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Fabrication of ZnO/Mg nanoparticles for catalytic pyrolysis Of *Phoenix dactylifera* seeds biomass

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In this study slow catalytic pyrolysis of *Phoenix dactylifera*(date palm seeds) was investigated in fixed bed reactor in the presence of doped ZnO/MgOnanoparticles. These NPs were prepared by using homogenous precipitation method. The effect of catalytic dosage of doped ZnO/MgO and ZSM-5 was studied on the conversion of biomass into pyrolysis products. By using doped ZnO/MgO the production of bio oil was increased, further increasing reduced bio oil yield. ZSM-5 caused slight increase in the yield of bio oil. The yields of bio char and syn-gas were also affected by variable dosage of catalyst.

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1. Introduction

Nanotechnology is playing tremendous role in many fields around the world, especially in the fields of science and engineering, its contribution is impeccable[1].NPs are extensively used in an extensive variety of probable purposes in pharmaceuticals, powder and paint, production of energies, manufacturing of eco-friendly products and provide healthcare facilities [2]. Among a number of energy sources, biomass is considered as a foremost source of energy for human beings. It is expected that biomass produces around 10– 14% total energy supply of the world[3, 4]. The term “Biomass” is employed for organic material (non-fossilized and eco-friendly)obtained from animals, plants, and microbes [5]. Biomass is taken as limitless and workable energy source[6]. Sources of biomass include sanitary solid waste, garbage, woody wastes, crops and their wastes, animal waste, and under water plants along with algae [7-9]. Being nonrenewable energy sources, fossil fuels such as coal, coke and natural gas will be exhausted; hence, they cannot be preferred over biomass. Moreover, using biomass instead of fossil fuels in energy generation is a cost effective process and more efficient to reduce the amount of CO_2 emitted in the atmosphere. In the process of pyrolysis, organic components in biomass are thermally decomposed [10]. In this process, breakdown of long chains of C, H and O containing compounds in biomass, occurs and they are converted into small molecules in the form of syngas, condensed vapors (e.g. bio-oils) and char under pyrolysis reaction conditions. Recently, various type of catalysts are used to improve the rate and efficiency of pyrolysis reaction, by breaking compounds having high molecular weight and converting them into hydrocarbon products having low molecular weight[11]. This technique is called as catalytic pyrolysis. In comparison, zeolites and metal oxide catalysts are employed to produce exceedingly homogenized and much more stable organic portion which is further upgraded by reduction and removal of oxygen from oxygen containing species [12, 13]. Zeolites mainly used are ZSM-5[14, 15], or metal oxides are Cu/Al_2O_3[16], ZnO [17], Na_2CO_3/γ-Al_2O_3etc[18].

In this paper, ZnO/MgO nanoparticles have been prepared by homogeneous precipitation method and further characterized. ZnO nanoparticles has a stronger tendency to show a special capability to destroy cancer causing HL60 cells[19]. The observed antibacterial properties, suggest the possible utilization of prepared nanoparticles in water purification[20]. The ZnO/MgO NPs are used as an effective catalyst for slow catalytic pyrolysis of *Phoenix dactylifera*(date palm

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seed). Date seed is found to be highly efficient as biomass as it has specific properties, for example, uniform pore size dispersal and cost effective raw materials which can be used at less temperature value (minimize energy usage). It has been reported that 1.67 billion tons dates are grown by top 10 date producer countries[21]. So, these date seeds can be frequently used as an energy source in different methods that is slow catalytic pyrolysis.

2. Experimental

2.1. Chemicals

Chemicals were bought from sigma Aldrich and were used without further purification. Some major chemicals used were, Zinc chloride ($ZnCl_2$), Magnesium chloride ($MgCl_2$), Ammonia (NH_3), Distilled water (H_2O). Firstly, date seeds were purchased from local market. They were washed with distilled water to remove impurities. Then they were dried in oven for 3 days in order to remove moisture from them then, date seeds were crushed into fine powder by using crusher. Finally, powder was stored in air-tight packets for further use.

2.2. Synthesis of ZnO/MgO Nanoparticles

80 mL of 1M $ZnCl_2$ and 80 mL of 1M $MgCl_2$ were added in beaker. Then, 10 mL of 25 % ammonia was added in above solution. The resulting solution was heated at 80 ^oC for two hours on hot plate with constant stirring. Then the solution was filtered and the precipitates were washed with distilled water. After that, precipitates were dried in hot air oven at 80^oC for one hour. Then, prepared sample calcined in muffle furnace at 350 ^oC for 2 hours. Clear white ZnO/MgO nanoparticles in powder form were prepared. Dried Nano particles were obtained which were stored in sample vial for further use. For UV-Vis spectroscopy, small amount of dried nanoparticles was diluted with distilled water and sonicated for 15 minutes, UV was done which confirms the synthesis of ZnO/MgO nanoparticles.

