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Sandia National Laboratories
Hydrogen System Engineering (Power Parks)
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H2 Program Progress Report Author: Andy Lutz

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 necessary to evaluate the efficiency and economics of hydrogen production 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.

The previous quarterly report described simulations of hydrogen production by pyrolysis and reforming, with comparison to experiments [3]. Following that analysis of pyrolysis, the analysis this quarter focused on a set of gasification experiments [4], in preparation for simulations of a process being pursued at the Hawaii Natural Energy Institute (HNEI).

Analysis of Biomass Gasification

The analysis this quarter focused on the equilibrium model of the gasification stage of the hydrogen production system. To establish the validity of the approach, the gas composition measured in experiments by Turns *et al* [4] are compared to computations of chemical equilibrium. Previous analysis established the validity of the equilibrium model for steam reforming [5] and pyrolysis [6], including the ability to model the fraction of char remaining from the pyrolysis.

Gasification is distinguished from pyrolysis in that air, or molecular oxygen, is included in the mixture to help the process of breaking apart the hydrocarbons in the biomass. There is concern that gasification may not approach chemical equilibrium at the temperatures of interest. The experiments controlled the temperature and the flows of biomass, oxygen, nitrogen, and steam. The oxygen and nitrogen were not mixed in the proportions of air, but the nitrogen was mainly added as a diluent, and to maintain nearly constant flow rates through the experimental reactor. The experiments included trials with individual parameter variations that examine the effects of temperature, steam, and oxygen. The variation of steam is quantified by the steam-to-biomass ratio (defined on a mass basis), where for a representative approximation to biomass the reaction

$$CH_{1.3}O_{0.7} + 1.3\ H_2O \rightarrow CO_2 + 1.95\ H_2$$

gives an ideal steam-to-biomass ratio of approximately 1. Practical operation requires more steam than this to allow for incomplete mixing and reaction.

The steam necessary to completely oxidize the carbon also depends on how much oxygen is present in the mixture. Combustion of the biomass follows the reaction.

$$CH_{1.3}O_{0.7} + 1.95\ O_2 \rightarrow CO_2 + 0.65\ H_2O$$

Following Turns *et al* [4] the equivalence ratio is defined as the actual oxygen-to-fuel ratio divided by the stoichiometric oxygen-to-fuel ratio. By this definition, equivalence ratios in the range $0 < ER < 0.4$ are fuel rich in that there is not enough oxygen present to completely oxidize the fuel (combustion literature often uses the inverse definition).

Figures 1 to 3 compare computations of chemical equilibrium (curves) to the experimental data (symbols). These compositions are for the gas mixture after gasification and removal of water and nitrogen. Taking the variations of equivalence ratio and steam-to-biomass ratio together, the trends of hydrogen, carbon dioxide, and carbon monoxide are captured with reasonable agreement. However, chemical equilibrium does not predict any methane formation at these conditions. The presence of methane at up to 10% in the experimental gas samples suggests that there are kinetic limitations on the conversion of methane.

The comparison in Figure 3 suggests that the temperature may play a role in understanding the departure from chemical equilibrium. The computations are extended to much lower equilibrium temperature, in order to find out if methane is predicted at any temperature. About 10% methane appears in the equilibrium mixture at about 500°C. In some cases, departures from equilibrium can be modeled by simply reducing the temperature input to the equilibrium solution by a temperature "offset". However, the temperature difference here is too large (nearly 250°C) to justify this approach.

A final comparison between the experiments and equilibrium solutions that is not shown in the figures is the amount of the biomass lost to char and/or tar formation. The experiments noted some char and tar formation, but did not measure these quantitatively. In contrast, the equilibrium solutions did not indicate that any solid carbon species (representing char) should exist at these conditions. The equilibrium model is capable of predicting about the right amount of char under pyrolysis conditions, but it appears that the presence of oxygen, either in the form of molecular oxygen or steam, moves the equilibrium away from solid carbon formation.

Future Activities

Future analysis of the gasification process will include a kinetic parameter, such as a reaction progress variable, that can be adjusted to capture the amount of char formation in the gasification reactor. Using this modification, a complete system model will be developed, based on the process being pursued by HNEI. The system model will be used to perform economic analysis for the cost of hydrogen from biomass gasification, for comparison with the targets in the DOE Multi-Year Program Plan.

References

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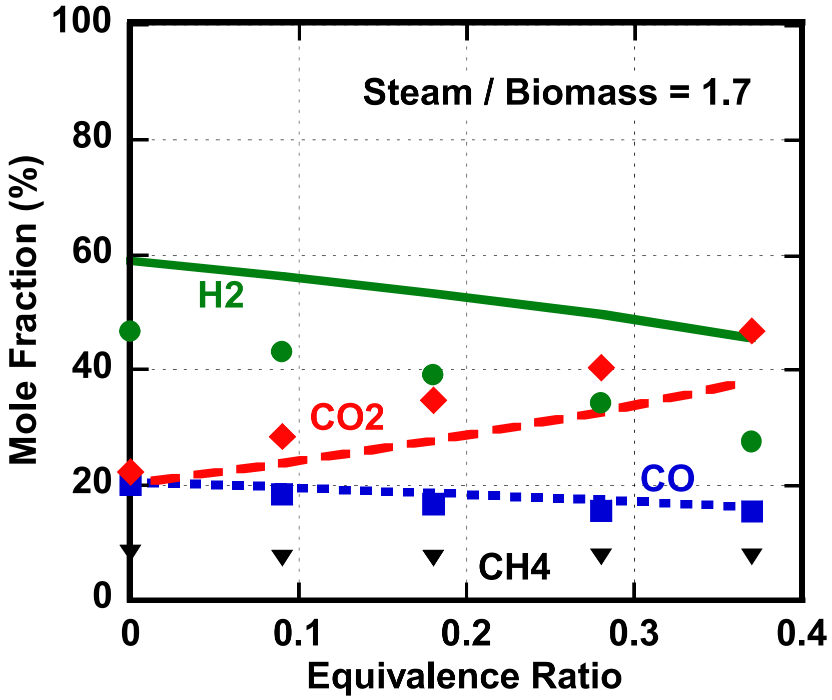

