Catalytic Biomass Reforming for Hydrogen and Hydrocarbon Production

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ABSTRACT

This paper reports synthesis of catalyst nanoparticles using sol-gel method involving the addition of metal salt precursor and a surfactant in ethanol followed by gelation using propylene oxide. As prepared gels were dried, calcined at $600^{o}C$ and characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The catalyst nanoparticles were used for thermochemical processing of liquefied biomass (750 mg/L) obtained after subcritical aqueous phase treatment of paper waste at $250^{o}C$ to investigate H_2 and hydrocarbon generation. The nanoparticles were centrifuged and the processed liquefied biomass obtained after thermochemical processing was analyzed using TOC analyzer and GC-MS. The catalyst nanoparticles were capable of producing H_2 and oxygenated hydrocarbons from a liquefied biomass containing dissolved organic carbon at a concentration of 750 mg/L.

Keywords: Nanoparticles, sol-gel synthesis, paper waste, H_2, oxygenated hydrocarbons.

1. INTRODUCTION

Biorefinery waste or wastewater containing dissolved organics can be further utilized for the production of H_2 and hydrocarbon fuels. In one of the studies by Tungal et al. [1], biorefinery waste from KL Energy Company based in South Dakota was processed in presence of $NiSO_4$ catalyst, which generated about 4 vol% H_2 continuously for 120 min at $250^{o}C$. Other types of solid wastes such as paper waste are also generated in large amounts and can be further utilized for the production of biofuels such as H_2 and hydrocarbons as shown by Tungal et al. [2].

Due to the increased energy demands and rapid consumption of fossil fuels, there is a need to find the alternative sources of energy. Biomass is a renewable source of energy and can be used to replace fossil fuels to meet future energy demands as it has a potential to generate not only hydrogen (H_2) and hydrocarbon (HC) fuels but can also produce bio-oil, biodiesel and bio-gasoline. In US, a large amount of dry biomass (400,000 ton) is produced per year [3]. Though biofuels are already being generated on commercial scale, the production can be further enhanced if waste biomass such as waste paper or paper pulp or biorefinery waste is further utilized [4].

Various processing technologies are being applied for the processing of biomass or waste biomass for the production of biofuels on commercial scale such as biological [5], biochemical [6], gasification [7,8], pyrolysis [9] and aqueous phase reforming [10]. In one of the studies by Kersten et al. [11], pine wood gasification has been performed using hot compressed water and production of H_2, CO, CO_2 and lower hydrocarbons have been showed. In another study by Zhang et al. [12], catalytic switchgrass has been treated in fluidized reactor at temperatures of 700-$760^{o}C$ and H_2 generation was reported. Muangrat et al. [13] studied H_2 production from food waste via hydrothermal gasification at 330-$390^{o}C$. Production of H_2, CO, CO_2 and CH_4 was reported from the hydrothermal pyrolysis of paper sludge [14].

Use of subcritical and supercritical is very advantageous over other conventional thermochemical processes such as pyrolysis [15] and gasification [16] as it eliminates the need of drying a biomass and thus saves energy as wet biomass can be directly processed for the generation of biofuels [17]. Subcritical aqueous phase liquefaction of biomass is gaining more attention as it operates at low to moderate temperatures of 125-$350^{o}C$ and pressures of 0.5-21 MPa [18] and for processing of biomass these temperatures can be easily achieved by using waste heat available in the industries. H_2 production has been shown from switchgrass using subcritical water at temperatures of 250-$350^{o}C$ and 20 MPa pressure and reported increase in hydrogen yields from 0.17 mol % at $250^{o}C$ to 0.9 mol % at $350^{o}C$ along with other products such as CO, CO_2 and CH_4 [19]. In another study by Cortright et al. [20], H_2 generation was achieved from biomass in water at moderate reaction conditions using heterogeneous catalyst such as 3 wt% platinum supported on alumina. Furthermore, higher hydrocarbons such as gasoline range hydrocarbons can be produced using suitable metal supported catalyst using Fisher Trospch synthesis [21]. It has been observed that the use of nanosize complex oxide catalyst with suitable morphology is very limited for real biomass processing though TiO_2 and ZrO_2 [22] have been used on sugars for the production of HMF and furfurals but not for H_2 and HC's production. This paper demonstrates the use of catalyst nanoparticles for H_2 and hydrocarbon generation from biomass substrates under subcritical water conditions.

