

Catalytic Subcritical Hydropyrolysis of Waste Biomass into Gasoline Range Hydrocarbons

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ABSTRACT

This paper reports the synthesis of catalyst nanoparticles using inorganic condensation method involving the use of poly(ethylene glycol) template and metal salt precursors. The powder obtained by this method was dried, calcined at 600°C for 4 h and analyzed using X-ray diffraction and transmission electron microscopy (TEM). The TEM images exhibited presence of nanosize catalyst particles. These catalyst nanoparticles were used to investigate H₂ and hydrocarbon generation from pine wood. The effectiveness of the catalyst nanoparticles towards H₂ and hydrocarbon generation was compared with the homogeneous NiSO₄ catalyst, which was also used for the liquefaction of paper waste. The liquid slurry obtained after biomass processing was further extracted in different organic solvents and analyzed by FTIR to investigate the formation of higher alkanes.

Keywords: Nanoparticles, inorganic condensation, NiSO₄, paper waste, pine wood, H₂, hydrocarbons

1 INTRODUCTION

Biomass is considered as an alternative source of energy and it has a great potential to generate different fuels such as hydrogen, bio-oil, diesel and gasoline, which can be utilized as a partial replacement for fossil fuels to meet future energy demands. H₂ is a sustainable, green fuel with energy density of 143 MJ/Kg [1], which is significantly higher than the energy density of oil (46.4 MJ/kg), natural gas (53.6 MJ/kg) and coal (32.5 MJ/kg) [2]. H₂ is considered as a future energy fuel and is receiving increased attention. On industrial scale H₂ is produced by gasification and reforming of fossil fuels [3]. Additional processes such as water-splitting [4], solar thermal processes [5] and reforming of biomass [6] are being considered for H₂ generation. Significant efforts are currently being directed to make use of renewable resources such as water and biomass for H₂ generation.

Biomass and waste biomass can be processed using various processing technologies such as biological [7], biochemical [8], gasification [9], pyrolysis [10] and aqueous phase reforming [11] for the production of H₂ [12]. Kersten *et al.* [13] performed gasification of pine wood using hot compressed water and showed H₂ as the major gas generated along with CO, CO₂ and lower hydrocarbons.

Hydrothermal gasification of waste biomass for hydrogen production was reported by Kong *et al.* [14]. In general, high temperature compressed fluids such as subcritical and supercritical water have one of the key advantages over other conventional thermochemical processes and that is the direct processing of wet biomass for H₂ production [15] eliminating the need of drying biomass as it is required for the gasification [16] and pyrolysis [17]. Hydrogen production from subcritical aqueous phase liquefaction of biomass is receiving more attention as it operates at low to moderate temperatures of 125-350°C and pressures of 0.5-21 MPa [18]. Cheng *et al.* [19] investigated switchgrass conversion in subcritical water at temperatures of 250-350°C and pressures of 20 MPa. These authors reported increase in hydrogen yields from 0.17 mol % at 250°C to 0.9 mol % at 350°C. Typically the rates of biomass reaction leading to the formation of H₂ or hydrocarbon fuels are slower in subcritical water; however, the rates can be enhanced by using a suitable catalyst.

Most of the studies so far have been focused on group VIII catalysts with platinum exhibiting highest activity. In one of the studies by Cortright *et al.* [20], 3 wt% platinum supported on alumina nanofibers was prepared by wet incipient method and it was used for hydrogen generation from aqueous solutions of biomass model compounds in water at moderate reaction conditions. These investigators demonstrated almost quantitative yields of H₂ from the reaction of aqueous sorbitol solution over Pt/Al₂O₃ catalyst at about 250°C. Efforts are also being made to develop thermochemical processes for the generation of CO and H₂ (syngas) from biomass substrates. The syngas can be further reacted following Fisher-Tropsch and/or water gas-shift reaction routes for the production of alkanes using heterogeneous catalysts.

