

Biofuels from Biomass by Catalytic Autothermal Reforming

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Goal

Systematically examine the catalytic partial oxidation in millisecond autothermal reactors of solid biomass and the liquid products formed by pyrolysis of solid biomass. Alcohols, polyols, esters, solid carbohydrates, and lignocellulose will be studied to try to maximize formation of either hydrogen and syngas or olefins and oxygenated chemicals.

DOE Interest

Renewable fuels will play an increasing role in US energy demands. This research explores the fundamental catalysis of conversion of solid and liquid and liquid biomass into useful fuels by catalytic autothermal reforming at millisecond contact times.

Recent Progress

Spatial Profiles in Millisecond Reactors. We have within the past two years developed a technique to measure spatial profiles within the working catalyst with minimal disruption of flow and temperature profiles. In the technique we developed, we drill a 650 μm hole in the ceramic monolith and fill the hole with a 600 μm quartz capillary (a GC capillary). The capillary protrudes above the catalyst to completely block gas bypass. One end of the capillary is sealed off and the other end leads to a computer driven motor drive assembly through which thermocouple (gas temperature) and a quartz optical fiber (surface temperature) can be inserted. A 200 μm hole is ground in the side of the capillary for gas sampling, and the capillary fiber also leads to a differentially pumped quadrupole mass spectrometer for gas composition measurements.

Autothermal Reforming of Bio Liquids. We have also examined many catalysts and supports for these reactions. Generally we find that Rh is the most robust catalyst and that Ce addition can improve syngas yields by several percent. Pt makes more olefins, and other metals such as Ni exhibit narrower windows of operation, generally because of formation of carbon and metal oxides. We have examined several supports including foam monoliths of alumina, zirconia, aluminosilicate, and fercalloy. We have also done extensive characterization of catalysts by microscopy, XPS, XRD, and surface area measurements. While optimizing catalysts and morphologies help define and optimize the catalyst, our major emphasis in this research program is to explore the **reaction engineering** and the **reaction chemistry** that enables extension of autothermal catalytic processes to more interesting and valuable applications involving biomass.

Autothermal reforming of Solid Biomass. Within the past two years we have successfully reformed solid biomass particles using related techniques. We have used Avacil cellulose (a food grade of 500 μm cellulose particles), as well as sugar, starch, lignocellulose (aspen wood), and polyethylene particles (not biomass but interesting as a prototype for plastics recycling). The process also involves reactive flash volatilization as with bio liquids, but the delivery and mixing methods are entirely different. Solids are fed from a hopper through a screw drive and mixed with air or O_2 to form a uniform distribution of particles in air or O_2 that then impact the hot front face of the catalyst where they almost instantly decompose and volatilize. As with liquids, we have successfully reformed these solids into nearly equilibrium syngas for $\text{C}/\text{O} < 1$ with no higher products formed and no carbon accumulation on the catalyst for periods of at least 24 hours.

Future Plans

We plan to continue research on each of these topics. Spatial profiles will be examined for more complex biomass systems to identify the intermediate species produced and the reaction networks involved. For bio oils we will examine more complex liquids to determine the products formed and their mechanisms for different reactant functional groups to determine the reactivity of mixtures. For solids we will examine components of lignocellulose to determine strategies for biomass gasification to particular products.

Publications (2007-2009)

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