Syngas Production from Cotton Stalks by Oxygen Gasification over Iron-Nickel Bimetallic Nano-Catalyst

Ganzory Mohamed, Amin Ashraf *, Radwan Aly M. and Hamad Mohamed A.
Chemical Engineering and Pilot Plant Department, Engineering Research Division, National Research Centre, 33 El-Bohouth St., Dokki, Cairo, EGYPT
*ashmukhtar@yahoo.com

Abstract
Gasification of cotton stalks was studied using Fe-Ni bimetallic nano-catalyst. Nano-bimetallic catalyst was prepared by supporting 10 wt.% Fe and 20 wt.% Ni on alumina or dolomite. The effect of nano-sized bimetallic catalyst on biomass gasification using oxygen as gasification medium was investigated by comparing gas yield and composition with and without catalyst. Alumina and dolomite were used as a support for the bimetallic catalyst to examine the effect of support on catalyst performance.

A remarkable effect of catalyst and support was observed. The produced gas volume was 320 and 297 ml for gasification with and without catalyst. For gasification without catalyst, the volume percentages of H_2, CO, CH_4 and CO_2 are 44.3, 33.5, 6.2, and 15.3 % respectively. Using Fe-Ni/dolomite, H_2 and CO volume percentages were 60 and 7.5 v.% respectively. Using Fe-Ni/alumina, H_2 and CO volume percentages were 25 and 57 v.% respectively.

Keywords: Gasification, Nano-catalyst, Syngas, Biomass.

Introduction

New alternative energy resources are necessary due to the limited supply and the increasing demands of fossil fuels. One of the most abundant materials is biomass. Biomass represents a potential solution for the diminution of fossil fuels. Using biomass to generate energy can decrease the environmental impact of the fossil fuels like greenhouse gas emissions. The amount of biomass available annually can place the biomass as the third energy source following to coal and oil. 35% of the global demand of energy in developing countries is generated from biomass which is corresponding to around 13% of the global energy demand. Several renewable energy resources were studied extensively; biomass appears as the most promising renewable energy source. This conclusion is based on the widely available quantities of biomass which can cover a large portion of the global energy demand[1-7].

As a CO_2 neutral and renewable energy source, biomass has attracted the research community for decades. Biomass was used for long time as an energy source; burning biomass is the oldest method to create energy. Burning biomass is not a viable option since it is associated with several technical and environmental problems. New and advanced practices must be established to consume biomass[5,8]. Biomass consumption and conversion can be achieved by gasification, pyrolysis, hydrolysis, and hydrogenation[9,10]. Efficient technologies should be developed to consume biomass to minimize biomass disposal complications in addition to generating revenue.

Gasification is one of the most promising processes for converting biomass to biofuels, namely syngas. Syngas is a mixture of carbon monoxide and hydrogen[11]. Gasifier is the unit at which biomass gasification takes place; Gasifiers are employed to replace burners of biomass. By producing syngas, gasifiers provide an alternative process for biomass conversion to avoid on-site power generation obligation of biomass burners[12]. Throughout gasification, biomass is converted to charcoal and a combustible gas using partial oxidation at a temperature range of 700-900˚C[12,13].

The charcoal is finally reduced to a gam mixture containing H_2, CO, CO_2, O_2, N_2, and CH_4[8,14]. The reactions encountered during the gasification process are listed below. Reaction 1 illustrates the overall process inputs and outputs while Reactions R2-R7 show the detailed reaction mechanism:

$$Biomass + Heat \rightarrow H_2 + CO + CO_2 + CH_4 + hydrocarbons + Char \quad (1)$$

$$C + O_2 \rightarrow CO_2 \quad \text{(Oxidation Reaction)} \quad (2)$$

$$C + \tfrac{1}{2}O_2 \rightarrow CO \quad \text{(Oxidation Reaction)} \quad (3)$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \quad \text{(Oxidation Reaction)} \quad (4)$$

$$C + CO_2 \leftrightarrow 2CO \quad \text{(Boudouard Reaction)} \quad (5)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \text{(Hydrogenation/reduction)} \quad (6)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(Water gas-shift Reaction)} \quad (7)$$

When biomass is heated to 120˚C, the biomass loses moisture. The volatile matter is devolatilized completely at 350˚C. Gasification of char takes place at temperatures above 350˚C[9]. The produced gas comprises the following constituents: volatile alkali metals, tars, ash, and syngas. The gasification commercialization is still not feasible due to the challenge of tars formation. Tar is a condensable material which may cause blocking and fouling for downstream equipment[15]. Commonly, tar usage may cause a sudden and complete shutdown of the industrial unit[11,15].