2.3. Pyrolysis Reaction

Pyrolysis was carried out in a fixed-bed stainless steel reactor functionalized to perform slow pyrolysis.10g of powdered *phoenix dactylifera* (date seed) was taken as biomass into the pyrolysis reactor tube. Then Nitrogen gas was supplied to it. Plaster of Paris was used to tightly seal the pyrolysis assembly. The output pipes were connected both with sample collection bottles and pyrolysis tube. Bottles were placed in an ice containing chromatographic tank where ice was filled to reduce temperature and condense vapors to liquid. The heat was supplied and temperature was set at 450^oC. Temperature rose at the rate of 10^oC per minute. The reaction time was 45-50 minutes. Finally, bio-oil was obtained, collected and then stored in a sample bottle whereas bio-char was obtained from pyrolysis tube and stored in air tight bags. And their percentage yields were calculated.The same above procedure was repeated with addition of 0.2 gram of catalyst (ZnO/MgO nanoparticles), along with 10g of biomass.Just like the reaction performed with 0.2 g catalyst; the same abovementioned procedure was repeated by adding 0.5 gram of catalyst (ZnO/MgO nanoparticles), along with 10g of biomass.The same above procedure was repeated with addition of 0.2 gram of ZSM-5 catalyst, along with 10g of biomass. The effect of these catalysts on yield was investigated.The conversion and product yields were calculated by fallowing equations:

$$\% \text{ Yield of bio oil} = \frac{\text{weight of bio oil}}{\text{Weight of Biomass}} \times 100$$

$$\% \text{ yield of biochar} = \frac{Weight\ of\ biochar}{Weight\ of biomass} \times 100$$

$$\% \text{ yield of syngas} = 100 - (bio - oil(\%) + biochar\ (\%)$$

2.4. Characterization

Double beam UV/VIS spectrophotometer with a resolution of 0.1nm(UVD-3500, Lambod, Inc., USA,) was used to characterize ZnO/MgO nanoparticles for their optical properties where FT-IR spectrophotometer (Cary 630, Agilient Technology, USA and Resolution is 0.05 cm^{-1}) was employed for functional group analysis of NPs and biochar.

3. Results and discussion

3.1. UV-Visible analysis

To verify the formation of ZnO/MgO NPs, UV–Vis spectroscopy was used where maximum absorption peak was measured and collective oscillations of conduction band electrons in response to electromagnetic waves were calculated. UV/Visible spectrometer has the ability to show the absorbance of the samples in the range of 200-800nm. The formation of metal oxide NPs by the reduction of the aqueous metal ions, during the precipitation reaction was easily verified by UV/Vis spectroscopic analysis. Because of the interaction of electromagnetic radiations, ZnO/MgO Nps display distinctive property of localized surface plasma resonance(SPR) that ultimately makes the conduction electrons to collectively oscillate. The shape and width of absorption band related to the size of NPs. In this paper, chemically synthesized ZnO/MgO NPs displayed maximum absorbance at 320nm due to surface plasma absorption of NPs as provided in Fig.1.

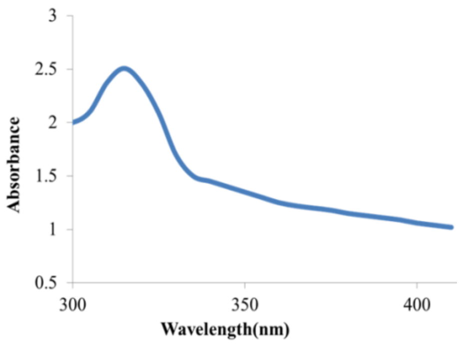

Fig. 1. Absorbance spectra of ZnO/MgO NPs.

