

High-temperature sorbents for desulfurization of biomass-derived syngas

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Introduction

The current focus of biomass conversion research and development is to produce fuel derived from cellulosic biomass, especially waste biomass or feedstock grown on marginal lands that generate little carbon today. Gasification of biomass feedstock to generate syngas for further downstream fuel synthesis is a viable and promising approach. Biomass feedstocks contain low percentages of protein-derived sulfur which is converted primarily to H_2S during gasification. The H_2S concentrations, on a dry basis, in biomass-derived syngas range from about 20–50 ppmv for hardwood to 500–600 ppmv for corn stover. The sulfur content of the syngas needs to be removed because it deactivates catalysts used downstream and is corrosive.

High temperature removal of H_2S offers the potential of better thermal efficiency in the overall biomass gasification to fuels process, reduced waste stream generation, and lower biofuel production cost than the use of a conventional amine-scrubbing process. Several types of sorbents have been developed over the last two decades to remove H_2S from dry coal-derived syngas at mid- to high- temperature ranges [1]. However, further research is necessary because biomass syngas contains much higher steam and hydrocarbon content than coal syngas. The work presented here used materials developed for coal syngas desulfurization as a starting point to begin sorbent development for biomass syngas desulfurization.

Materials and Methods

Several zinc-, manganese-, and ceria- based sorbents were studied. The goals of these experiments were to establish a set of process boundaries where the sorbents would function in an environment simulating biomass-derived syngas, to understand the mechanism of sulfur removal, and to design sorbents specific to biomass-derived syngas. The composition of the syngas used for reaction studies was modeled after that produced from hardwood gasification in the 0.5 ton per day thermochemical biomass conversion pilot plant at the National Renewable Energy Laboratory (NREL).

The sorbents were tested in a microactivity test system equipped with on-line gas analyzers. The sorbent, supported on quartz wool, was packed into a one-inch diameter quartz tube which functions as a downflow packed reactor. Mass flow controllers provided precise gas flow rates and the reactant gas of desired composition was mixed in a gas manifold just prior to entering the quartz reactor tube. Steam was introduced to the system via an HPLC pump and ultrasonic nozzle set up. The reactor tube was heated by a rapid heating furnace. Reactant gases and steam exiting the reactor tube were cooled in a condenser to remove water vapor and condensable materials. A Nafion membrane drier with nitrogen as a sweep gas was used downstream of the condenser to remove additional moisture from the exit gas stream. The exit

gas was analyzed by a Varian CP4900 Micro-GC equipped with four columns that provided permanent gas, hydrocarbon, and sulfur species analyses.

Steam, when present, was typically at 62 volume %, similar to the conditions used in the pilot plant. Gas containing steam is denoted “wet” in the Results and Discussion session. The total steam to carbon ratio was $\text{S:C} = 5:1$. The H_2S concentrations selected for the experiments were 99.5 to 995 ppmv on a dry basis, which bracket the concentrations of H_2S found in biomass-derived syngas while offering a range suitable for both studying breakthrough phenomena and obtaining initial mechanistic process understanding. The experimental results were modeled using HSC Chemistry software.

Results and Discussion

A zinc oxide-based material was able to lower H_2S concentrations efficiently from an input gas stream which contained 544 ppmv H_2S on a dry basis. Another zinc-based material, zinc titanate, showed limited performance in both an inert gas environment and model syngas that contained steam. A manganese sorbent was efficient in wet nitrogen (Figure 1), dry nitrogen, and dry syngas environments at 650 °C. However, this material did not perform well in wet syngas (Figure 1). A ceria-based material also showed promise for sulfur sorption. We are conducting further experiments and modeling to elucidate the differences in sorption efficiency in different environments and to improve sorbents performance.

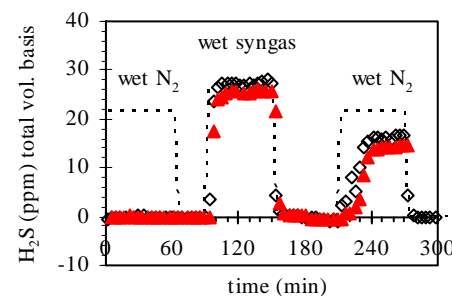


Figure 1. H_2S concentrations in outlet process gas (symbols) with manganese sorbent in 62% steam and 650 °C as a function of wet inert versus wet syngas environments. Dashed line is the “effective” H_2S concentrations at the sorbent bed. The open diamonds and solid triangles are duplicate experiments.

Significance

This work demonstrates that removing gas phase sulfur species from biomass-derived syngas using mid- to high- temperature sorbents is a viable approach though further research is necessary to design sorbents that can operate in the high steam, high hydrocarbon environments specific to biomass-derived syngas generated via indirect steam gasification.

References

1. Torres, W., Pansare, S.S., and Goodwin, J.G., Jr., *Catalysis Reviews* 49, 407 (2007).