



Biodiesel production optimization from waste cooking oil using nano heterogeneous catalyst

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Abstract

Energy demand, specifically petroleum fuels, demand around the world is increasing rapidly and become scarcer and more expensive. New type of renewable energy sources has been forced to be investigate by scientific community. Due to greenhouse effect brought about by the growing usage of fossil energies and thus to increase the time over which fossil fuels will still be available. Biodiesel become more attractive because of its environmental benefits and it is obtained from renewable resources. Due to waste cooking oil availability in Egypt, the production of biodiesel interest is growing. This study discusses the preparation of nano catalyst from saw dust by physical and chemical activation and their characterizations, also its application as a heterogeneous catalyst for biodiesel production from waste cooking oil by transesterification with methanol to give the corresponding mono alkyl esters. The following variables effects on the yield of the biodiesel produced was studied. These variables are the reaction time (0.5–2 .5h), catalyst concentration (3–10wt %), temperature (27 “room temp.”–60 °C) and methanol : oil molar ratio (6:1– 14:1). As a result, it was found that the chemical activation catalyst is more effective than physical activation catalyst and the maximum percentage yield was obtained under the conditions of methanol: oil molar ratio of 8:1, catalyst (5%) and 50± 1 °C temperature for 1.5 hr .The yield of biodiesel was determined according to GC-MS. From the results it was clear that the produced biodiesel fuel by the nano catalyst prepared in this work was in the recommended standards range of biodiesel fuel.

Key words: biodiesel, heterogeneous catalyst, fuel emission , fuel properties, waste cooking oil, transesterification

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1. Introduction

Due to the depletion of the world's petroleum reserves and the increasing environmental concerns, there is a great demand for alternative sources of petroleum-based fuel, including diesel and gasoline fuels [1]. Today, the transportation sector worldwide is almost entirely dependent on petroleum-derived fuels. Around the world, there were about 806 million cars and light trucks on the road in 2007 [2]. These numbers are projected to increase to 1.3 billion by 2030 and to over 2 billion vehicles by 2050 [3]. The petroleum is a finite source for fuel that is rapidly becoming scarcer and more expensive [4]and is one of the main causes of anthropogenic carbon dioxide (CO₂) emissions to the atmosphere. One-fifth of global CO₂ emissions are created by the transport sector [5], which accounts for some 60% of global oil consumption [6]. Also, the presence of sulphur in

diesel fuel has limited its use extensively due to corrosion and environmental pollution. The scientific community was forced to investigate new types of renewable energy sources, mainly because of the greenhouse effect brought about by the growing use of fossil fuels and thus to increase the time over which fossil fuels will still be available [7]. Bio-fuels are alternative to petroleum-based transportation fuels which can help to reinforce energy security and reduce the emissions of both greenhouse gases (GHGs) and urban air pollutants. This current alternative diesel fuel can be termed as biodiesel [8] which is considered to be a possible substitute of conventional diesel. Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acid with a great number of advantages specifically it is biodegradable, non-toxic, renewable and has reduced emission of CO, SO₂ due to the absence of aromatics and sulphur, and also reduced volatile organic compounds and unburned

hydrocarbons as compared to conventional diesel [9,10]. Also it has higher cetane number and flash point greater than 423 K compared to 350 K for petroleum-based diesel fuel [11]. The use of biodiesel can extend the life of diesel engine because biodiesel has more lubricating properties than petro diesel [12, 13]. Numbers of methods are currently available and have been adopted for the production of biodiesel fuel such as direct use and blending of raw oils [14, 15], micro-emulsions [16], thermal cracking [17, 18], and transesterification [19]. The most commonly used method for converting oils to biodiesel is through the transesterification of animal fats or edible and non-edible oils. [20-22]. The catalyst presence is necessary to increase the reaction rate and the transesterification reaction yield. Catalysts mainly used can be classified according to its chemical presence in the transesterification reaction: homogeneous or heterogeneous catalysts. Currently, homogeneous catalysts applications dominate the biodiesel industry due to their simple usage and less time required for oil conversion [23,24]. People around the world use edible oils for cooking, after which the oil is discarded. The amount of heat and water increases the hydrolysis of triglycerides and the percent of free fatty acid (FFA) in the oil [25]. Due to high FFA content in low cost feedstocks, the alkali catalyzed transesterification reaction to produce biodiesel gives low biodiesel yield. To solve this problem, production of biodiesel by a two-step catalytic process has been recently developed. In the first step, a feedstock pretreatment is performed in which the free fatty acid content is reduced by the use of an acid catalyst such as sulfuric acid or ferric sulfate and in the second step called transesterification a heterogeneous catalyst is used [26]. This work aims to prepare a new nano heterogeneous catalyst from waste (saw dust) by two methods and use it to produce biodiesel by transesterification from waste cooking oil. Also, to study the different variables affecting the catalysis process, namely reaction time, methanol: oil molar ratio, temperature, percentage of catalyst to determine the optimum conditions for biodiesel production.

