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*RESEARCH ARTICLE*

# SYNTHESIS AND CHARACTERIZATIONS OF NEEDLE- SHAPED CUO NANOPARTICLES FOR BIODIESEL APPLICATION

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## Abstract

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Biodiesel is a green and clean burning alternative fuel for conventional fuels. This study compares the catalytic transesterification of coconut oil by using CuO nanocatalyst with the conventional base catalyst (NaOH). The needle-shaped CuO nanoparticles were synthesized by simple precipitation method. All the characterization studies (UV-Vis, FTIR, XRD, and FESEM with EDX) were proved the formation of CuO nanoparticles. The XRD study revealed the formation of CuO nanostructures with the monoclinic phase. The crystallite size of CuO was estimated to be 48 nm using Debye-Scherrer's formula. The surface morphology of the obtained CuO nanoparticles is needle-like in shape. The conversions of FAMEs were verified by using both FTIR and GCMS analysis. The investigation of producing biodiesel using GC-MS spectroscopy indicated that fatty acids were transformed into corresponding methyl esters. From this study, it has been concluded that CuO nanocatalyst could be a good promising catalyst for the green and eco-friendly production of biodiesel.



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## Introduction:-

It is an undeniable fact that recently so much of attention is drawn to the field of renewable energy as an alternative to the traditional energy sources [1]. This was necessitated and encouraged due to the issues like shortage of petroleum, hike in fuel price, greenhouse gas emissions and global warming [2-4]. Biodiesel is one of the promising options for the alternative renewable fuels that can be used in existing engines [5]. Adding to the benefits, it is biodegradable, environmentally friendly, non-toxic and has potential in reducing levels of pollutants [6-8].

Vegetable oils are becoming a promising source for the production of biodiesel. Among the available edible oils, coconut oil is considered to be one of the potential sources for the biodiesel production [9]. The transesterification reaction of oil and alcohol with a homogeneous catalyst is the common method for the production of biodiesel. [10-13]. The homogeneous catalysts have many limitations, such as requiring large amounts of water, difficulties in product separation and environmental pollution caused by the liquid wastes etc. [14]. But the heterogeneous catalysts based biodiesel preparation is considered to be a green and environmentally friendly method [15-17].

The focus on the development of new heterogeneous nanomaterials as a catalyst is a novel concept. It has been reported that the main advantage of nano-sized materials is its large surface area [18]. The Nanocatalysts have many



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advantages such as high catalytic activity, reusability, high resistance to saponification reaction and simpler in purification processes etc. [19, 20]. There have been very few studies on nano metal oxides catalysed transesterification to produce FAME (Fatty Acid Methyl Ester) [21-23]. Among the availing transition metal oxides, CuO is one of the potential p-type semiconductors and gains considerable attention due to its excellent optical, physical and magnetic properties [24-27].

This study compares the catalytic transesterification of coconut oil by using CuO nanocatalyst with the conventional base catalyst (NaOH). The CuO nanoparticles were synthesized by simple precipitation method. The characterization of CuO nanoparticles was studied using FTIR, UV-Vis spectroscopy, XRD, FESEM and EDX. The obtained biodiesel was examined with Gas Chromatography-Mass Spectrometry (GC-MS) and the infrared spectroscopy (FTIR).

## Materials and Methods:-

### Materials:-

All the reagents were of analytical grade and were used without further purification. Copper acetate [Cu $(CH_3COO)_2$] was obtained from Sigma Aldrich, Germany. Methanol (99.9% purity), ethanol and sodium hydroxide (NaOH) were obtained from Merck, Germany. Coconut oil was purchased from a local market. For the entire experiment, double distilled water was used.

### Preparation of CuO Nanocatalyst:-

CuO Nanocatalyst was synthesized by direct precipitation method using copper acetate and NaOH as precursors. In this work, the aqueous solution (0.2 M) of copper acetate was prepared with deionized water. The NaOH solution was slowly added into the copper acetate solution and mixed together by constant stirring for 30 minutes with the help of a magnetic stirrer. It was kept at room temperature for 4 hours for the completion of the reaction. A large amount of black precipitate was formed. The nanostructures were collected after centrifugation (4000 rpm). The obtained nanoparticles were washed with absolute ethanol and distilled water several times to remove the possible residual impurities. The particles were dried in an oven at 800C for 3 hours. After grinding, a dark brown nanopowder was obtained.

