Biomass Gasification Research in the SEAS Combustion and Catalysis Lab

One of the goals of the Combustion and Catalysis group at Columbia SEAS is to develop environmentally benign technologies that use alternative and unconventional sources to produce a sustainable energy supply. We are investigating CO₂ management strategies that can mitigate GHG emissions contributing to global warming. One of the current areas of investigation to produce a carbon-free energy source is the development of fuel processing technologies that combine catalytic combustion with gasification of biomass feedstocks to produce H₂ and electricity.

In the U.S., renewable energy accounts for only a few percent of the total energy consumption with one third of the renewable sources attributable to woods, grasses, and agricultural and forestry wastes and residues. Woody biomass includes trees, shrubs and bushes. Non-woody biomass includes grasses, straw, stems, roots, leaves, water plants, starchy fruits such as bananas and plantains, fibrous seed plants such as cotton, fleshy root plants such as cassava, and energy crops such as sugarcane. The plant material typically used as biomass fuel includes fast growing trees (having a high energy density, simple genetic composition and cultivated to be disease resistant and environmentally tolerant), woods, grasses, grains, vegetable plant oils, agricultural residues, forestry residues, and food processing waste such as nuts, seeds, shells and cereal husks and corn cobs. Through Atomic Absorption Spectroscopy and Scanning Electron Microscope-Energy Dispersion X-Ray Spectroscopy we have observed significant differences in the chemical composition of woods and grasses from the analyses of the pre- and post-combusted biomass feedstocks. The molecular composition of woods and grasses is similar since they are both ligno-cellulosic in structure.

Biomass fuels, that constitute one group of the more promising renewable energy sources available, can alleviate the immediate need to meet increasing energy demands in an environmentally responsible way. The thermal processing of plant biomass, whether by pyrolysis, gasification or combustion involves returning to the environment the carbon that has been removed during the growth of the tree or grass. For this reason biomass is considered a carbon neutral energy source. Considering the viability, growth and sustainability of emerging economies, the international community is looking to biomass as a means by which rural infrastructure can be developed through job creation, land reclamation and the economics of co-production of energy and food crops.

Hydrocarbons produced from biomass can help alleviate the energy shortage by serving as an alternate source of energy and chemicals as fossil fuel reserves become depleted. Low energy intensive agriculture such as biomass from agricultural waste and fast growing disease resistant trees are promising feedstocks to fuel future biorefineries just as fossil fuels currently feed petroleum refineries. Biomass can be used to generate synthesis gas for production of methanol or liquid hydrocarbons that can be processed into a wide variety of fuels and petrochemicals.

The thermo-chemical conversion treatment of the biomass feedstocks that we have been investigating include the processes of pyrolysis and gasification. Pyrolysis involves the breakdown of the biomass by heat in the temperature range of 200-500°C where the majority of mass loss is due to devolatilization and the products include gases, charcoal and liquid bio-oil. Gasification, that is one of the most important energy conversion
processes for biomass fuel production, involves thermal degradation of the pyrolyzed biomass either in the presence of very limited oxygen or in an oxygen-free environment. Temperatures range from 700-1100°C, char oxidation occurs with CO\(_2\) or H\(_2\)O, and the fuel gas product is optimized to produce CO, a minimum of waste CO\(_2\) and H\(_2\)O, and a maximum of H\(_2\).

The gasification process can produce a clean stream of H\(_2\) for use in fuel cells until an alternative technology for production of H\(_2\) possibly involving direct solar conversion becomes economically viable. The H\(_2\) rich, medium heating value synthesis gas is a clean stream with minimum tar, soot and particulates. A knowledge of the competing reactions occurring at the high gasification temperatures allows us to vary those parameters (such as T, p, H\(_2\)O concentration, feedstock, reaction times) that can optimize methane conversion, H\(_2\) production and either power or heat retrieval from the gasification process.

Thermogravimetric analysis of several biomass samples has shown a similar mass decay with increasing temperature. Initial mass loss is due to devolatilization, followed by decomposition and finally char burnout. The result of biomass gasification is the producer gas consisting mainly of CO, H\(_2\) and CH\(_4\). Additional significant volatile products include CO\(_2\), acetic acid, acetaldehyde, phenol, formaldehyde, formic acid and acetone. Depending on the particular composition of the biomass (hemicellulose, cellulose, lignin), varying percents of the evolved gas species are observed.