3.2. FTIR Analysis of ZnO/MgO NPs

For the functional group analysis of NPs Fourier transform infrared spectrometer (FTIR) was done. Generally,metal oxides give absorption bands below 1000 cm-1(fingerprint region)arising from inter-atomic vibrations. The peak observed at 3446.54 is due to O-H stretching assigned to the water adsorption on the metal surface (figure 2 (a)). The peaks at 1613.97 correspond to Zn-O stretching. The peak at 2163cm^{-1}indicates the presence of C≡C stretching. The peak observed at 1613cm^{-1} is for C=C (in ring). The peak at 1040cm^{-1} is due to presence of Amine group. The metal-oxygen frequencies observed for the respective metal oxides are in accordance with literature values reported by Kumar *et al*[22].. FT-IR analysis of biochar without catalyst was shown in figure 2 (b). A band at 3194cm-1 indicates OH cm^{-1} stretching.A band at 1156 cm^{-1} stretching of date palms, indicates the possibility of C-O stretching, or alcohol-OH, or carboxylic acid. There was a sharp band at 2163 cm^{-1} of date palms that is related to C triple bond C of alkynes. There was a band at 1574 cm^{-1} which is related to C-C alkenes and aromatic rings. The FT-IR spectrum showed a band at 1156 cm^{-1} which is related to the possibility of the presence of C-O stretching. Stretch occurred at 745 cm^{-1} is because of out of plane bending of double bond C-H.This band is a major band that is considered as an important functional group and the responsible for interactions that may be occurred. The obtained results agree with that of the graphic structure is symmetrical and little change in dipole moment occurs during vibration.The FTIR spectra of date seeds derived biochar were in good agreement with the results reported by

Bouchelta *et.,al*[23].Moreover, figure 2 (c) displayed the FT-IR spectrum of biochar with ZnO/MgO NPs catalyst. A band at 3332cm-1 indicates OH cm-^{1} stretching.A band at 2163 cm^{-1}shows the possibility of C double bond stretching, indicating presence of alkenes. There was a sharp band at 2163 cm^{-1} of date palms that is related to C triple bond C of alkynes. There was a band at 1556 cm^{-1} which indicates the presence of nitro group. The FT-IR spectrum showed a band at 1150 cm-1 which is related to the possibility of the presence of C-O stretching, or indicates the presence of esters, alcohols and phenols. Stretch occurred at 747 cm^{-1} is because of out of plane bending of double bond C-H.This band is a major band that is considered as an important functional group and the responsible for interactions that may be occurred. Metal oxides generally give absorption bands in fingerprint region i.e. below 1000 cm-1 arising from inter-atomic vibrations, indicating the presence of ZnO/MgO NPs in composition of biochar. The obtained results agree with that of the graphic structure is symmetrical and little change in dipole moment occurs during vibration.

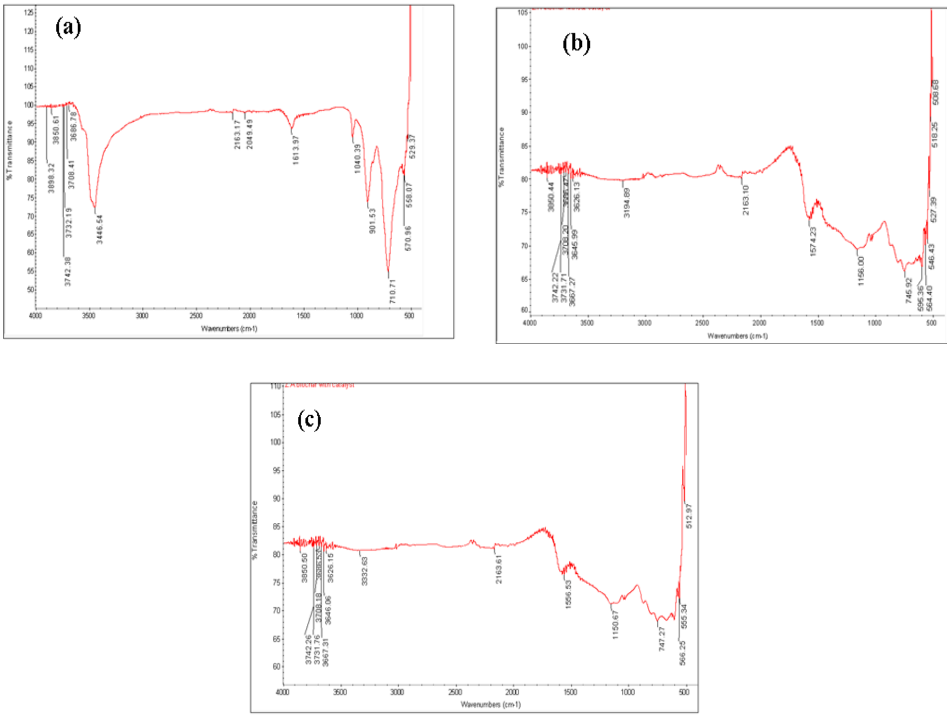

Fig. 2. FT-IR spectrum of (a) ZnO/MgO NPs (b) biochar without catalyst (c) biochar With ZnO/MgO NPs catalyst.

