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Biodiesel production from waste cooking oil using green synthesized nanoFe_2O_3 and CuO impregnated nanoFe_3O_4

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Abstract : A comparative study of biodiesel production from waste cooking oil using green synthesized nano Fe_2O_3 and CuO impregnated nano Fe_3O_4 was carried out. Biodiesel is an alternative to fossil fuel which provides solution to many environmental problems. Nano Fe_2O_3 was green synthesized usingCalotropis gigantean milk as a reducing and gelling agent at 60°C.CuO impregnated Fe_3O_4 was synthesized using green synthesized Fe_2O_3 and Copper nitrate solution. The synthesized powders were characterized by powder XRD, FTIR and FESEM. The effects of reaction time (2 to 6 h),reaction temperature (60◦C), methanol/oil molar ratio (6 to 25), catalyst loading (3wt%), and reusability of catalyst (1 to 4 times) on the conversion to biodiesel were studied.
Keywords: Biodiesel, Nano Fe_2O_3,Waste Cooking Oil,Transesterification

Introduction

Recently, there is a growing need for the alternate liquid fuel to meet the huge demand of fossil fuels.Biodiesel an environment friendly renewable fuel possess similar properties as fossil fuels [1]. Biodiesel are produced by transesterification reaction of vegetable oil and animal fat with small chained alcohol (methanol or ethanol) in the presence of a catalyst [2]. The catalysts used for transesterification reaction are of two types i) Homogeneous and ii) Heterogeneous. Compare to homogeneous catalyst, heterogeneous catalyst are found to be more advantageous such as no by product formation, purity, reusability and can be easily separated from the medium[3].Various literature reports on heterogeneous catalyst for biodiesel synthesis are CaO[4], MgO[5], many alkaline earth metal oxides [6] etc. Among the heterogeneous catalyst used for transesterification reactions, Nano Fe_2O_3 and CuO impregnated nano Fe_3O_4 catalyst have not been explored. Nano $Fe_2O_3$are synthesized by various methods which includes hydrothermal, sol-gel, coprecipitation, sonochemical, polyol, solvothermal etc[7-12]. All the above methods are time consuming, cost effective, toxic chemicals, solvents etc. So there was a need for an alternative method which includes non-toxic, low cost, low temperature etc.

Recently, the utilization of Plant extracts for synthesizing nanometal oxides have drawn the attention of researchers due to its environment benign approach [13]. The CalotropisGigantea plant is a dry waste land plant available throughout India. It belongs to the Asclepiadanceae family. Leaf extracts of Calotropisgigantea have been employed for synthesizing ZnO[14], Fe_2O_3[15] , CuO [16]nanoparticles etc. To the best of our knowledge

Calotropis gigantean milk has been used for the first time as a gelling and stabilizing agent for the synthesis of Fe_2O_3 and Fe_3O_4 impregnated CuO nanoparticles.

Waste cooking oil causes environmental pollution and converting it into biodiesel protect environment and meet the energy shortage. Waste cooking oil was chosen as a feedstock for the synthesis of biodiesel due to its high quantity of free fatty acid compared to vegetable oils, low cost of biodiesel production. Recent reports on Fe based nanocatalyst for the synthesis of biodiesel from waste cooking oil are Ferric-Manganese Promoted Molybdenum Oxide / Zirconia,Lipase immobilized on magnetic nanoparticles,Fe_2O_3-MnO-SO_4^{2-} / ZrO_2, iron nanoparticles [17-20].

In the current work, we propose a rapid, nontoxic, green method of preparing Fe oxide based nanoparticles for converting waste cooking oil to biodiesel. The main aim of the project was to study the effect of 3% catalyst loading (nano Fe_2O_3 and Fe_3O_4 impregnate CuO), molar ratio of oil to methanol and the reusability of catalyst within 8hr reaction time on the biodiesel production.

Experimental

Materials

Ferric chloride hexa hydrate ($FeCl_3.6H_2O$, AR), ferrous chloride tetra-hydrate ($FeCl_2.4H_2O$, A R) and ammonia (NH_3) were purchased from SR Chemicals.