Using catalyst in gasification is important for two reasons: tar removal from the product stream and increasing the quality of the produced gas[16]. Different catalysts were employed for catalytic conversion including nickel, olivine, limestone, and dolomite[12,16]. The effect of nano-structured materials was studied in the literature. Li et al[17] studied the effect of nickel oxide nanoparticles supported on γ-Alumina on oxygen-steam gasification of rice husk leading to 10 v.% in hydrogen percentage and over all gas yield.

Li et al[18] investigated the effect of nano tri-metallic (Ni-La-Fe) supported on γ-Alumina in steam gasification of saw dusts. The results indicated a great enhancement in gas yield and 99% tar removal efficiency at 800°C. Ismail et al[19] showed the effect of CaO and MgO nanoparticles on the gasification of oil palm empty fruit bunch resulting in a significant increase in the hydrogen production. Sina et al[20] used ZnO and SnO_2 nanoparticles for gasification of cellulose. The results showed that ZnO resulted in increasing the hydrogen yield while SnO_2 increased the ethane and propane yield. Throughout this study, catalyst and support material effect was examined. Iron and nickel nano-particles as a bimetallic catalyst, were used for biomass gasification with air. Nano-sized Fe-Ni/alumina (Al_2O_3) and Fe-Ni/ dolomite ($CaMg(CO_3)_2$) catalysts were prepared. Non-catalytic thermal gasification was conducted to investigate the catalyst effect. The effect of the catalyst/support matrix was studied by comparing the gas yield and the gas composition observed with each catalyst.

Material and Methods

Raw material analysis: The biomass (cotton stalks) is analyzed before the gasification reactions using an elemental analyzer (Vario El Elementar) to determine percentage of carbon, hydrogen, nitrogen, and sulphur in biomass. Oxygen percentage is assumed to be the balance.

Catalyst preparation: 10 wt.% Fe and 20 wt.% Ni nano-catalysts are supported on dolomite and alumina supports using wet impregnation method. 2.15 gm of nickel nitrate, 1.58 gm of iron nitrate and 6 gm of urea (precipitation agent) are dissolved in 50 ml distilled water using a magnetic stirrer at room temperature until a homogeneous solution is obtained. The mixture is added to 1.5 gm dolomite (Alumina) in another beaker forming a brown precipitate. The mixture is heated in a water bath (100˚C) for 2.5 hr. Then, the mixture is filtered and the agglomerate is heated at 110˚C in the drier for 5 hrs. The agglomerate is ground in a ball mill and calcined at 500˚C for 1 hr in the muffle.

Catalyst characterization: The catalyst is characterized using Transmission Electron Microscope (Jeol-Jem-2100 HR) operated a 200 kv to investigate the structural properties of the catalyst particles.

Biomass gasification: A bench scale fixed bed reactor is used for biomass gasification using oxygen as gasification medium. Three experiments are conducted, the first experiment (EX1) is considered as the control experiment performed using 0.5 gm cotton stalks without a catalyst at 800˚C. The second experiment (EX2) is carried out in the presence of 10 % Fe and 20% Ni nanoparticles supported on dolomite at 800˚C. The third experiment (EX3) is carried out in the presence of 10 % Fe and 20% Ni nanoparticles supported on alumina at 800˚C. The biomass is charged in the reactor with the catalyst, then the reactor is sealed and checked for leakage.

The reactor is heated to 800˚C at a heating rate of 10°C/min. Then, the reactor is kept at 800˚C for 1 hr. The temperature is controlled using a K type thermocouple inserted in the reactor and protected with a quartz tube to prevent any catalytic interference of the thermocouple material. After cooling down, the produced gas is collected and analyzed using gas chromatography equipped with MS.

Results and Discussion

Raw material composition: The weight percent of biomass elements was determined using elemental analysis. Carbon and oxygen represent the majority of the biomass weight (around 90%). Nitrogen, hydrogen and sulfur represent lower percentages of the biomass weight. Table 1 shows the weight percentage of the different elements in biomass used.