In our previous studies [1,2], subcritical water was used in presence of water soluble nickel catalyst for the production of hydrogen in the gas phase and oxygenated

hydrocarbons in the liquid phase from biorefinery waste as well as office paper waste. In this study, NiO nanoparticles were utilized for the high-pressure hydrothermal processing of liquefied biomass obtained from office paper waste with the objective of achieving reduction in total organic carbon (TOC) with simultaneous production of H_2 and hydrocarbon fuels.

2. EXPERIMENTAL

2.1 Synthesis of Catalyst Nanoparticles

Catalyst nanoparticles were synthesized via sol-gel synthesis method using $NiCl_2.6H_2O$ and Brij-76 surfactant. In the synthesis performed, specifically, 1.0 g of $NiCl_2.6H_2O$ in 2-3 ml of ethanol was sonicated for 10 min. To this sonicated solution, Brij-76 (30 wt% of $NiCl_2$) was added and it was further sonicated for 10 min. Next, propylene oxide was added to achieve the gel formation. The gel was washed with ethanol several times and dried at 100^oC. The dried powder was calcined at 600^oC, using ramp $40^oC/min$ with no hold time.

2.2 Characterization of the Catalyst

The calcined catalyst powders were characterized using X-ray diffraction ($10^o \leq 2\theta \leq 70^o$ and scanning speed of 2° per minute), and transmission electron microscopy (TEM). The sample for TEM analysis was prepared by sonicating the catalyst powder in isopropanol for 2 hrs and finally dropping it onto a carbon grid. The grid was dried at room temperature before performing the TEM analysis.

2.3 Liquefaction of Paper Waste and Hydrogen and Hydrocarbon Generation

Slurry of office paper waste (15 wt% in 150 ml of de-ionized water) was loaded in the PARR high-temperature high-pressure batch reactor and heated to 250^oC under continuous stirring at 1300 rpm. It took about 1 hr to reach the set temperature of 250^oC. Without providing any residence time, the reactant contents were cooled down and the processed slurry was recovered. The slurry was centrifuged to collect water soluble components and residue. The liquid thus obtained without any residue was analyzed using TOC analyzer, which indicated total organic carbon concentration of about 750 mg/L. To this low organic carbon containing liquid, 100 mg of NiO nanoparticles were added and contents were then heated to 250^oC in N_2 environment. Once the set temperature was reached, a gas sample was withdrawn and analyzed by Chrompak packed column installed in gas chromatograph, Agilent 7890A, 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 90 min and while the reaction was in progress gas samples were withdrawn at 30 min time

interval and analyzed using GC. During the course of reaction, liquid samples were also collected and analyzed using TOC analyzer for carbon content and GC-MS for oxygenated hydrocarbon compounds. The entire processing, sampling and analysis sequence is depicted in Figure 1.
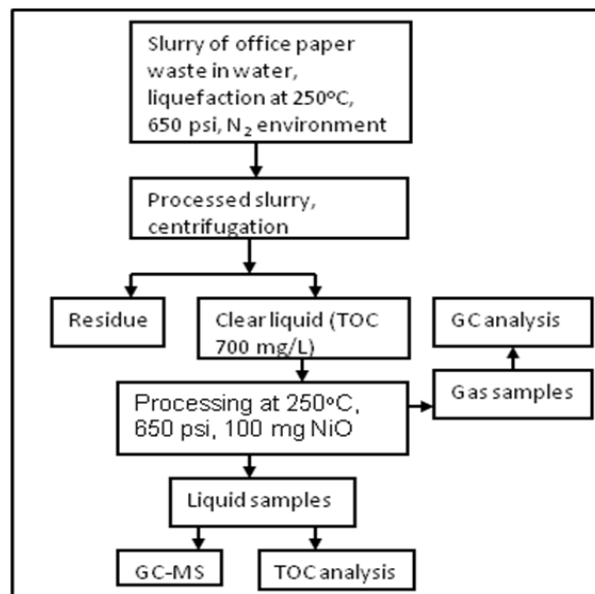

Figure 1: Flow diagram showing processing, gas and liquid sampling and analysis sequence.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Catalyst Nanoparticles

The compositional purity of calcined powders were determined using Rigaku Ultima-Plus X-ray diffractometer (*CuKα* radiation, λ=1.5406 Å, 40 kV, 40 mA) and a graphite monochromator. The parameters such as 2θ, scanning speed and width of $10^o \leq 2\theta \leq 80^o$, 2° per minute and 0.020^o, respectively, were used for the X-ray diffraction measurements. The XRD pattern of calcined catalyst powder is presented in Figure 2a. The 2θ values corresponding to the three major peaks were found to be consistent with those reported by other investigators. Quantitative estimation of the phases present in the powders was performed using the JADE software, v. 7.5 (Materials Data Inc.) following the 'Reference Intensity Ratio' (RIR) method. Using this method, the catalyst powder was found to contain NiO in the amount of 82.5wt%. Other impurities were not fully characterized.