Synthesis of hematite nanoparticles

In the current work, hematite nanoparticles (α-Fe_2O_3) were synthesized as follows: 100ml of 1M $FeCl_2.4H_2O$ and 1M $FeCl_3.6H_2O$ (1/2 molar ratio) was mixed homogeneously in a 500 mL beaker and heated at 80℃ under mild stirring using magnetic stirrer under ambient condition. After 10 minutes, 10 mL of the Calotropis gigantean milk was added to the mixture, immediately the yellowish colour of the mixture changed to brown colour. After 5 minutes, the pH was adjusted to 9.8 by the addition of 10 mL of aqueous ammonia to the mixture for allowing the hematite formation**.**Then the mixture was allowed for heating at 80^0C for 3hrs and the particles were washed with distilled water, dried and analysed by XRD, FTIR and SEM.

Synthesis of CuO impregnated magnetite nanoparticles

The prepared α-Fe_2O_3 nanoparticles were immersed into 100ml of 1.6 M Cu $(NO_3)_2$ solution for 12 h at ambient temperature. After immersion, filtered and dried at 60ºC for 24 h and calcined in air for 30 min at 550ºC in a muffle oven to decompose the impregnated copper nitrate into insoluble copper oxide.

Pre-treatment of waste cooking oil

Waste cooking oil obtained from the restaurant was filtered with filter paper to remove cooking debris. Then the oil was heated at 110^0C to remove the water content.

Synthesis of Biodiesel

The catalyst testing was carried out by loading the various amount of catalyst (either α-Fe_2O_3 or CuO impregnated Fe_3O_4 nanoparticles) with waste vegetable oil(obtained from local hotels) and methanol in a 1000ml three-necked round bottom flask equipped with heating mantle, reflux condenser and digital thermometer. The temperature of the reaction was maintained at 65^oC. To prevent the methanol loss during a reaction, a water-cooledcondenser was used to condense the vapours and reflux it back into the reactor. The reaction was started by charging about 3 wt % of synthesized catalyst and the reaction was carried out for a period of 2-6hrs.The reaction samples were withdrawn periodically,and after filtration and separation of the residual methanolanalyzed by gas chromatography(Varian 3400) with an FID detector.

Results and Discussion

Physiochemical properties of hematite and CuO impregnated magnetite nanoparticles

XRD patterns of α-Fe_2O_3 and CuO impregnated Fe_3O_4 are shown in Fig.1 &2. All the diffraction peaks of α-Fe_2O_3 are indexed based on JCPDS No-89-0599. The Xray diffraction pattern depicted in Fig.2

corresponds to CuO impregnated Fe_3O_4(JCPDS No-82-1533).The impregnation of CuO by annealing the Fe_2O_3nanoparticles results in the interconversion of alpha Fe_2O_3 into Fe_3O_4 nanoparticles. The results are in agreement to the literature reports[21].