2. Material and Methods

2.1 Materials:

Saw dust (used as the heterogeneous nano catalyst) was collected from carpenters wastes. It was activated using two methods as follow:

2.1.1. Chemical activation:

It is screened to 300 micrometer particle size, washed with distilled water and dried. Then, the dried saw dust is mixed with hot sulfuric acid and stirred mechanically until the slurry mixture is completely solidified. The product is placed in the Muffle furnace until it becomes black. After cooling the mixture to room temperature, it washed with distilled water and KOH solution is added to the mixture until it completely covered it. The mixture is washed again by distilled water. The solid mixture is dried in a dryer and stored in a closed container for characterization.

2.1.2. Calcinations method (physical activation):

The saw dust screened to 300 micrometer particle size, washed with distilled water and dried. The sample is

calcinated at 600, 700, 800, 900 and 1000 °C in the Muffle furnace until it becomes completely black. The prepared catalyst samples are denoted as C600, C700, C800, C900 and C1000 (numbers 600-1000 represent the temperature of calcinations). All Chemicals used are A.R. reagent and the glassware are Pyrex washed with soap, rinsed thoroughly and then washed with deionized water.

- Methanol: Anhydrous methanol (Fluka CO., ASSAY > 99.8%) most commonly used due to low cost, availability and its physical and chemical advantages (polar and shortest chain alcohol).
- Anhydrous Na₂SO₄ (>99%) which is used for water removal from biodiesel produced.

2.2. Characterization methods

The two types of catalyst surface morphology was analyzed using different magnifications of scanning electron microscopy (SEM, JEOL JSM 6360LA). Surface structure of the solid materials was studied using Fourier Transform Infrared Spectroscopy (FTIR-8400S, Shimadzu-Japan). The FT-IR spectrum of catalysts was recorded between 500 and 4000 cm⁻¹ wave numbers. The pore structure development was analyzed using X-ray Diffract meter (XRD) [Bruker axis Advance powder diffractometer, Siemens X-ray gun, CuKα Bruker axis Diffrac PLUS software (0.3° step angle, 7s, step time, 2θ = 5°-80°, generator: 40kV at 40mA)]. It is generally accepted that is influenced by many factors, including inorganic impurities and the initial structure of the carbon precursor. Also, determination of particle size diameter was done by using "N5 Submicron particle size analyzing -Pekmon Coulter-USA" was measured

2.3 Feed Stock Preparation

At the beginning, the acid value of the waste cooking oil is determined. Then the esterification process is carried out using concentrated sulfuric acid to reduce the fatty acid content. It was found that the most recommended percent of sulfuric acid is 1 wt % of oil. Esterified oil is used to produce biodiesel by transesterification using the prepared heterogeneous catalyst.

2.4. Method

2.4.1. Waste Cooking-oil Transesterification

A 100 ml of esterified oil were heated in a 3-neck round bottom flask and stirred in a water bath equipped with a magnetic stirrer (at 600 rpm) at 60 °C. Catalyst in a of ratio (% by weight of oil) was added to alcohol (molar ratio to oil) in a separate flask and carefully shake. Mixture was added to the heated oil. Leaving the product in a separating funnel for 12 hours, the ester layer was separated, washed with hot water for 5-6 times and dried using anhydrous Na₂SO₄. The conversion was determined using gas chromatography and Mass Spectrometers [GC-MS] then the yield of biodiesel produced was calculated.

3. Results and Discussion

3.1. Characterization of the catalyst Produced

3.1.1. Particle size:

The particles size distribution of the prepared catalyst by physical activation were in the range 8.4 to 29.2 nm depending on the temperature. While the particles size prepared by chemical activation were 36 nm (Table 3.1). All the catalyst produced by physical or chemical activation were in nano range. the particle size produced by the physical activation at 700 °C was selected to be used during this study.