Catalyst characterization: The TEM analysis indicates the formation of nanoparticles of iron and nickel supported on alumina and dolomite as shown in figure 1. Figure 1a and figure 1b show TEM images for the Fe-Ni nanoparticles supported on dolomite. The size of the catalyst particles ranges between 20-40 nm. Figure 1c and figure 1d show TEM images for Fe-Ni nanoparticles supported on alumina. The size of the catalyst particles Fe-Ni/Al_2O_3 ranges between 4-20 nm. TEM results indicate the formation of nano- catalyst particles over both catalysts.

Biomass gasification

Effect of Catalyst: For gasification without catalyst (EX1), the volume of the gas produced was about 297 ml and the volume percentages of H_2, CO, CH_4 and CO_2 are 44.3%, 33.5 %, 6.2 % and 15.3 % respectively. However, when the Fe-Ni/dolomite catalyst was used (EX2), the volume of the gas produced was increased to 320 ml and the composition of the gas was changed. The percentage of H_2 in the gas increased to 60%, while that of CO decreased to 7.5% and the CO_2 increased to 25% and the CH_4 ratio was nearly remained constant as illustrated in figure 2.

Table 1
Elemental Analysis of biomass samples (wt %)

Biomass type	N %	C %	H %	O %	S %
Cotton Stalk	0.9	45	6	44	0.6

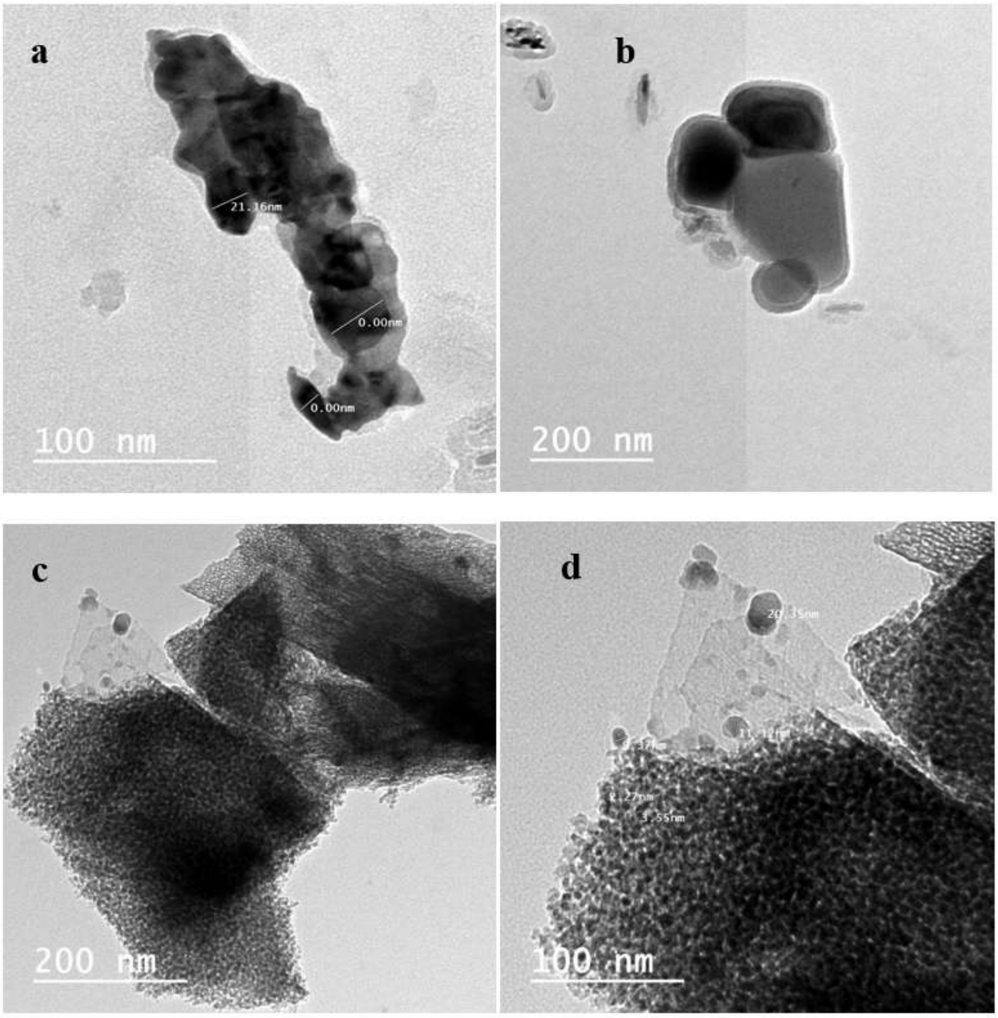

Figure 1: TEM images for the Fe-Ni bimetallic nano-catalyst, (a, b) supported on Dolomite and (c, d) supported on Alumina