Figure 1. Species mole fraction from the gasification of biomass at 850°C, steam-to-biomass ratio of 1.7 (by mass), and varying equilivalence ratio. Curves are chemical equilibrium; symbols are experimental data from Turns et al [4].

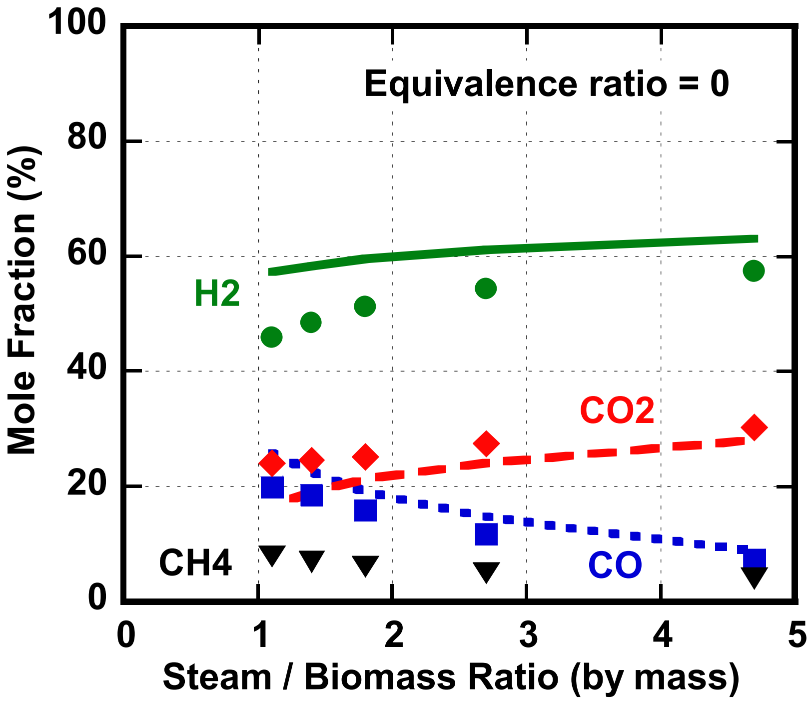

Figure 2. Species mole fraction from the gasification of biomass at 800°C, equilivalence ratio of zero (no oxygen) and varying steam-to-biomass ratio. Curves are chemical equilibrium; symbols are experimental data from Turns et al [4].

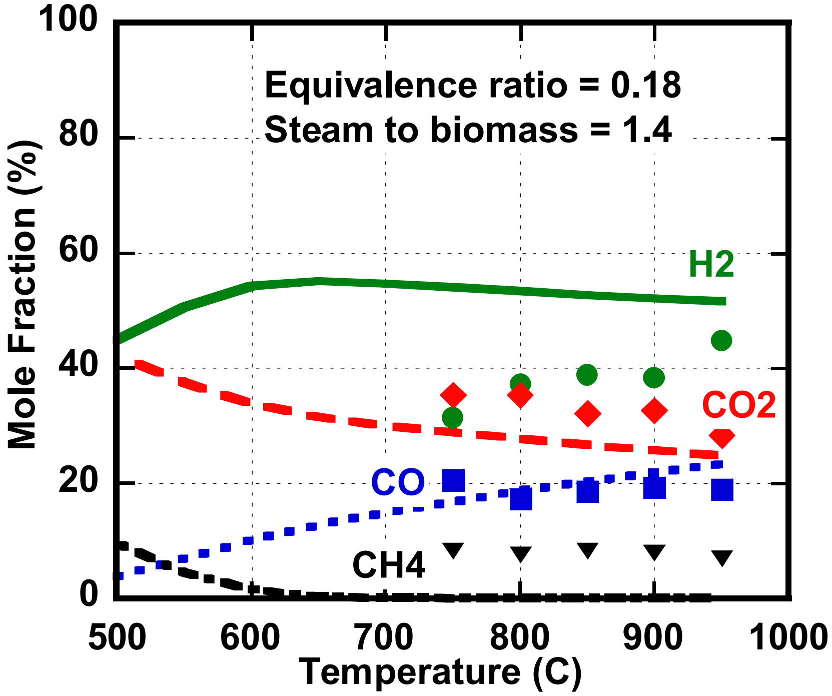

Figure 3. Species mole fraction from the gasification of biomass at equivalence ratio of 0.18, steam-to-biomass ratio of 1.4 (by mass) and varying temperature. Curves are chemical equilibrium; symbols are experimental data from Turns et al [4].