3.3. Percentage yields of pyrolytic products

Fig. 3 (a) showed slow Pyrolysis of Phoenix dactylifera in the absence of a catalyst. So without a catalyst, by-products obtained at 450 ^{O}C were: bio-oil, biochar and bio-gas to be 46.60%, 28.40% and 25%, respectively whereas with 0.2g of ZnO/MgO NPs the by-products obtained were55.30%, 30.90% and 13.80%, respectively as provided in Fig. 3 (b). Slow catalytic pyrolysis of Phoenix dactylifera with 0.5g ZnO/MgO NPs produced bio-oil, biochar and biogas to be 43.30, 30% and 51.01%, respectively at 450 ^{O}C (Figure 3 (c) whereas,with0.2g ZSM-5,by-productsobtained were:51.30%, 28.50% and 26.20%, respectively at 450^{O}C (Fig. 3 d).

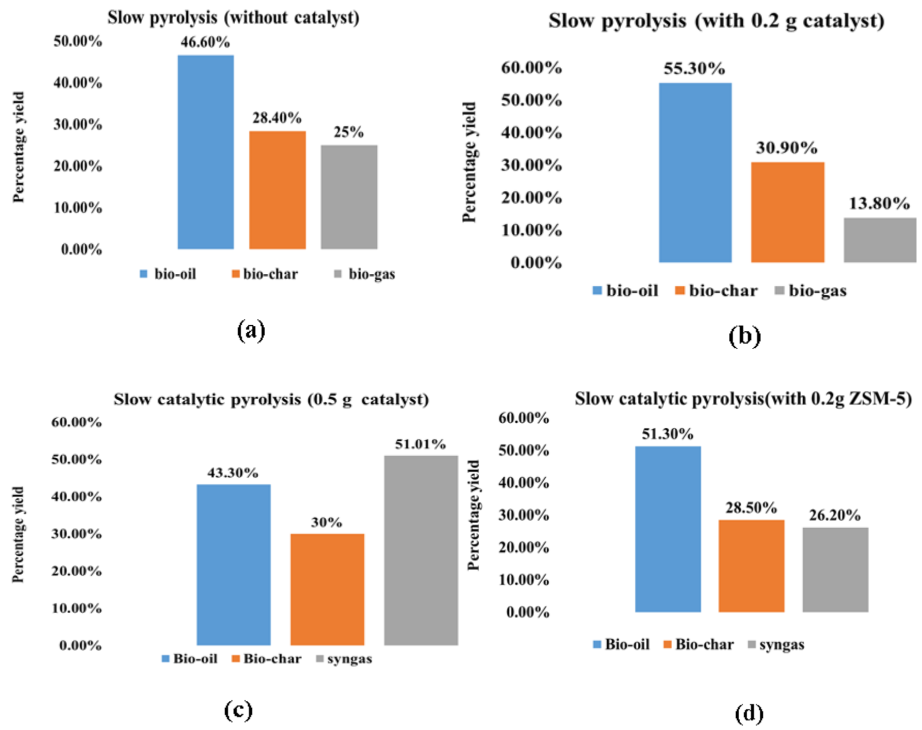

Fig. 3.Slow Catalytic Pyrolysis of Phoenix dactylifera (a) without catalyst (b) 0.2g ZnO/MgO NPs (c) with 0.5g ZnO/MgO NPs (d) with 0.2 g ZSM-5

4. Conclusion

Doped ZnO/MgO nanoparticles have a characteristic property of having large surface area which makes them effective to be used as catalyst. The present research focused on the fabrication of one the most important and remarkable ZnO/MgO nanoparticles by using the homogenous precipitation method. UV–Vis spectroscopy was employed to verify the formation of ZnO/MgO NPs by measuring maximum absorption peak at 320nm. For the functional group analysis of NPs, Fourier transform infrared spectrometer (FTIR) was done. In the present research work these doped nanoparticles were applied for the catalytic pyrolysis of biomass. Seeds ofdate palm tree (*Phoenix dactylifera)* contain excellent properties to be utilized as biomass in catalytic pyrolysis for bioenergy production.

Being plant waste; date seeds are highly cost effective biomass to produce bio-oil, biochar and syngas, with least hazardous effects on the environment. All reactions were carried out at 450^{o}C. Pyrolysis reaction was also performed with 0.2g ZSM-5 catalyst and yields of pyrolysis products were compared. The product yields were highly affected by changing catalyst and amounts of catalyst used. With any catalyst, yield of bio-oil was 46.6%. The maximum yield (55.4%) of bio-oil was attained with 0.2g of ZnO/MgO NPs where as 0.2g of ZSM-5 caused 5% increase in bio-oil yield i.e 51.3% bio-oil. An unexpected decrease of bio-oil yield (43.3%) took place with 0.5g dose of ZnO/MgO NPs.FT-IR analysis of obtained biochar was also done for its functional group analysis.

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