Gasification using steam results in increased H\(_2\) content of the synthesis gas produced. This is the preferred outcome when a H\(_2\) rather than a CH\(_4\) stream is the desired fuel product. At gasification temperatures, in the 800-1200°C range, the dominant reactions driving the biomass gasification process are the Boudouard reaction

\[ \text{C } + \text{CO}_2 \rightarrow 2\text{CO} \]

the steam gasification reaction

\[ \text{C } + \text{H}_2\text{O} \rightarrow \text{CO } + \text{H}_2 \]

the pyrolysis of the ligno-cellulosic biomass components to release CO and CO\(_2\), the decomposition of oxygenated minerals releasing O\(_2\) and the oxidation of the char to release CO and CO\(_2\). Optimum H\(_2\) production for a given biomass feedstock occurs within the temperature range of 850-1050°C, above which H\(_2\) dissociation competes with H\(_2\) formation to decrease the optimum H\(_2\) yield attainable. We plan to study H\(_2\) evolution as a function of gasification T and p and rate of heating for various amounts of recycled gas to optimize H\(_2\) production. Many competing reactions are occurring at these elevated gasification temperatures, but the thermodynamically favored products are CO and H\(_2\). Enhanced H\(_2\) production is possible either through recycle or injection of CO or CO\(_2\) or through elevated reaction pressures.

Enhanced production of CO and H\(_2\) would indicate improved tar conversion of the biomass material resulting in less residue for waste treatment. This is one area that we would like to investigate in addition to the study of the mineral content of the alkaline residue that has proven to be highly corrosive to the experimental apparatus. High ash content, due to oxidized minerals that we found to be more prevalent in the grasses than in
the woods, can lead to slagging during gasification as a result of melting and agglomeration of the ash residue.

Many biomass fuels contain high mineral content. We found the grasses to possess significant alkali levels, with potassium found as most likely to be responsible for the highly corrosive behavior of grasses as compared to woods. Facilities using biomass fuels have found that the high potassium content posed a potential fouling and slagging problem while high chlorine levels were responsible for low temperature pit corrosion. We have looked into ash residue formation during gasification and combustion of various biofuels and will perform further chemical analyses to better understand the connection between biomass mineral content and suitability as a fuel or energy source.

We are currently looking at enhanced H\textsubscript{2} production from gas recycle, a comparison of gasification products for different woods and grasses, and the connection between variation in chemical composition of biomass feedstock and levels of production of the various evolved gas species from the gasification process. The important physical properties of the biomass fuels that we are investigating include the moisture/volatiles/ash content and the thermal characteristics that include the ash melting temperature, heat capacity, conductivity and heating value. The important chemical properties of the biomass fuels that we are investigating include the levels of K/Na/Cl/F/S responsible for the corrosive behavior, the levels of Mg/Ca/K/Na/Heavy Metals that determine the ash melting behavior, and the feedstock's chemical composition that determines the C : H : O ratio responsible for the fuel's heating value and which is helpful in determining possible reactions or mechanisms that the particular fuel is undergoing as a result of the steam gasification process.

There is an opportunity in the Castaldi Combustion Lab for 3 groups of 3-4 (max) students to conduct biomass gasification research using the Thermogravimetric Analyzer and Gas Chromatograph. The following is a list of activities that need to be performed:

1. For a given biomass feedstock- a literature search of its ligno-cellulosic composition
2. For the particular biomass fuel- several gasification experiments (4-5) for varying levels of CO\textsubscript{2}/N\textsubscript{2}/H\textsubscript{2}O
3. A plot of TGA data for the mass decomposition vs. temperature due to varying amounts of CO\textsubscript{2} gas
4. A plot showing the amount of volatile products detected by the GC (CO, CH\textsubscript{4}, H\textsubscript{2}) as a function of varying levels of CO\textsubscript{2} gas
   The data will be collected, analyzed and plotted in an excel spreadsheet.
5. The final summary will interpret the results of the 4 graphs and give a short description of the chemical composition of the particular feedstock