Recently, there is a major emphasis on the use of a bifunctional catalyst for the selective enrichment of higher hydrocarbons during biomass pyrolysis. Typically, the morphology (e.g. porous) as well as metal or metal oxide surface reactivity offer bifunctionality to the catalyst surface. In this regard, various metals such as Fe, Co, Ru etc. and mesoporous oxides have been explored by researchers for the production of gasoline range hydrocarbons. Ngamcharussrivichai *et al.* [21] investigated a bifunctional catalyst, Co/MCM-22, for Fisher-Tropsch synthesis at 230°C and 1 MPa pressure with the motivation of achieving the production of gasoline range hydrocarbons. From the current literature, a very limited efforts have been

observed that making the use of nanosize complex oxide catalyst materials for H_2 and hydrocarbon generation from hydrolysis of biomass substrates. This paper demonstrates the use of catalyst nanoparticles, for H_2 generation from biomass substrates under subcritical water conditions and compares the H_2 generation ability of nanoparticles with homogenous $NiSO_4$ catalyst.

2 EXPERIMENTAL

2.1 Synthesis of catalyst nanoparticles

Catalyst nanoparticles were synthesized via inorganic condensation method using PEG 400 and chloride salts of copper and nickel. In the synthesis performed, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $NaOH$ (1:1:1.2 weight ratio) were first ground into fine powder. After the addition of PEG-400, the mixture was pulverized using pestle and mortar for 30 minutes until black slurry was obtained. To this slurry, 500 ml of DI water was added and it was further sonicated for 2-3 hours in a sonic bath. This was then centrifuged for 10 minutes to recover the powder. The powder thus obtained was washed with 500 ml ethanol, dried at $100^\circ C$, and finally calcined at $600^\circ C$ for 4 hours.

2.2 Characterization of the catalyst

The calcined powders were characterized using X-ray diffraction ($10^\circ \leq 2\theta \leq 70^\circ$ and scanning speed of 2° per minute), and transmission electron microscopy (TEM). A sample for TEM analysis was prepared by dropping 2-propanol based dispersion of catalyst particles onto a carbon grid. The grid was dried at room temperature and used for the TEM analysis.

2.3 Hydrogen generation set-up

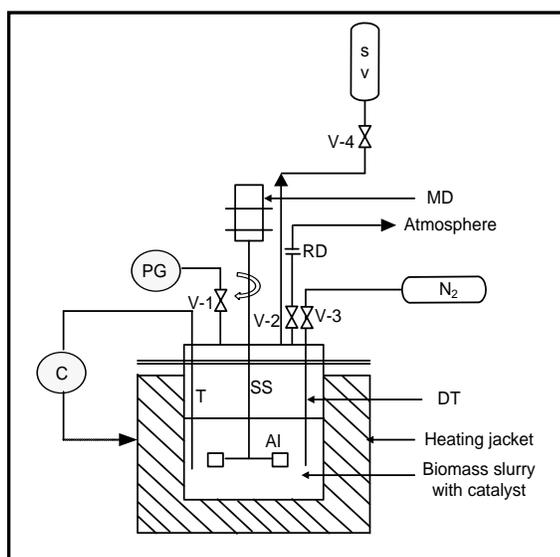


Figure 1: Reactor set-up for high-temperature and high-pressure catalytic hydrothermal processing of a biomass.

Slurry of a biomass (15 wt% in 150 ml of de-ionized water) was prepared in distilled water containing 5 wt % catalyst and loaded in the PARR SS316 reactor as shown schematically in Figure 1. The slurry was stirred at 1300 rpm and heated to different temperatures. Once the set temperature attained, a gas sample was withdrawn and analyzed by Chrompak capillary column installed in gas chromatograph, HP6890A, equipped with thermal conductivity detector (TCD). This time was referred as 'zero' time for a reaction. Next, the reaction was continued at the set temperature for 120 min and while the reaction was in progress gas samples were withdrawn at 30 min time interval and analyzed using GC. The effluent gases from the reactor were also analyzed using the Chrompak capillary column installed in the gas chromatograph, HP6890A.

3 RESULTS AND DISCUSSION

3.1 Synthesis and characterization of catalyst nanoparticles

Catalyst nanoparticles were synthesized using an inorganic condensation method as per the procedure described in Section 2.1. The reaction of $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $NaOH$ is exothermic in nature and leads to the formation of $Cu(OH)_2$ and $Ni(OH)_2$, which on dehydration at higher temperatures produces a mixture of oxides. During the synthesis, PEG gets adsorbed on the surface of the colloids in the solution and restricts the growth of colloid into macrostructure leading to nanoscale morphology. In other words, PEG provides a template for the growth of nanoparticles [22].

