, 1.0 and 1.5 % catalyst loadings of fly ash-KNO₃. From Figures 13 to 15, it was observed that with increasing in the mole ratios of reactants, the conversion of WCO was also increasing. At higher loadings of the catalyst, the effect of mole ratio is more than that of lower loadings.

Figure 13: Effect of molar ratio for the conversion of WCO for 0.5% loading of fly ash-KNO₃ at 60°C.

Figure 14: Effect of molar ratio for the conversion of WCO for 1.5% catalyst loading of fly ash-KNO₃ at 60 °C.

Figure 15: Effect of molar ratio for the conversion of WCO for 1.0% loading of fly ash-KNO₃ at 60 °C.

4.3. Effect of Catalyst Loading

For the reaction, larger amounts of catalyst lead to higher yield of esters in a lesser reaction time. In the reaction, three amounts of catalyst loadings are tested i. e, 0.5, 1.0 and 1.5 % of total reaction mixture weight for the three catalysts. The observations are presented in the Figure16. From the figure, it was observed that with increase in catalyst loadings, the

conversions are increased for the three catalysts. For the 1.5 % catalyst loading of the three catalysts was resulted in maximum conversions of WCO. From the above study, it could be concluded that the fly ash – KNO₃ catalysts gave just 47 % conversion of the WCO respectively.

Figure 16: Effect of catalyst loading for the conversion of WCO with fly ash-KNO₃ catalyst at 60 °C and molar ratio of methanol to WCO is 9:1.

5.0 CONCLUSIONS

The production of the biodiesel from WCO with methanol was carried out with Flyash-KNO₃ catalyst in conventional batch reactor. The prepared Catalyst was characterized by FTIR, XRD and SEM. Performance of the prepared catalysts was evaluated by varying the temperature, molar ratios and catalyst loading for the production of biodiesel from WCO. The conversion of WCO increased with increasing the temperatures, molar ratio and catalyst loading. The maximum conversion of 47% WCO was obtained at temperature of 60°C, molar ratio of 9:1 (methanol to WCO) within 90 min at 1.5 % catalyst loading.

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