3.1.2. Surface morphology

For sawdust Treatment, different levels of magnification factor of SEM images were taken in order to show the major features of the fibers morphology after treatment. Figure (3:1-a, b) shows the SEM for untreated sawdust with magnification factor 10000 and 35000 respectively. Figure (3. 2- a,b,c,d) show the SEM for catalyst produced from sawdust by chemical activations with magnification factor 10000 and 35000 and by physical activations at 700 °C with magnification factor 10000 and 35000 respectively that show the total surface of treated fibers as flocculated particles. By increasing the magnification factor (from 10000 to 35000) as in Figures; the high surface roughness leading to increase the surface area was noticed.

3.1.3. FTIR Analysis

FTIR analysis permits spectrophotometric observation of treated Sawdust in the range 400- 4000 cm^{-1} , and a direct identification of the organic function on the surface. Treated Sawdust examination provides surface groups information that might have participated in the adsorption process and also indicates the surface site(s) on which adsorption can take place. In Figure 3.3, IR indicate the participation of the specific functional groups in adsorption interaction for chemical activation while Fig.3.4 indicates the participation of the specific functional groups in adsorption interaction for physical activation at 700 °C. Also, IR spectrum show that the most prominent peaks in the spectrum originate from OH vibrations (3300 - 3450 cm^{-1}), C-H asymmetric and symmetric stretching vibrations at (2935-2300 cm^{-1}), at (700- 1300) may be stretching of C-C group while at (400-700 cm^{-1}) the aromatic region related to C-O group.

3.1.4. X-ray Diffract meter (XRD)

Generally, sawdust surface has a relatively smooth structure with some pores and occasional crevices and also covered with silica agglomeration. Figures 3.5 and 3.6 can clearly indicates that chemical and physical activation resulted in a porous structure and the opening of these pores were on the surface of the catalyst respectively.

3.2. Biodiesel production:

3.2.1 Effect of Time

One of the most important factors affecting the conversion of biodiesel is the reaction time. Figure 3.7 shows the effect of time on the production of biodiesel. The reaction was carried out at temperature of $60 \pm 1^\circ\text{C}$, stirring speed of 600 rpm, methanol to oil molar ratio of 12:1 and 5 wt% of catalyst. Using the catalyst activated physically, the maximum conversion obtained is 65.5% while using chemically activated catalyst gives a maximum conversion of 90%. These results indicates that the yield of the biodiesel produced by these catalyst is more better than that different heterogeneous catalysts reported in the literature from waste cooking oil [27,28].

3.2.2. Effect of Catalyst Percentage

Transesterification can be carried using different types of catalyst. Figure 3.8 shows the effect of catalyst amounts (at $60 \pm 1^\circ\text{C}$ with stirring at 600 rpm and alcohol/oil molar ration (12:1) for 1.5 hrs) on the percentage yield of biodiesel. From Figure, it was found that an optimum amount of catalyst of 5% wt based on oil can be achieve maximum % yield of biodiesel of 65.5% using physical activated catalyst and 90% using chemical activated catalyst. The decrease of yield on increasing the catalyst beyond 5% (based on oil wt.) can be attributed to adsorption process on catalyst surface may be taken place.

3.2.3. Effect of Methanol/Oil Molar Ratio

The effect of alcohol/oil molar ratio (moles of alcohol/moles of oil; 6:1, 8:1, 10:1, 12:1 and 14:1) on the percentage yield of biodiesel was studied. Figure 3.9 indicates that the production of biodiesel increased with increasing the molar ratio to certain ratio (12:1) then decreased. Using physically activated catalyst, the % yield of biodiesel produced increased from 42.7 to 65.5% until 12:1 ratio then decreased to 60% when the methanol/oil molar ratio increase to (14:1), this may be attributed to increasing the amount of alcohol will drive the reaction to more products as expected. In case of using chemically activated catalyst, the % yield of biodiesel produced was relatively slightly changed. This may be due to the high activity of the catalyst prepared as shown by high yield of biodiesel produced, so the methanol/oil molar ratio (8:1) is considered the optimum for chemical activation catalyst. The present results show that the present catalysts are out perform heterogeneous catalysts reported in the literature for producing biodiesel from waste cooking oil [27,28].