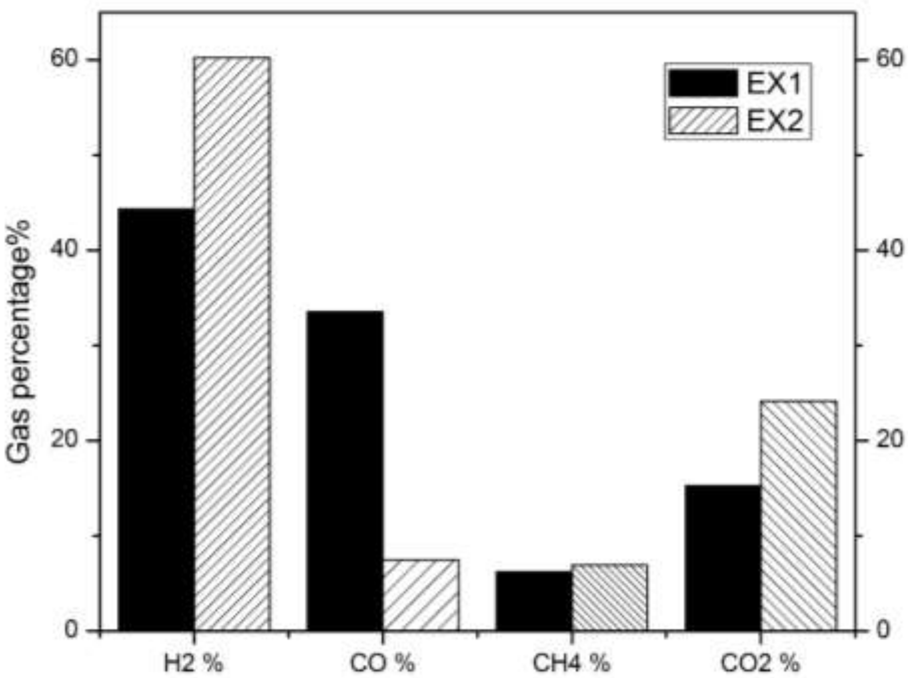

Figure 2: Effect of Fe-Ni/Dolomite catalyst on the percentage of gases produced from biomass gasification

Using Fe-Ni/Alumina (EX3), the volume of the gas was 320 ml and the H_2 percentage sharply decreased to 25.4 %. On the other hand, the percentage of CO was significantly increased to 57% while the CH_4 and CO_2 ratio decreased to 4% and 13.4 %, respectively as illustrated in figure 3. Figures 2 and 3 indicate that catalysts have improved the overall gas yield. In addition, the catalyst has affected remarkably the composition of the produced gas.

Support effect: By comparing Fe-Ni/Dolomite catalyst (EX2) and Fe-Ni/Alumina catalyst (EX3) experiments, same yield of gas was obtained in both experiments (320 ml). However, the composition of the produced gas was significantly different. Using Fe-Ni/Dolomite catalyst (EX2), H_2 volume percentage was about 60% compared to 25% obtained with Fe-Ni/Alumina catalyst (EX3). Using Fe-Ni/Dolomite catalyst (EX2), CO volume percentage was about 7.5% compared to 55% obtained using Fe-Ni/Alumina catalyst (EX3). The results indicate that hydrogen production is more favored when Fe-Ni/Dolomite is used. In case of Fe-Ni/Alumina catalyst, the carbon monoxide production is more favored as illustrated in figure 4.