### Transesterification process:-

The transesterification reaction was performed in Teflon-lined stainless steel autoclave. The sample was loaded (1:4 oil to methanol, 0.75 wt % catalyst) into the autoclave and kept in an oven for 2 hrs. After the completion of the reaction, the mixture was cooled to room temperature and the biodiesel phase was separated. At the end of the experiment, the autoclave was cooled and the catalyst was separated from the reaction mixture by centrifugation and filtration.

## Results and Discussion:-

### Characterization of CuO nano catalyst:-

### UV-Vis analysis:-

In order to explore the optical properties of CuO nanoparticles, the optical absorption spectra were taken using the UV-Visible spectrophotometer. Fig.1 shows the obtained peak at 380 nm which is assigned to the surface plasmon resonance band of the CuO nanoparticles and is in coincidence with the literature values [28].

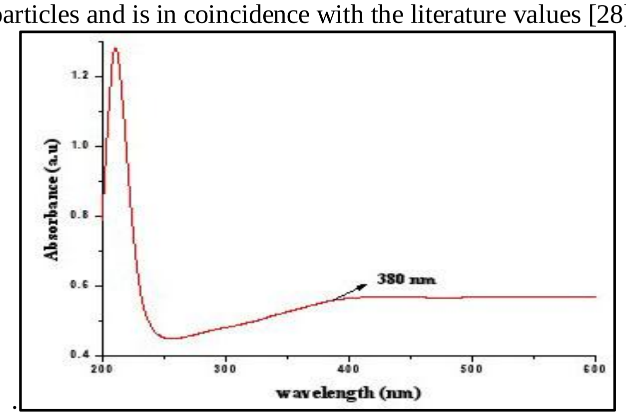



**Fig.1:-**UV-Vis analysis of CuO nanoparticles

**FTIR Analysis:-**

Fig. 2 shows the peak at 1606.75 $cm^{-1}$ which indicates the presence of primary amines and the C-H stretches of alkanes appearing at 1373.34 $cm^{-1}$. The three infrared absorption peaks reveal the vibrational modes of CuO nano structures. The major peaks were found with 503.82 $cm^{-1}$, 696.13 $cm^{-1}$ and 931.76 $cm^{-1}$ respectively. The vibration at the region of 503.82 $cm^{-1}$ has been attributed to CuO. The EDX analysis was used for further confirmation of the structure.

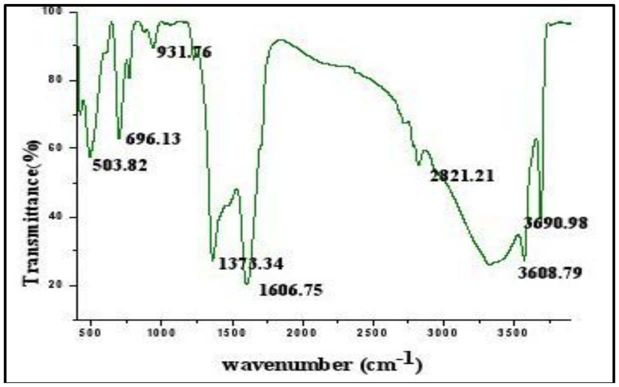



**Fig 2:-**FTIR pattern of CuO nanoparticles

**XRD analysis:-**

From fig.3 it can be clearly appreciated that all the peaks in the XRD patterns are consistent with the JCPDS data (89-5895) and the results were found to be in agreement with the reported diffraction pattern of CuO nanoparticles [29]. The major peaks located at $2\Theta$ = 32.47°, 35.58°, 38.75°, 48.81°, 53.27°, 58.24°, 61.47°, 66.23°, 68.05°, 75.05° and 82.92° are assigned to (110), (002), (111), $(\bar{2}02)$, (020), (127), $(\bar{1}13)$, (022), (220), $(\bar{2}22)$, $(\bar{3}13)$ plane orientation. The spectrum is identical to that of pure CuO, indicating the formation of single-phase CuO with monoclinic structure. The average crystallite size of the CuO nanoparticles calculated by Debye–Scherer's formula is 48 nm.