The calcined powder was analyzed using TEM and the TEM image obtained is shown in Figures 2b. TEM analysis revealed a majority of nanoparticles in the size range of 8-30 nm. Controlled synthesis, which is currently underway, is expected to improve the particle size distribution.
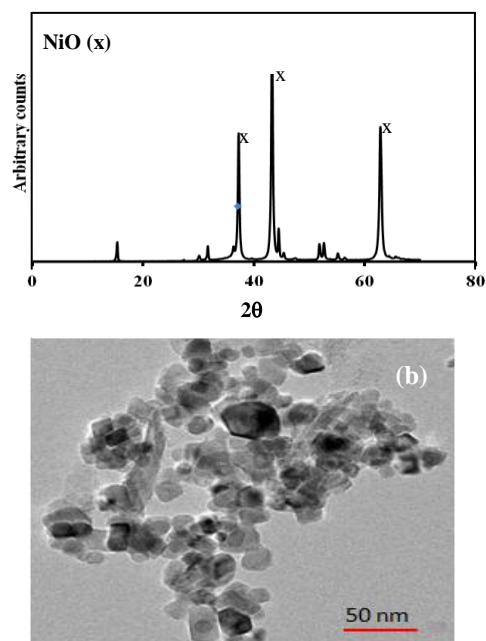
Figure 2: a) X-ray diffraction pattern of catalyst powder prepared by sol-gel method exhibiting NiO (82.5wt %) and b) TEM image showing nanoparticles.

3.2 Effect of NiO on Liquefied Biomass Obtained from Office Paper Waste

Slurry of office paper waste (15 wt% in 150 ml of de-ionized water) was loaded in a batch reactor and heated to $250^{o}C$ under continuous stirring at 1300 rpm. Without providing any residence time, the reactant contents were cooled down and the processed slurry was recovered and centrifuged. The clear liquid thus obtained was analyzed using TOC analyzer, which indicated total organic carbon concentration of about 750 mg/L. To this low organic carbon containing liquid, 100 mg of NiO nanoparticles were added and contents were then heated to $250^{o}C$ in N_2 environment. At the set temperature the reaction was continued for 90 min and while the reaction was in progress, the liquid samples were withdrawn and analyzed using TOC analyzer. The TOC values obtained are shown in Figure 3. TOC values were found to decrease with increase in reaction time. About 43 % reduction in TOC was observed at the end of 90 min reaction time from an initial value of about 750 mg/L. It will be possible to achieve higher TOC reduction with increase in reaction temperature, catalyst concentration and reaction time. By using the processing approach investigated here, it will be possible to achieve the discharge standards with respect to chemical oxygen demand (COD) and biological oxygen demand (BOD) of the liquefied biomass slurry that need to be treated in a wastewater treatment facility of a biorefinery prior to its disposal.

While the reaction was in progress at $250^{o}C$ in presence of NiO, gas samples were also withdrawn and analyzed with GC as mentioned earlier in the Experimental section.

The effect of NiO catalyst on H_2 generation during hydrothermal processing of office paper waste at $250^{o}C$ is shown in Figure 4. It can be observed that the H_2 generation
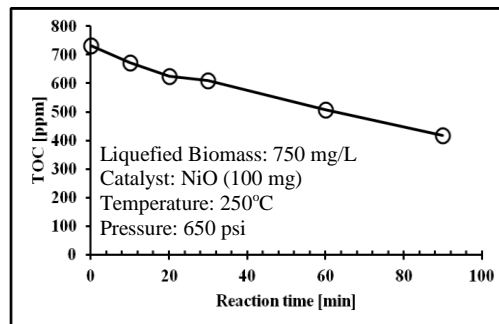

