Biomass pyrolysis and in line air-steam reforming as a potential strategy to progress towards sustainable ammonia production

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Highlights

- An environmentally friendly NH_3 production process from biomass was proposed
- A H_2/N_2 ratio above 3 was obtained under autothermal conditions
- The results evidence the potential of biomass pyrolysis reforming for NH_3 synthesis

1. Introduction

The steady growth in world population has increased the need for ammonia-derived products, especially fertilizers [1]. Current ammonia production is highly energy intensive and emits huge amounts of CO_2 due to the use of natural gas [2]. Therefore, progress on the sustainability of the process is urgently required. Biomass pyrolysis and in-line oxidative-steam reforming (P+OSR), using air as oxidizing agent is an encouraging process for the renewable and sustainable ammonia production. Thus, this work studies the potential of this process to produce a stream containing H_2 and N_2 (from the air) in a 3:1 ratio suitable for the Haber-Bosh process.

2. Methods

First, the thermodynamic assessment was performed to ascertain the most suitable ER (Equivalence Ratio) to obtain a gas stream with a suitable H_2/N_2 ratio. The simulations of the process were carried out using AVEVA Pro II software by varying the amount of air incorporated into the inlet stream of the reformer of biomass volatiles. Thus, the thermodynamic analysis was conducted based on Gibbs free energy minimization method, which is based on solving material and energy balance corresponding to equilibrium conditions.

The basis considered in the simulation was 100 kg h^{-1} of biomass (pine sawdust) fed into the pyrolysis-reforming process, however only the volatile stream of pyrolysis products (gases and bio-oil) is fed into the reforming reactor (Gibbs free reactor). The composition of the volatile stream was that obtained in a previous experimental biomass pyrolysis study carried out using the same reactor and conditions to the one followed in this experimental study [3]. Furthermore, the inlet stream of the reforming reactor contained also air and steam, with their amounts being fixed by ER (calculated with respect to the volatiles introduced into the reforming stage) and steam/biomass (S/B) ratios. Thus, while the S/B ratio and temperature were remained constant (3 and 600 ºC, respectively), the influence of air was examined for ER values ranging 0.13 to 0.17. ER values lower than 0.13 were not considered in the simulation because it is the minimum ER required for autothermal operation [4].

Based on the simulation results, the integrated process of biomass pyrolysis and in line air-steam reforming (P+OSR) was conducted in a bench-scale plant, which combines a conical spouted bed reactor (CSBR), where the pyrolysis takes place, and a fluidized bed reactor (FBR) in which occurs the catalytic air-steam reforming of the volatiles.

Pine sawdust (1-2 mm) was used as raw material. ReforMax® 330 commercial catalyst was employed in the reforming step, which contains 14 wt% NiO supported on Ca doped alumina. The experimental conditions was selected in accordance to the results obtained in the previous thermodynamic study. Thus, the temperature in the pyrolysis and steam reforming reactors were 500 °C and 600 °C, respectively. The experiments were carried out by continuously feeding 1 g·min^{-1} of biomass, with a S/B ratio of 3 and a space time of 15 $g_{catalyst}·min·g_{volatiles}^{-1}$. It is to note that this space time results in nearly complete conversion of the biomass derived volatiles [5], so enables to compare the experimental results with those obtained from equilibrium simulation. The effect of air addition was analyzed using different ER ratios (0.13, 0.15 and 0.17). The volatile stream leaving the reforming reactor was quantified in-line by means of a GC Varian 3900, whereas the permanent gases were analyzed off-line in a microGC (Varian 4900).

3. Results and discussion

The simulation replicates the typical reactor arrangement used in industrial processes, which usually adds shift reactors in series (P-OSR+shift) to maximizing the H_2 production, as all the produced CO was fully converted into H_2 and CO_2 through Water Gas Shift reaction. Thus, as showed in Figure 1, an increase in ER resulted in a decrease in the H_2/N_2 ratio. This can be attributed to two factors, i.e., the promotion of oxidation reactions, which are detrimental for H_2 production, and the addition of a higher amount of N_2 into the reforming step. Concerning the two reactor configurations (Figure 1a), P-SR+shift provided slightly higher H_2/N_2 ratios, which in fact includes the shift reactor specifically used in industry for H_2 production. However, regardless of the configuration, a suitable H_2/N_2 ratio (>3) required for the ammonia production is attained with ER=0.13, which corresponds to autothermal conditions at 600 ºC with S/B=3, according to the assess of the reaction enthalpy which has been also made. Nevertheless, it should be pointed out that ER=0.15 led to the attainment of an almost optimum H_2/N_2 ratio (3) when the shift reactor is used. In respect of the experimental results of the Figure 1b, which are the theoretical results after converting the produced CO into CO_2 and H_2, a H_2/N_2 ratio above 3 was achieved under autothermal conditions (ER=0.13), which confirms the potential of this process for producing an adequate gas stream for ammonia production in a sustainable manner.

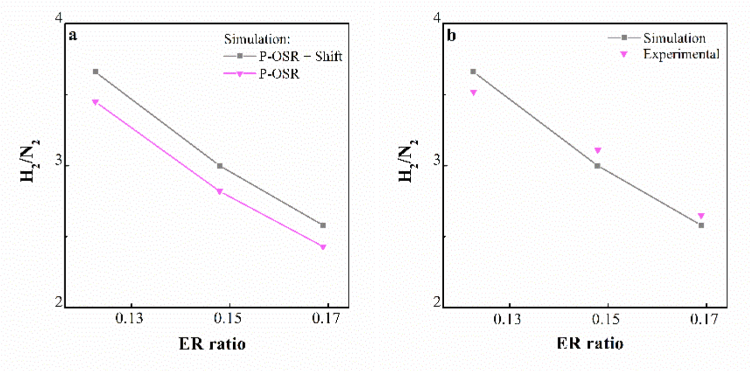

Figure 1. H_2/N_2 ratios in the air-steam reforming of biomass pyrolysis volatiles at different ER ratios: a) using simulated P-OSR and P-OSR+shift configuration and b) when the CO shift reaction is considered to the both cases (simulation and experimental).

4. Conclusions

Overall, the integration of biomass pyrolysis and in-line air-steam reforming into the Harber-Bosch process is a promising alternative to address the environmental concerns related to the conventional processes for H_2 production, as it contributes to pursuing renewable and sustainable ammonia production. This innovative process allows attaining yields of up to 558 g NH_3 $kg_{biomass}^{-1}$, making it a highly efficient and environmentally friendly approach.

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Keywords
Ammonia; Hydrogen; Biomass; Air-steam reforming