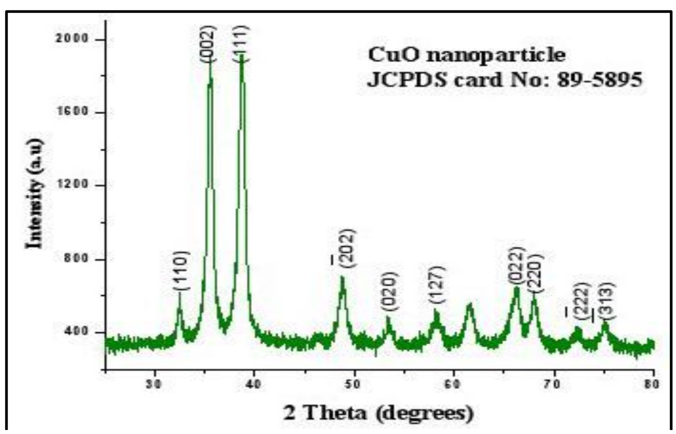



**Fig 3:-**XRD pattern of CuO nanoparticles

**FESEM with EDX Analysis:-**

Fig.4 (a) illustrates the surface morphology of the obtained CuO nanoparticles. The surface morphology of the obtained CuO nanoparticles is needle like in shape.

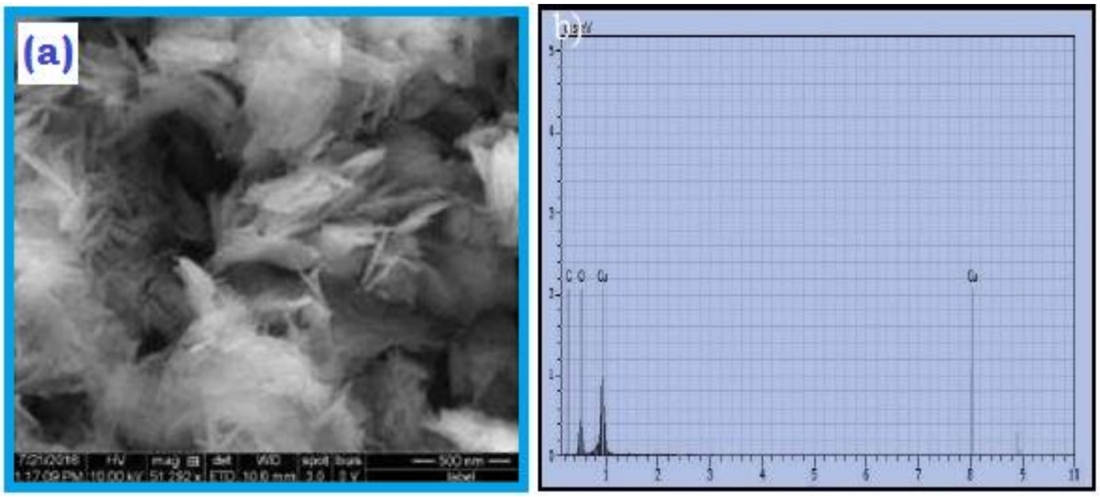



**Fig 4:-**FESEM & EDX images of CuO nanoparticles

The corresponding EDX spectrum is shown in fig.4 (b) which confirmed the elemental presence of Cu (75.92 %) and O (21.60 %) as the major constituent along with C (2.48 %) in fewer amounts.

**Analyses of transesterification products:-**

**Visual analysis:-**

Fig.5 displays the color of synthesized biodiesel with two different catalysts. It is noted that the NaOH (Fig. 5a) biodiesel sample is slightly brighter than that of nano catalyzed based one (Fig.5b). The advantages of using CuO nano catalysts include ease of separation and purification of the reaction products. So, it could be considered as a green and environmental friendly catalyst for biodiesel production.