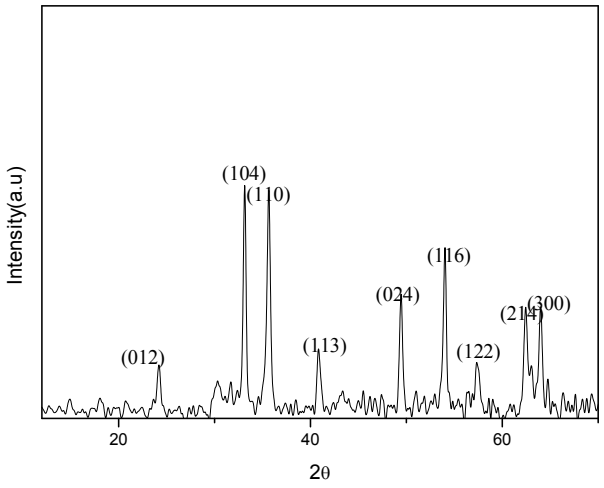


Fig.1. XRD pattern of alpha Fe_2O_3

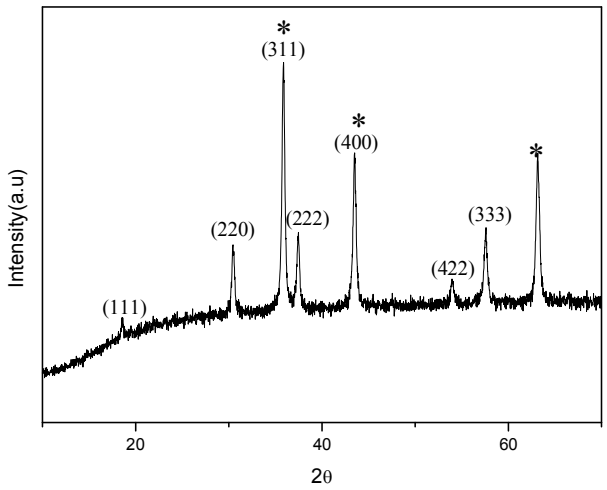


Fig.2. XRD pattern of Fe_3O_4 (inset * indicates CuO impregnation)

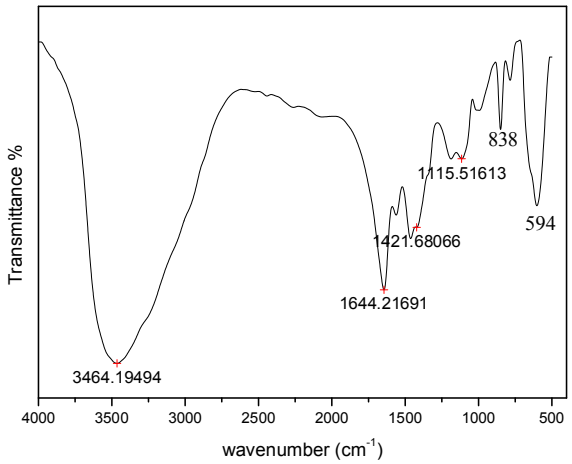


Fig.3. FT-IR pattern of α- Fe_2O_3

Fourier transform infrared (FT–IR) studies were performed to ascertain the metal–oxygen bonding of the synthesized hematite and CuO impregnated magnetite nanoparticles. The FT– IR spectra of as synthesized α-Fe_2O_3 sample are shown in figure 3. The α-Fe_2O_3 shows the absorption in the region 3464, 1644, 1421, 1115,838 and 594 cm^{-1}. The peaks at 594 cm–1 correspond to the metal–oxygen vibrational modes. The metal–oxygen frequencies observed for α-Fe_2O_3 nanoparticles are in accordance with reported literatures [21]. The peak at 3464 cm^{-1} and 1644 corresponds to hydration peaks.Fig.4 depicts the FT– IR spectra of as synthesizedCuO impregnated magnetite nanoparticle. The absorption band at 549.96 corresponds to the Fe-Obonds of Fe_3O_4 nanoparticles. The slight shift in absorbance is due to the impregnation of CuO nanoparticle.

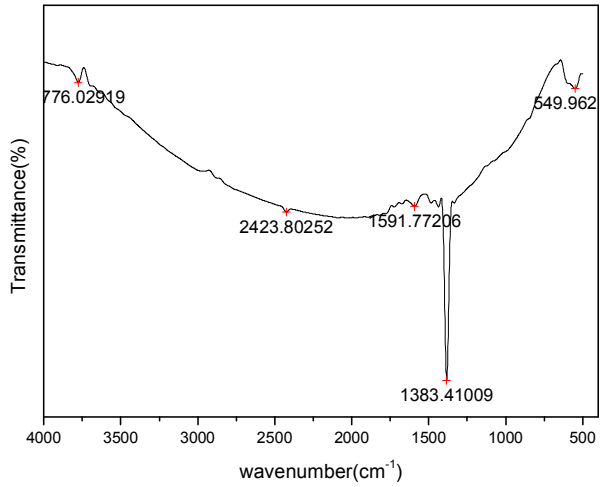
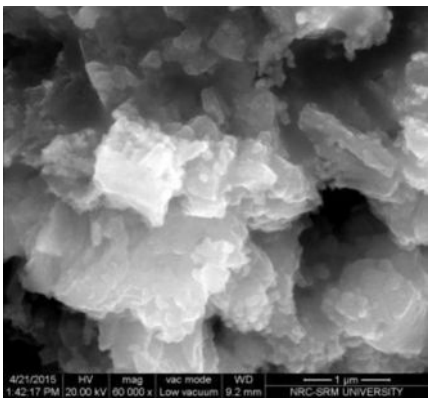