As-synthesized catalyst powder was dried and calcined at $600^\circ C$ for 4 hrs. The compositional purity of the calcined powder was determined using the powdered x-ray diffraction. The X-ray diffraction pattern of the calcined catalyst powder is presented in Figure 2, which indicates a mixed phase composition containing $Ni_{0.9}Cu_{0.1}O$ and CuO in the weight ratio of 1:1.

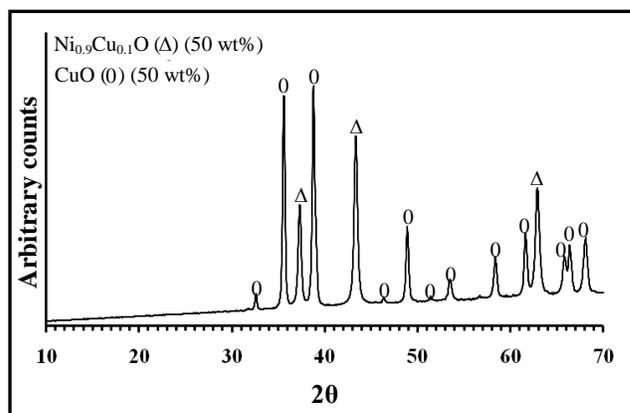


Figure 2: X-ray diffraction pattern of catalyst powder exhibiting mixed phase containing $Ni_{0.9}Cu_{0.1}O$ and CuO .

The calcined powder was analyzed using TEM and the TEM image obtained is shown in Figures 3, which shows nanoparticles in the size range of approx. 18-50 nm.

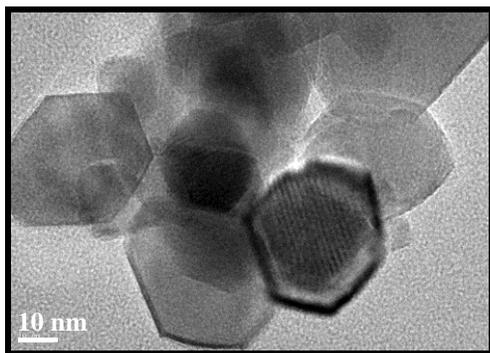


Figure 3: TEM image showing catalyst nanoparticles of the mixed phase composition containing $\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}$ and CuO .

3.2 H_2 generation from waste biomass and pine wood using NiSO_4 and nanoparticles of mixed phase containing $\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}$ and CuO

The effect of 5 wt% NiSO_4 catalyst on H_2 generation during hydrothermal processing of office paper waste at 250°C is shown in Figure 4. It can be observed that the H_2 generation increases almost linearly with the reaction time and reaches to about 6vol% in 90 min. The other product gases observed were CO_2 , CO and CH_4 . It is possible to achieve reaction of CO and H_2 selectively over a catalyst bed for higher hydrocarbon formation following Fisher Tropsch reaction. The brown colored product slurry obtained after biomass processing was extracted in hexane, toluene, dichloromethane, ethyl acetate and methanol and evaporated. The residue obtained after evaporation was further characterized using FTIR, which indicated the presence of higher alkanes in all the extracts except the methanol one. From the product slurry, bio-char and bio-oil were also recovered.

The H_2 generation ability of catalyst nanoparticles of the mixed phase composition containing $\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}$ and CuO was investigated. Pine wood slurry was prepared in distilled water (15 g/150 ml) and mixed with 5 wt% catalyst nanoparticles. The slurry was loaded in the reactor and heated to 250°C in N_2 environment. At the set temperature, the reaction was continued for 90 min. During the reaction, the gas samples were withdrawn after every 30 min time interval and analyzed for H_2 content using HP 6890A gas chromatograph equipped with thermal conductivity detector (TCD) and Chrompak capillary column. The H_2 volume generated at 250°C from the wood substrate is also shown in Figure 4. It can be observed that, at 'zero' reaction time the H_2 level was 2.5 vol%, which increased to 7 vol% after 30 min. In the case of paper waste, the H_2 level was 0.8 vol% at zero reaction time, which increased to 2.5 vol% after 30 min. For the pine wood, the H_2 volume was further decreased to 5 vol% and remained practically constant until 90 min.