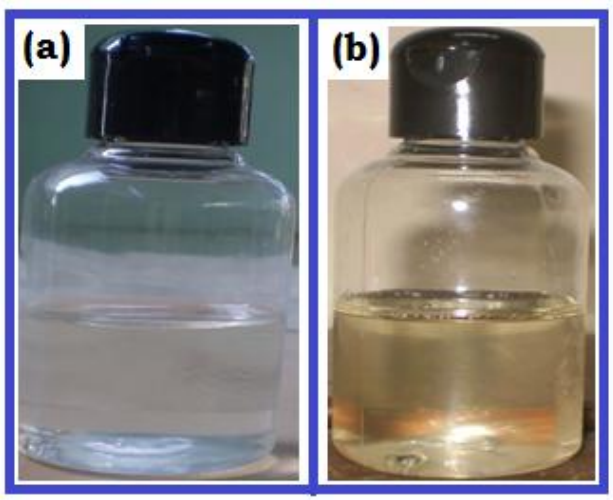



**Fig 5:-**Coconut oil biodiesel sample

**GC-MS Analysis:-**

The GC chromatogram of FAME of coconut oil using NaOH and CuO catalyst are visualized in Figs 6 & 7. The FAME conversion has calculated up to 79.52% and 86.56% by using two different catalysts NaOH and CuO respectively. The GC-MS result shows the chemical composition of FAMEs of coconut oil biodiesel in tables 1. In table 2, the GCMS results of produced FAME are compared with previous works.