4.2.4. Effect of Temperature

The temperature effect (temperature range : 27, 40, 50, 60 °C) on the % yield of biodiesel in presence of 5% catalyst at 600 rpm is shown in Figure 3.10. Transesterification reaction can take place at different temperatures depending on the properties of reactants. As shown in figure for physical activation catalyst, as the temperature increased, the yield of the biodiesel produced increased, so the recommended temperature is 60 °C but for chemical activation catalyst increasing temperature has slight effect on the yield of biodiesel produced, so the most economical temperature is 50 °C.



Waste cooking oil



Biodiesel produced

Figure 2.1 General transesterification reaction with methanol.

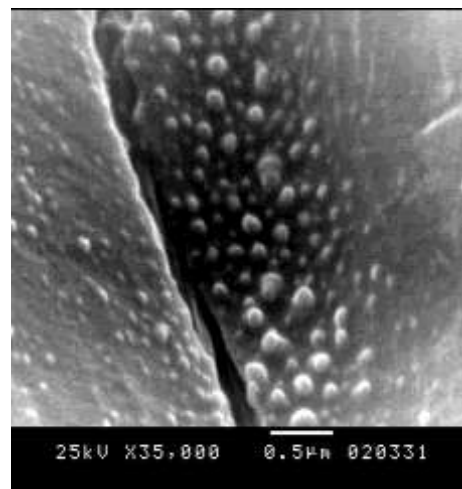
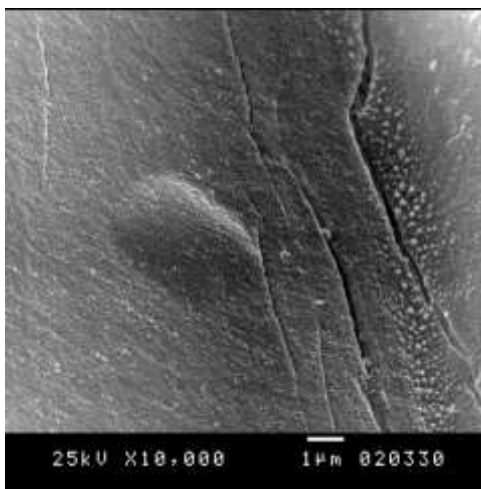