Fig.4.FT– IR spectraof CuO impregnated magnetite

Fig.5 shows the SEM image of alpha Fe_2O_3nanoparticles where productions of horizontal flakes of different sizes are observed with pores. The flakes are agglomerated horizontally and the average size of the flakes is around 100nm.Figure.6 shows SEM image of CuO impregnated Fe_3O_4 nanoparticles. The presence of CuO and annealing modifies the morphology of Fe_2O_3nanoflakes into elongated rectangular rods.



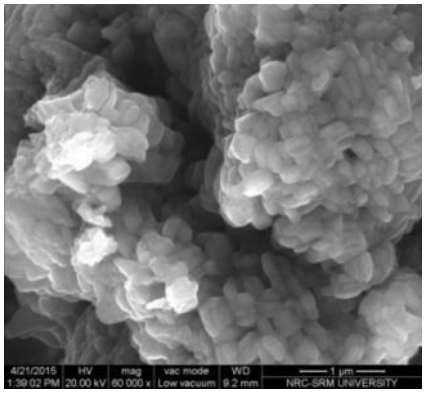


Fig.5 SEM image of α-Fe_2O_3nanoflakes **Fig.6 SEM image of CuO impregnated Fe_3O_4 nanoparticles**

Catalytic effect on biodiesel synthesis

Fatty acid profile of the biodiesel prepared from waste cooking oil using α-$Fe_2O$and CuO impregnated Fe_3O_4as catalystwas determined by GC-MS analysis. The individual peaks of the chromatogram were analysed and the fatty acids were identified using MS database(Fig.7&8). Relative percentages of esters were calculated and the results were shown in table1.

