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The Department of Energy's Hydrogen, Fuel Cells, Infrastructure and Technology program's Technology Validation activity is demonstrating hydrogen production systems. In addition to demonstrating the technologies, the projects provide data on the efficiency and economics. The data collected from a facility are evaluated for comparison to targets established in the multi-year program plan [1]. The objective of this project is to provide consistent analysis of the hydrogen systems being demonstrated. To perform the analysis, we have developed a library of components in the Simulink [2] language that are assembled into system models.

This quarterly report describes preliminary analysis of a process that uses biomass to produce hydrogen with fertilizer as a co-product. The process is being demonstrated by Day *et al* [3], using peanut shells as the biomass feedstock. Background material on the pyrolysis and reforming processes is provided by Evans and Czernik [4]. While the hydrogen yield of the original peanut shell pyrolysis demonstration was relatively low (4% H2 by mass), the potential benefits of the co-product sales and the elimination of the waste peanut shells make the process interesting.

The schematic of the process as analyzed is shown in Figure 1. The upper section of the schematic depicts the conversion of the biomass into hydrogen by pyrolysis and steam reforming. The lower section of the schematic shows the integrated production of ammonia for combination with the char to produce a slow-release fertilizer.

The model of pyrolysis and reforming follows the engineering experiments described by Evans and Czernik [4]. The biomass is heated by mixing and entrainment with the products of propane combustion. In the model, the amount of stoichiometric propane/air mixture is determined by the pyrolysis temperature. The model represents the pyrolysis reactor using chemical equilibrium. The thermodynamic properties of the biomass are approximated using the heating value of 19 MJ/kg, which is representative of wood chips, and a chemical composition approximated by $C_{10}H_{13}O_7$. The char formed by pyrolysis is represented by solid carbon. Figure 2 shows the variations in the fraction of the biomass that remains as char and the net heat that must be added to maintain the reaction at a constant temperature. At the nominal pyrolysis temperature of 823 K (550 C), the reaction is slightly exothermic, and the char fraction is a little above 30% (by mass). This char fraction is consistent with the experimentally observed range of 28 to 31% [4].

The gas mixture from the pyrolysis stage is mixed with steam, which provides thermal energy and additional hydrogen for the reforming step, as shown in Figure 1. The reforming reaction is simulated by chemical equilibrium at the nominal temperature of 850 C, with an additional water-gas shift reaction imposed on the resulting mixture (not shown in schematic). For a steam flowrate equal to the biomass input rate, the resulting steam-to-carbon ratio is 3.9, consistent with the measured values in the range 3.2 to 4, and the hydrogen yield is 6.1% of the biomass feed, consistent with the measured values in the range 5.6 to 6.7% [4]. The comparisons to the experimental conditions show that the chemical equilibrium model simulates the catalytic reactors for both pyrolysis and reforming within a reasonable approximation. Note that a hydrogen yield of about 11% can be obtained by running the pyrolysis reactor at higher temperature. However, the low-temperature char has the right material properties for use as a fertilizer [3].

In order to produce ammonia to combine with the char for fertilizer, separation of hydrogen and nitrogen are modeled in the second row of the schematic in Figure 1. The mixture is compressed to 200 atm and heated to 500 C. Chemical equilibrium predicts the ammonia yield at these conditions to be 27% (by mass), which is consistent with the range of per-pass conversion rates of 10 to 35% reported by Spath and Dayton [5]. After the ammonia is separated, the remaining hydrogen and nitrogen can be recycled to the compressor (not shown in the schematic) and reused in subsequent passes. Matching the production of ammonia and char to the proportions of the fertilizer [3] leads to a net hydrogen yield of 4.3% (by mass) from the original biomass source.

The model approximates the heat integration between the biomass pyrolysis and the ammonia production. The hydrogen production requires a net heat of 2.9 MJ per kg of biomass processed. Assuming ideal heat exchange, potentially half of the heat requirement, 1.7 MJ, can be offset by the exothermic ammonia process. The remaining heat is assumed to be provided by combustion of an extra quantity of the biomass; in this case some 6% extra biomass is required to balance the energy. The largest heat load is the requirement of providing the superheated steam to drive the reforming step: 4.5 MJ/kg of biomass processed for the steam-to-carbon ratio of 3.9. Since steam-to-carbon ratios as high as 5 may be necessary in practice [4], this load could increase.