Figure 3-1,a, b: SEM for pure saw dust with magnification factor 10000 & 35000

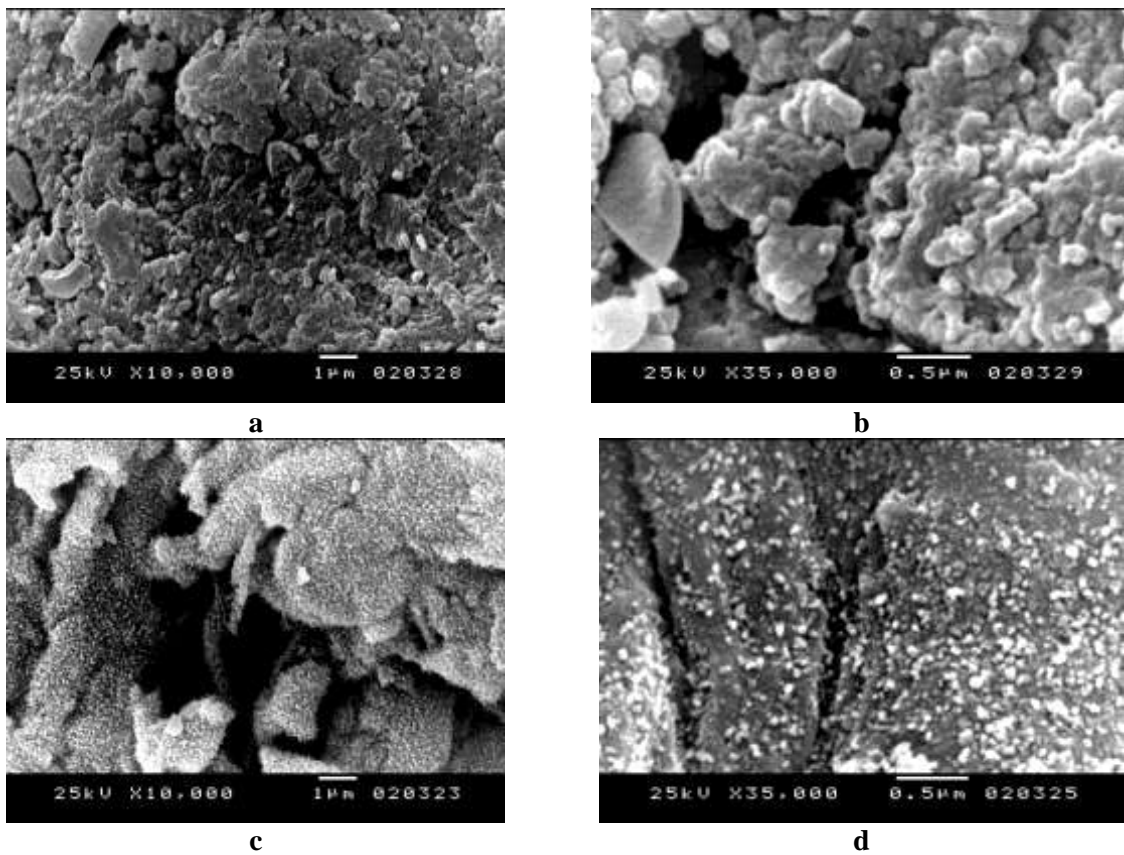


Figure 3-2, a, b : SEM for chemical activation with magnification factor 10000 & 35000

(c,d) SEM for physical activation with magnification factor 10000 & 35000

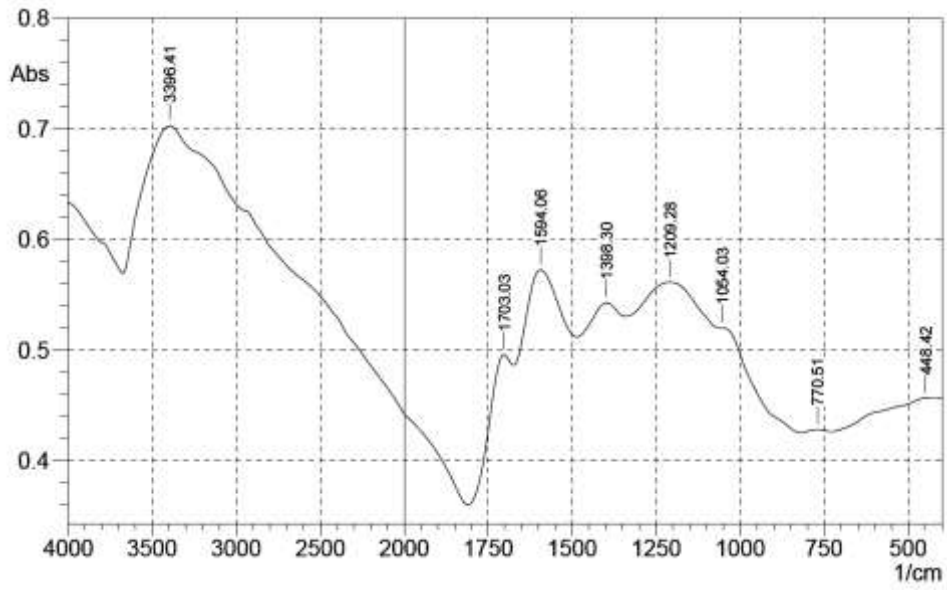


Figure 3.3: FTIR for catalyst produced from Sawdust by chemical activation.

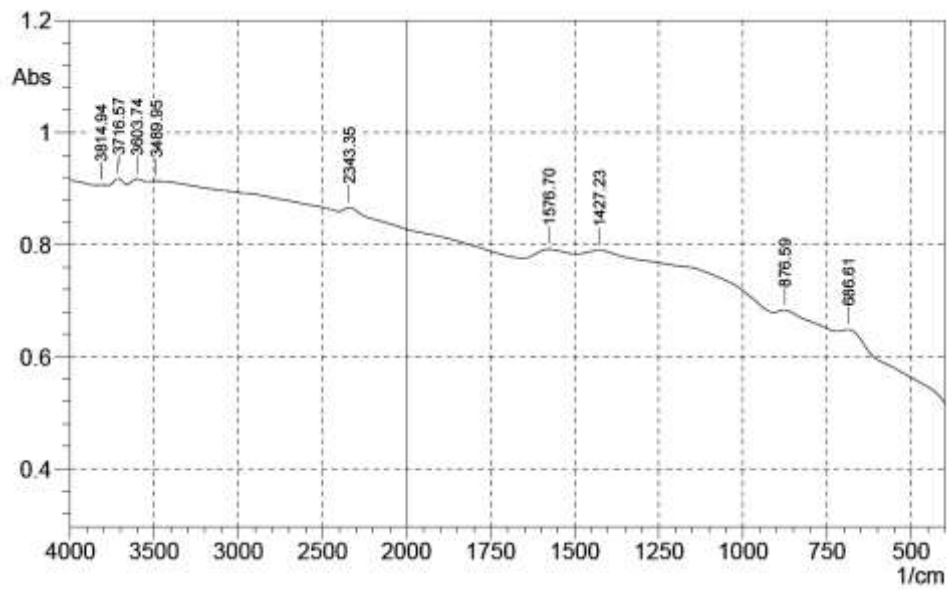


Figure 3.4: FTIR for catalyst produced from Sawdust by physical activation at 700°C.