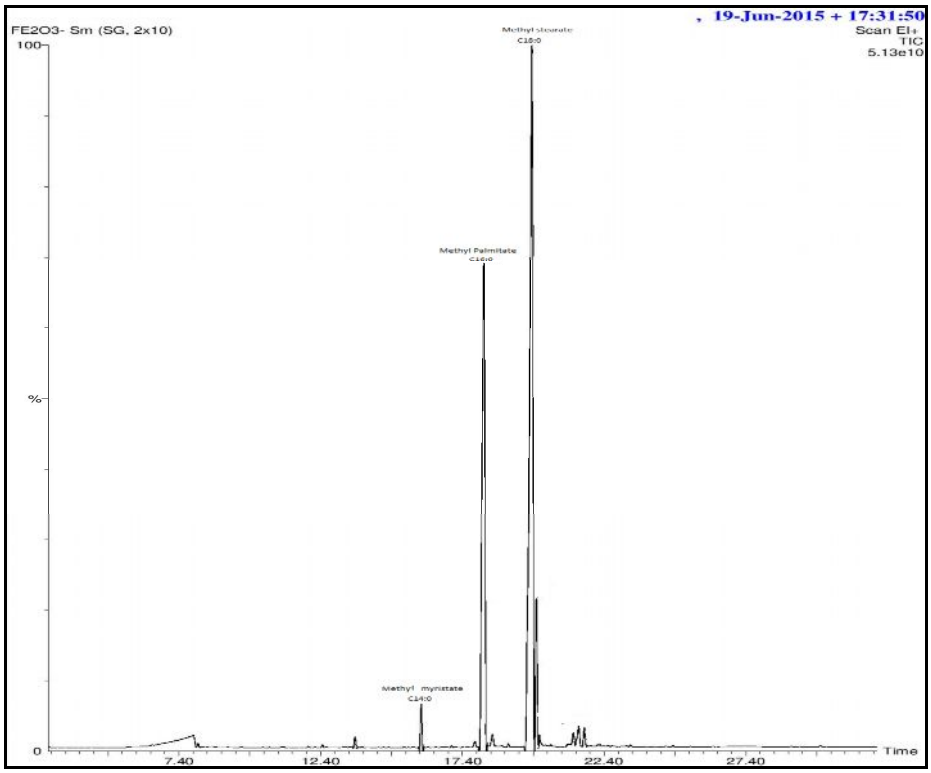


Fig.7 GC Chromatogram of Biodiesel produced using α-Fe_2O_3

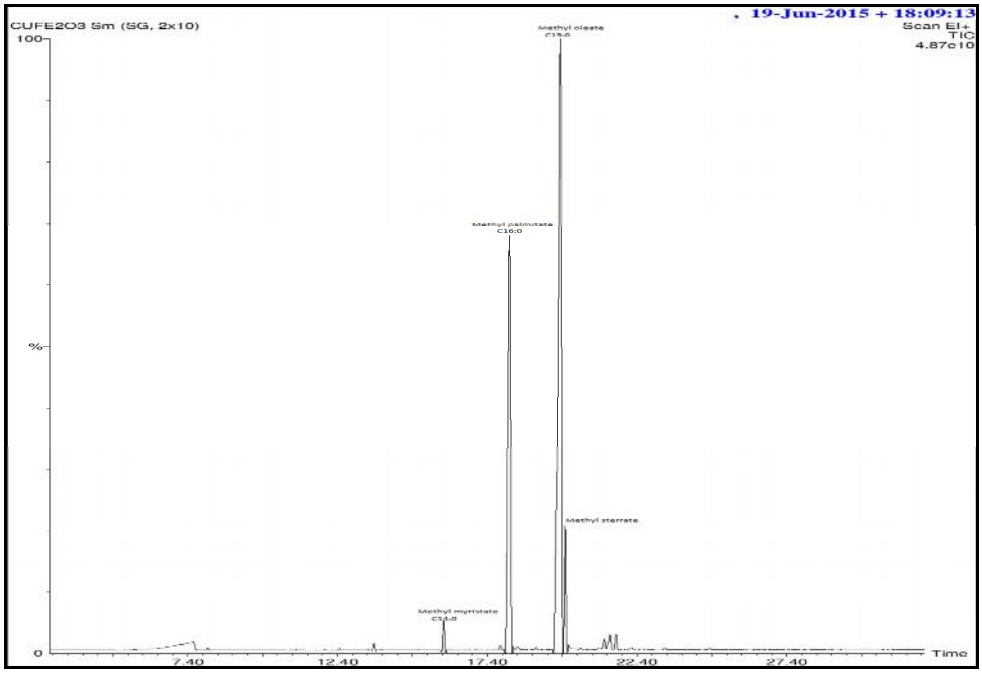


Fig.8 GC Chromatogram of Biodiesel produced using CuO impregnated Fe_3O_4 nanoparticles

Table1: Fatty acid Profile of biodiesel using catalyst

Retention Time	FAME	Wt %	Catalyst
15.9	Methyl myristate	1.5	α-Fe_2O_3
18.2	Methyl palmitate	33.1	
19.8	Methyl sterrate	54.4	
15.9	Methyl myristate	1.2	CuO impregnated Fe_3O_4
18.1	Methyl Palmitate	32.4	
19.8	Methyl oleate	51.6	
20.0	Methyl sterrate	5.0	

The molecular ion peaks of methyl palmitate, methyl oleate, methyl stearate and methylmyristateare observed at 270, 296, 298, and 242 respectively as expected. The optimum molar ratio of oil: methanol and reaction time was 1:15 and 6 hrs.The yield was found to be 90% and 88% for 1% CuO impregnated Fe_3O_4nanoparticlesand Fe_2O_3. The impregnation of 1% of CuO has increased the yield of Biodiesel. The amount of CuO has increase the yield because of basicity.

Conclusions

α-$Fe_2O_3$and CuO impregnated Fe_3O_4 nanoparticles were green synthesized. Biodiesel wasproduced from waste cooking oil and methanol using the green synthesized catalysts. The reaction conditions were optimized. Both the catalyst were efficient and reusable in the production of biodiesel of international standard. The yield of 90% was achieved when the reaction was carried out using CuO impregnated Fe_3O_4 nanoparticles content of 3%, with a molar ratio of methanol to oil of 15:1, a reaction temperature of 60 °C, and a reaction time of 6h.

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