The heat required to drive the endothermic conversion steps makes the thermodynamic efficiency of the process relatively low. Considering the hydrogen production alone, the 6.1% hydrogen yield on the pyrolysis/reforming process has a thermal efficiency of about 22%, based on the lower heating values. The potential offset of the reforming heat from integrating the ammonia production increases the efficiency to 29%. These efficiency estimates include the electrical work required to power compressors for the hydrogen/nitrogen mixture and perform separations of hydrogen, nitrogen, and ammonia. The relatively low process efficiency may be considered acceptable if the economic and environmental benefits of the process prove favorable.

The economic analysis of the cost-of-hydrogen produced from the integrated plant depends on the capital cost, the feedstock cost of the biomass, and the sale price of the fertilizer. The cost of the biomass feed is 40 \$/ton [7, 8], which assumes there are processing and drying costs even for biomass residues. The capital cost of the integrated process contains a high degree of uncertainty, because such a plant has not been demonstrated. Capital costs for a pyrolysis-oil reforming station are provided by Mann [6] for a 1500 kg-H_2/day facility. At the hydrogen yields considered here, that would amount to 25 tons of biomass per day. Using this facility as a basis, but adding capital for the pyrolysis reactor, the capital cost of the hydrogen production is estimated to be 3.7 M\$. The largest uncertainty is the additional capital cost of the ammonia production facility. Based on handbook correlations for ammonia plants [9], we estimate an additional 1.7 M\$ in capital cost for the additional equipment, bringing the total capital cost of the integrated plant to 5.4 M\$. Operation and maintenance costs are simply scaled to the capital by 10% per year. The other economic analysis parameters use the default values consistent with the H2A methodology [10].

To estimate the value of the novel slow-release fertilizer, an ammonia price of 1500 \$/ton is used, based on the market price of 600 \$/ton for urea, which is about 40% nitrogen [8]. This approximation yields a credit of 3.25 \$/kg of hydrogen for the co-product ammonia/char fertilizer. The break-down of the cost-of-hydrogen is shown in the table below. While the combination of capital and O-&-M is the largest contribution, the co-product credit is next, being about twice the electricity and biomass costs combined. Nevertheless, the net hydrogen cost is above 3 \$/kg.

	H_2 Cost (\$/kg)
Capital + O&M	4.85
Biomass feed	0.94
Electricity	0.63
Co-product credit	-3.27
Net H2 Cost	3.15

Parameter studies on the costs of capital equipment and the biomass feedstock show that the net hydrogen cost is a simple linear function of these variables. The hydrogen cost increases 52 cents for each million dollars in capital cost. The hydrogen cost increases 23 cents for each 10 \$/ton increase in the cost of biomass feed. For example, if the minimum biomass cost was reduced from the nominal value of 40 \$/ton to the minimum value of 10 \$/ton suggested by Spath *et al* [7], the net hydrogen cost would be reduced by 69 cents to 2.46 \$/kg.

Given the large contribution of both the capital cost, and the co-product credit, future efforts will attempt to obtain estimates with less uncertainty. In addition, future analyses are planned to compare this process to gasification processes, including the alternative of making ethanol by a thermochemical process from the syngas instead of hydrogen.