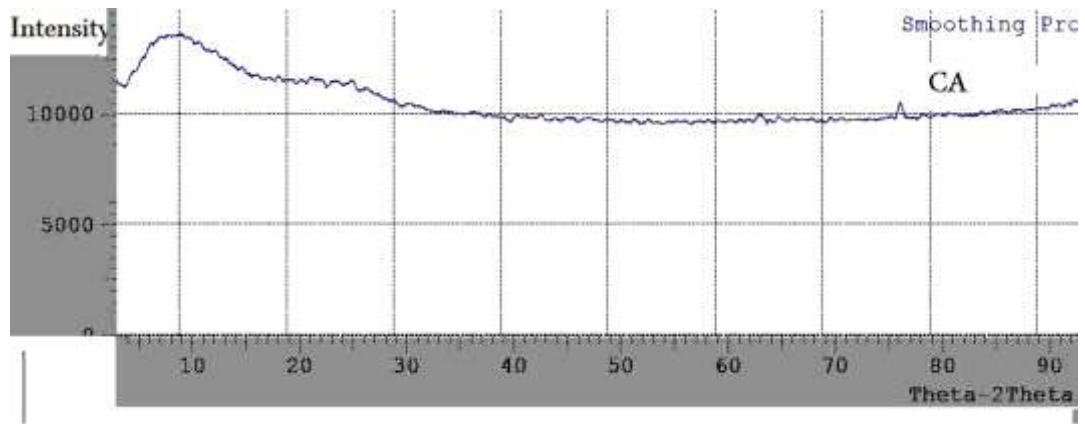


Figure 3.5: .X-ray Diffract-meter for catalyst produced from Sawdust by chemical activation.

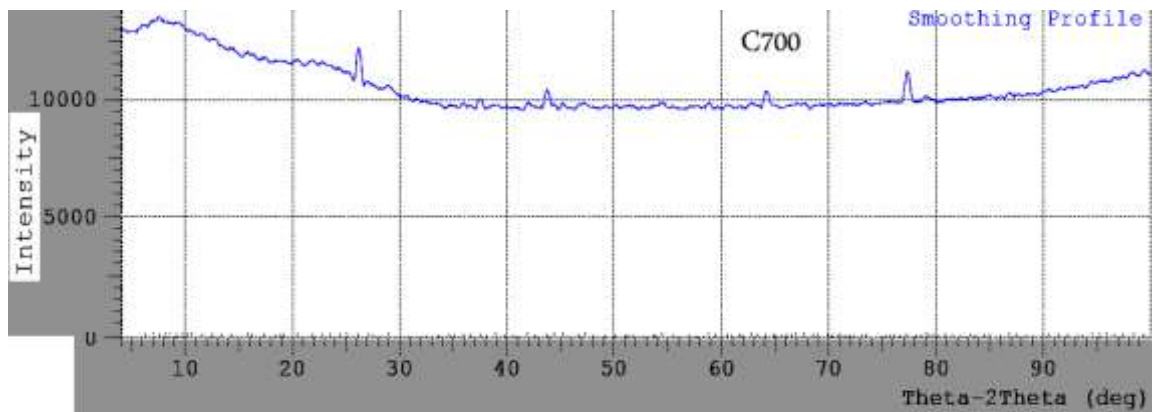


Figure 3.6: X-ray Diffract-meter for catalyst produced from Sawdust by physical activation at 700°C