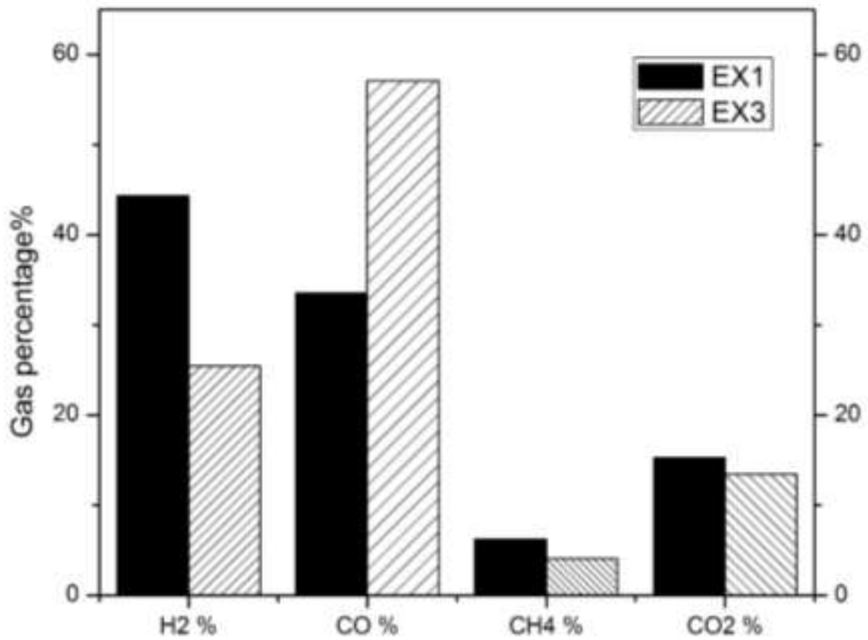

Figure 3: Effect of Fe-Ni/Alumina catalyst on the percentage of gases produced from biomass gasification

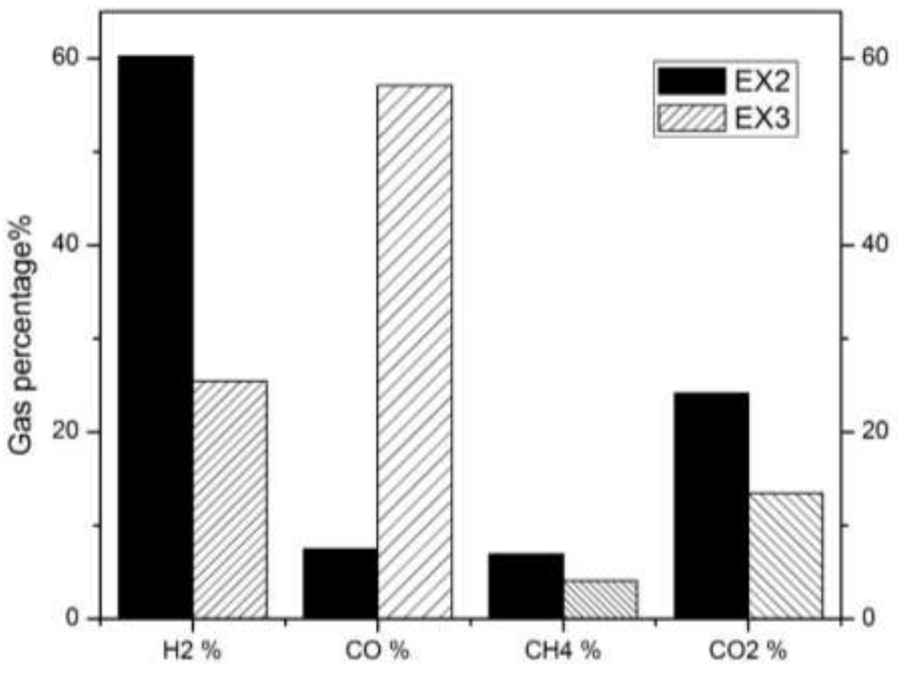

Figure 4: Effect of using Fe-Ni/Dolomite catalyst compared to Fe-Ni/Alumina catalyst on the composition of gases produced from biomass gasification

Conclusion

The effect of iron and nickel nano-particles as a bimetallic catalyst on cotton stalks gasification process using air as gasification medium was studied. The effect of the catalyst on gas yield from biomass as well as the gas composition was investigated. TEM has indicated the formation of nano-catalyst particles for both catalysts. The gasification results showed that both catalysts have increased overall gas yield to 320 ml compared to 297 ml non-catalytic gasification (for 0.5 gm of cotton stalks).

The catalyst has affected the produced gas composition. Hydrogen production is more favored when Fe-Ni/Dolomite catalyst is used. While carbon monoxide production is more favored when Fe-Ni/Alumina catalyst is used.

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