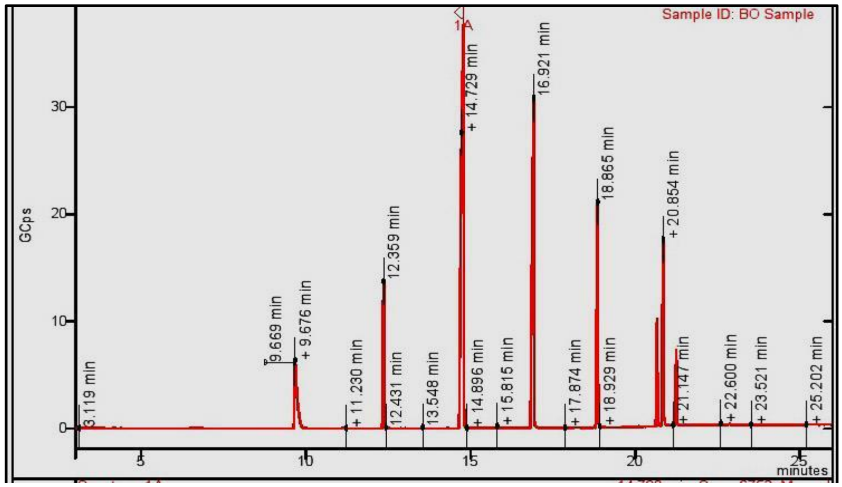



**Fig 6:-**GC Chromatogram of coconut oil using NaOH catalyst

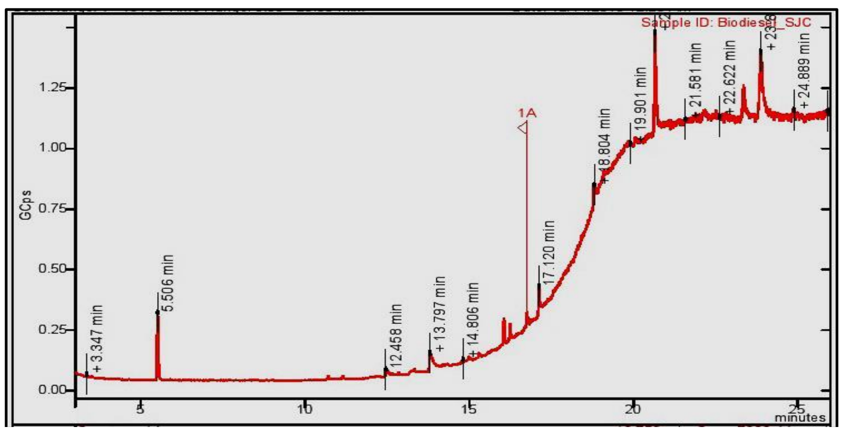



**Fig 7:-**GC Chromatogram of coconut oil using CuO catalyst

**Table 1:-** FAME composition of Coconut oil biodiesel

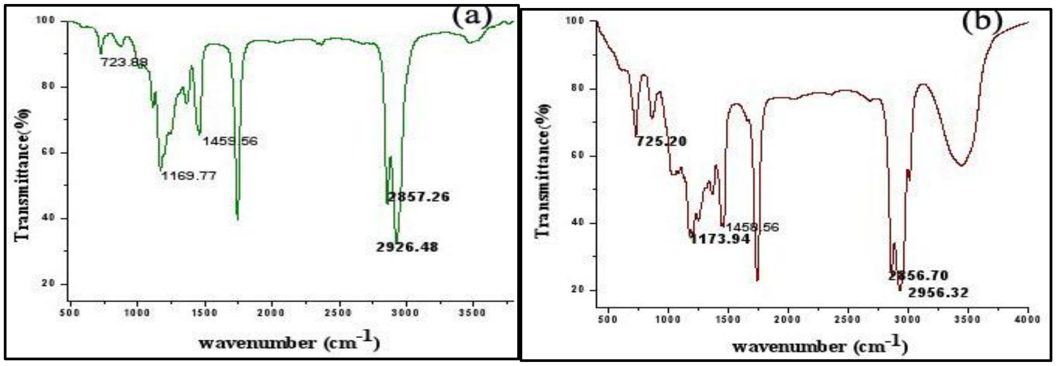
| FAMEs | Using NaOH catalyst | Using CuO nano catalyst |
|---|---|---|
| **Total FAME conversion (%)** | **79.521** | **86.574** |
| Others | 20.479 | 13.426 |

**Table 2:-** Comparison table of GCMS result with literature

| Catalyst | Oil/methanol | FAME content (%) |
|---|---|---|
| KOH | 1:7 | 82.5 [30] |
| $TiO2/SiO_2$ | 1:4 | 88.44 [31] |
| ZnO | 1:6 | 98.9 [32] |
| CaO | Excess | 91.5 – 95.7 [33] |
| NaOH | 1:3.5 | 79.52 (present work) |
| CuO nanoparticles | 1:3.5 | 86.56 (present work) |

**FTIR Analysis:-**

The FTIR spectrum of produced biodiesel from two different catalysts is shown in fig. 8. Biodiesel samples found in table 3 are very much similar to that of standard petro diesel and biodiesel samples [34]. The observed bands at 1459.56 $cm^{-1}$ and 1458.56 $cm^{-1}$ attribute to methyl group. The bands at 1169.77 $cm^{-1}$ and 1173.94 $cm^{-1}$ for ester group reveal the formation of biodiesel. The presence of two groups namely methyl ($CH_3$) and ester (C-O ester) in samples indicates that the transesterification of coconut oil occurred due to the addition of methanol and CuO nanoparticles [19].




**Figs8:-**a & b. FTIR spectra of NaOH and nano CuO catalysed biodiesel

**Table 3:-** Comparison table for FTIR spectrum peak area data

| Petro-diesel ($cm^{-1}$)[a] | Biodiesel standard ($cm^{-1}$)[a] | Biodiesel from coconut oil using NaOH catalyst ($cm^{-1}$) | Biodiesel from coconut oil using CuO nano catalyst ($cm^{-1}$) |
|---|---|---|---|
| 2915.86 | 2924.14 | 2926.48 | 2956.32 |
| 2849.66 | 2849.66 | 2857.26 | 2856.70 |
| 1451.03 | 1732.41 | 1459.56 | 1458.56 |
| 1376.55 | 1169.66 | 1169.77 | 1173.94 |
| - | 741.48 | 723.88 | 725.20 |

[a] Data from Hussain et al [34]

## Conclusion:-

The production of biodiesel from coconut oil was successfully completed by using CuO nano particles as a heterogeneous catalyst. The nano catalyst was characterized using different techniques which were confirming the formation of CuO nanoparticles. From the XRD, the average crystallite size of CuO was estimated to be 48 nm. The surface morphology of the obtained CuO nanoparticles is needle like in shape. From the GC-MS analysis, 86.56% and 79.52% of FAME components were calculated for CuO and NaOH catalysed biodiesel respectively. The presence of two groups, namely methyl ($CH_3$) and ester (C-O ester) were verified from FTIR analysis. This study recommends that the CuO nanocatalysts could be a promising option for the production of biodiesel with green and clean technology.

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