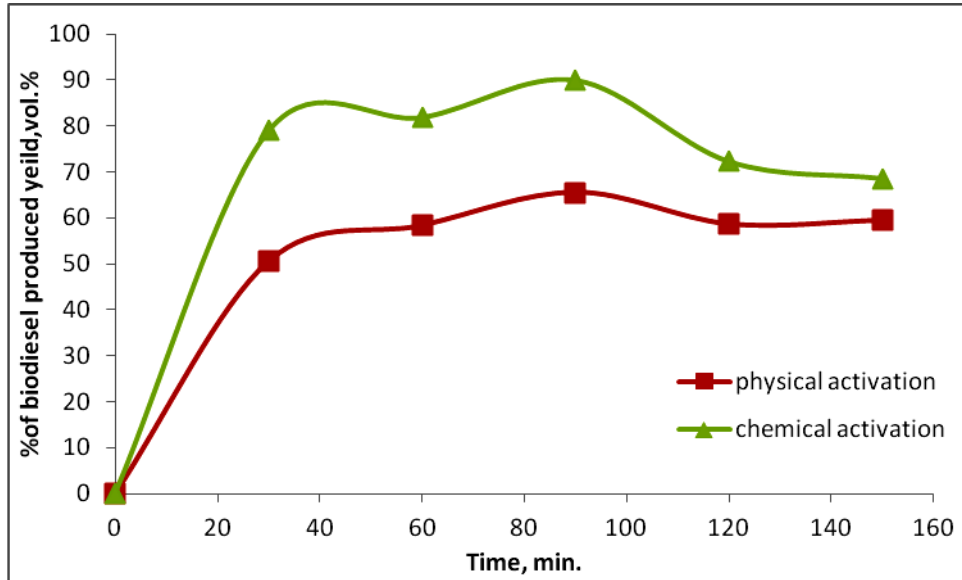


Figure 3.7 Effect of time on biodiesel yield at 60°C, 5% catalyst (by wt of oil), (12:1) methanol: oil molar ratio, 600rpm

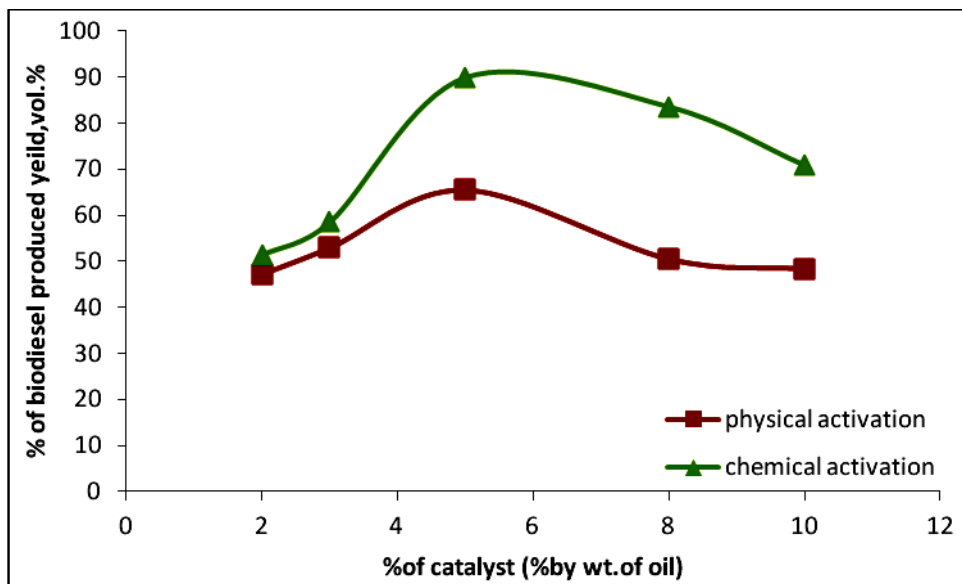


Figure 3.8 Effect of catalyst percentage on biodiesel yield at 60°C, 1.5hr, (12:1) methanol: oil molar ratio, 600rpm