References

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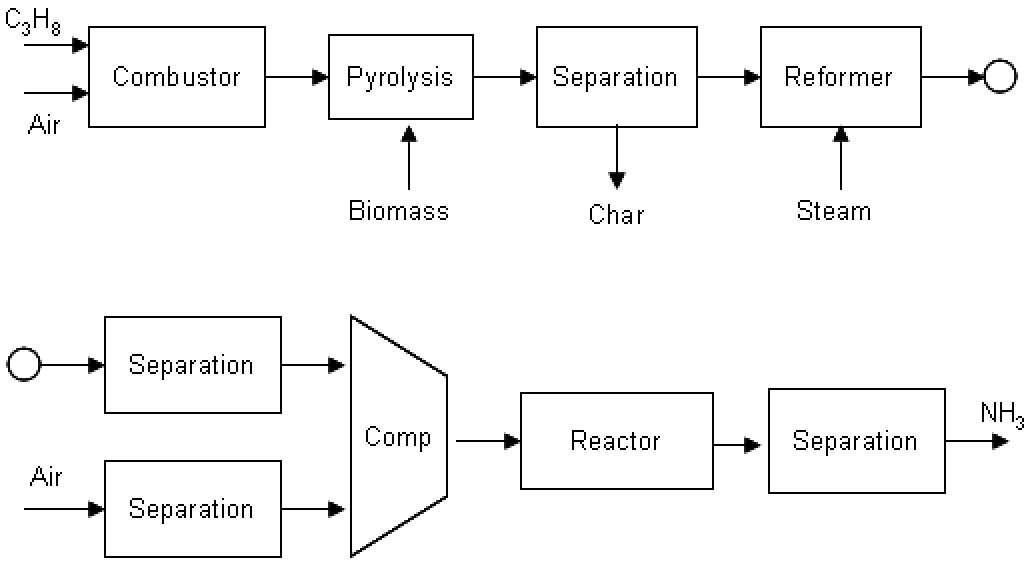

Figure 1. Schematic of the biomass pyrolysis process with ammonia production.

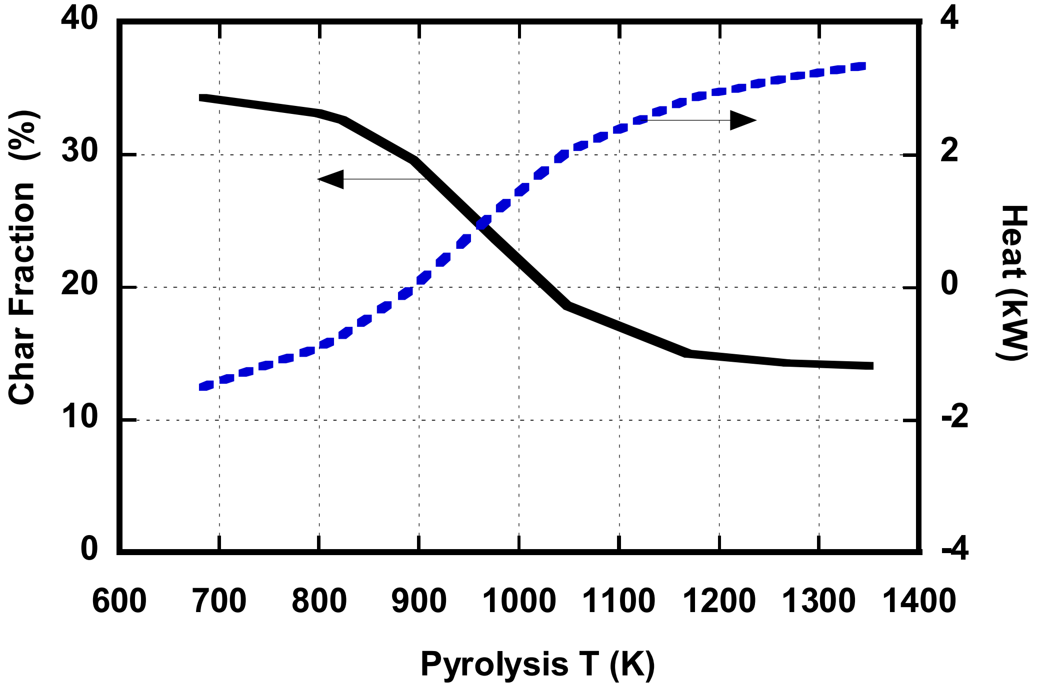

Figure 2. Model predictions of the char fraction (solid curve) as a percentage of biomass weight and heat (dashed curve) as a function of pyrolysis temperature. Net heat is positive when heat input is required to reach equilibrium at the fixed temperature.