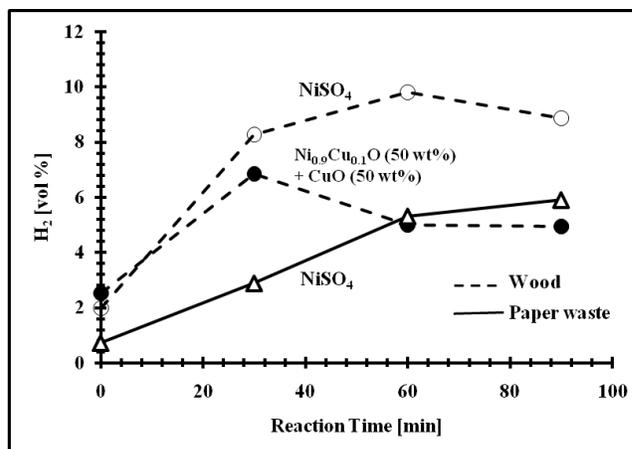


Figure 4: H_2 production during hydrothermal processing of waste paper and pine wood at 250°C using 5 wt % NiSO_4 homogeneous catalyst and nanoparticles of mixed phase composition containing $\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}$ and CuO .

It can also be observed from Figure 4 that the levels of H_2 production are almost similar for both biomass substrates using homogeneous NiSO_4 and nanoparticles of $\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O} + \text{CuO}$ after 60 min of reaction time. When 5 wt% NiSO_4 was utilized for hydrolysis of wood substrate, higher H_2 generation was observed as compared with H_2 generation observed using 5 wt% catalyst nanoparticles (Figure 4). It is to be noted that regardless of biomass and catalyst, the product gases were found to contain additional gases such as CO_2 , CO , and CH_4 . As waste paper contains a major portion of cellulose, a higher H_2 generation was anticipated in a shorter time period as compared with the wood, which has complex structure by nature containing cellulose, hemicellulose and lignin. Overall, the formation of H_2 , CO , CH_4 and CO_2 gases might be attributed to the dehydrogenation of acids, aldehydes, and ketones derived from sugars as well as to the water-gas-shift reaction.

This study reveals that the catalyst nanoparticles of mixed phase containing $\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O} + \text{CuO}$ were effective in breaking down the complex biomass substrates leading to the formation of H_2 as well as hydrocarbons. After the reaction performed, the reactor contents were cooled down to room temperature and blackish brown slurry was recovered. The slurry was filtered and analyzed using HPLC, which showed the presence of sugars, acetic acid, ethanol, furfural and HMF. The bio-oil was recovered from the slurry and residue was discarded.

The main advantage of using catalyst powder is its separation ability from the processed slurry. In the case of homogeneous NiSO_4 catalyst, however, an additional ion-exchange unit may be needed for the removal toxic metal ions.

4 CONCLUSIONS

Considerable H_2 vol% generation was observed with both paper waste and pine wood substrates using

homogeneous NiSO₄ and catalyst nanoparticles of mixed phase composition containing Ni_{0.9}Cu_{0.1}O and CuO. Still higher H₂ levels were possible using higher concentration of a catalyst as well the biomass loadings. Using catalyst nanoparticles, 7 vol% H₂ was achieved from wood, whereas in the case of waste biomass, the maximum H₂ vol% level was never reached to 7vol% even after 90 min of reaction using NiSO₄. Regardless of biomass and catalyst types, the product gas was found to contain mainly H₂, CO₂, CO, and CH₄. The CO and H₂ gases from the product gas stream can be reacted further to produce gasoline range hydrocarbons, which will require the use of multiple catalysts with proper selectivity. The liquid slurry obtained after biomass processing was extracted in different solvents and evaporated. The FTIR analysis of the residue collected after evaporation of extracts in organic solvents confirmed the presence of higher alkanes.

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