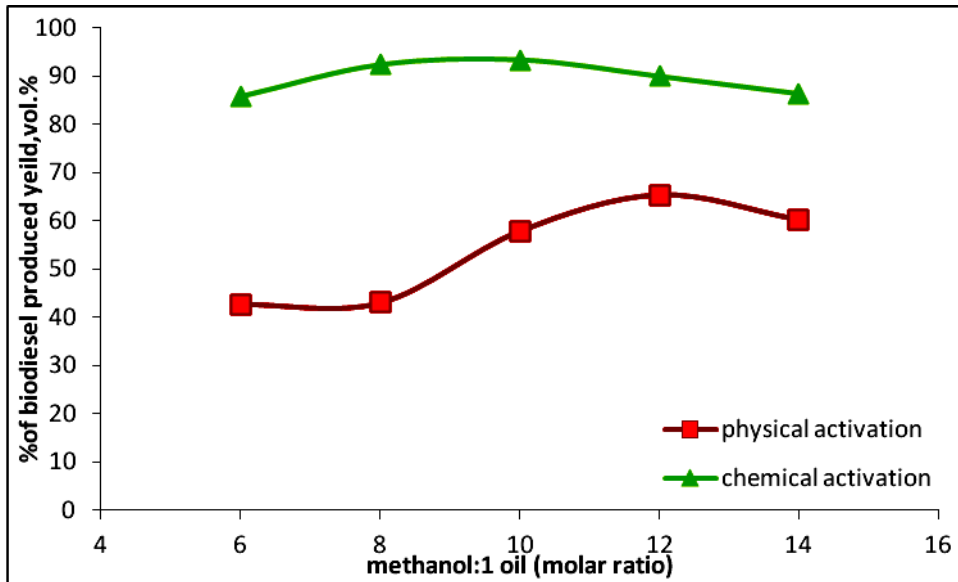


Figure 3.9 Effect of methanol: 1 oil (molar ratio) on biodiesel yield at 5% catalyst (by wt of oil) , 1.5hr, 60 C, 600rpm

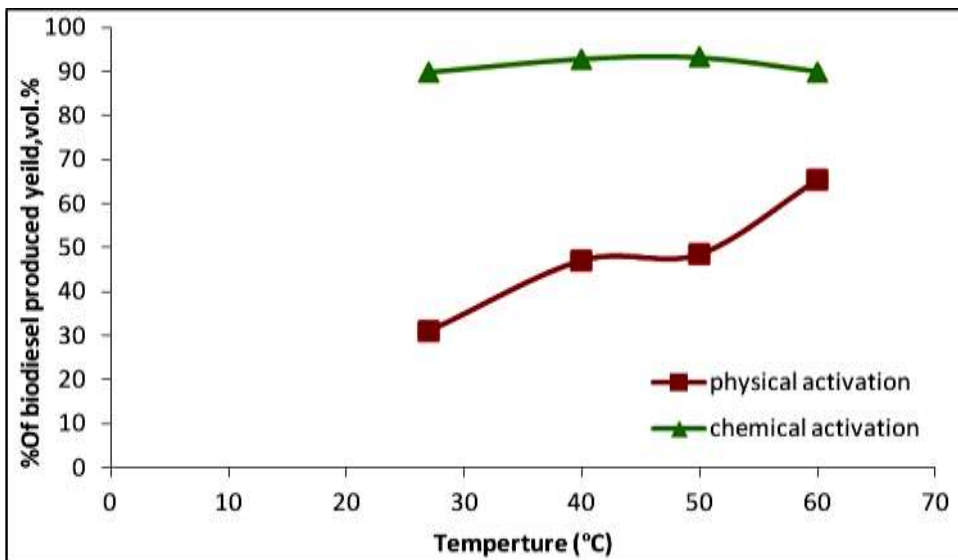


Figure 3.10 Effect of Temperature on biodiesel yield at 5% catalyst (by wt of oil), 1.5hr, (12:1) methanol: oil molar ratio, 600rpm.

So, it is clear that temperature effect on biodiesel produced is may be due to effect on reaction rate. Finally ,all the results have shown that the catalyst prepared from waste saw dust by chemical activation gave results better than basic and acid catalysts as shown in literature [Table 4.1 and 4.2]. The high yield in these tables is basically due to high temperature applied.

4. Conclusions

This study revealed that biodiesel produced from waste cooking oil can be used as an alternative fuel in conventional diesel engines. The results showed that the production of biodiesel by transesterification with methanol in presence of two types of nano heterogeneous catalyst produced from saw dust is affected by reaction time, methanol: oil molar ratio, catalyst percentage and temperature. The best yield percentage was obtained using a methanol: oil molar ratio of 8:1, as catalyst (5%) and 50 ± 1 °C temperature for 1.5 h at 600 rpm for chemical activation, while the best yield percentage was obtained using a methanol: oil molar ratio of 12:1, as catalyst (5%) and 60 ± 1 °C temperature for 1.5 h at 600 rpm for physical activation . The yield of biodiesel was determined according to GC-MS. Finally, the present results show that, the catalyst prepared from waste saw dust by chemical activation is superior to basic and acid catalysts. From the results it was clear that the waste cooking oil can be used as a source for production of biodiesel fuel by the nano heterogeneous catalyst.

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