Figure 3: TOC reduction during NiO catalyzed subcritical aqueous phase processing of liquefied biomass obtained from hydrothermal processing of office paper waste at $250^{o}C$.

increases almost linearly with the reaction time up to 90 min. It can also be observed that at 'zero' reaction time the H_2 level was almost 0 vol%, which increased to 0.04 vol% after 90 min of reaction time. Higher H_2 volume generation can be achieved if paper waste is processed directly in presence of homogeneous catalysts such as $NiSO_4$, $NiCl_2$ and $Ni(NO_3)_2$ [1,2]. The other product gases observed were CO_2, CO and CH_4. The generation of CH_4 was found to be almost negligible.
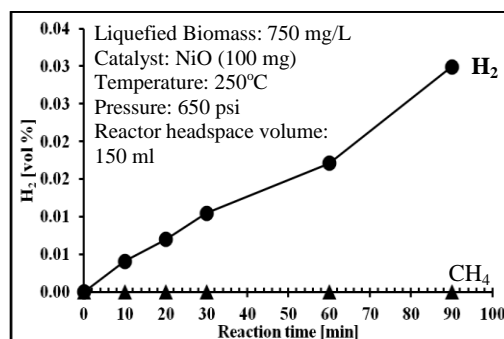

Figure 4: H_2 production during NiO catalyzed subcritical aqueous phase processing of liquefied biomass (750 mg/L) at $250^{o}C$.

Figure 3 shows that the TOC values are decreasing with the increase in the reaction time. This infers that the carbon was lost in the gas phase, which was evident from the production of CO and CO_2 in the gas phase (Figure 5). As the liquefied biomass was processed under N_2 environment, it was obvious that the oxygen from the biocrude was lost in the product gases, CO and CO_2. It may also be possible to treat the liquefied biomass in presence of oxygen, which will oxidize dissolved organic carbon to CO_2 and water. However, the production of H_2 and hydrocarbon fuels under hydrothermal conditions will be beneficial as they can be further utilized as energy sources.
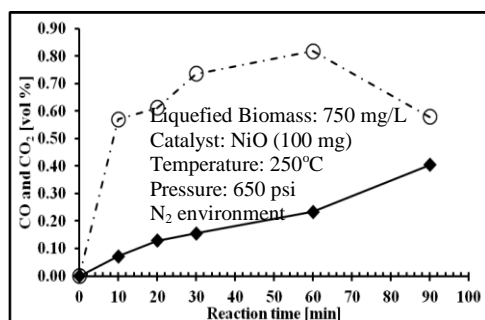
Figure 5: CO and CO_2 production during NiO catalyzed subcritical aqueous phase processing of liquefied biomass (750 mg/L) at 250^oC.

The biocrude obtained during NiO catalyzed subcritical aqueous phase processing of liquefied biomass (750 mg/L) at 250^oC was analyzed using Agilent GC-MS equipped with HP-5 MS column and the products obtained are listed in Table 1, which shows oxygenated hydrocarbons.

Retention time (min)	Compounds
7.329	2-(1-Methylpropyl)-cyclopentanone
8.117	1-Methyl-2-propyl-cyclohexane
8.251	1-(2,2-Dimethylcyclopentyl)-ethanone
20.162	2,6-Diisopropylnaphthalene

Table 1: Liquid products analyzed by GC-MS.

The treatment temperature of 250^oC can be easily achieved using the waste heat, which is generally available in industries. Therefore, it will be possible to achieve self-sustainable processing approach, which not only will treat the biorefinery wastewater containing low dissolved organics but will generate H_2 and hydrocarbon fuels.

4. CONCLUSIONS

Catalyst nanoparticles synthesized using surfactant assisted sol-gel method indicated 82 wt% NiO phase with majority of particles in the range of 8-30 nm. When NiO nanoparticles were used for subcritical aqueous phase processing of liquefied biomass (approx. 750 mg/L) at 250^oC, about 43 % reduction in TOC was observed with the production of H_2 and oxygenated hydrocarbons in gas and liquid phases, respectively. Preliminary GC-MS analysis indicated the presence of oxygenated hydrocarbons, which include 2-(1-methylpropyl)-cyclopentanone, 1-(2,2-di-methylcyclopentyl)-ethanone etc in the liquid phase. It appears that using NiO nanoparticles, a biorefinery wastewater containing typically a low organic carbon concentration can be sustainably treated to meet the effluent discharge standards with simultaneous generation of biofuels.

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