Influence of CO_2 Injection on Biomass Gasification

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The impact of CO_2 cofeed (0−50% by volume) on steam gasification of biomass was investigated via thermogravimetric analysis−gas chromatography (TGA-GC). H_2, CO_2, CO, and CH_4 gas evolution as a function of temperature were quantified for various S/C and CO_2/C ratios. CO evolution enhancement became significant at temperatures above 700 °C for all woods and grasses studied. H_2 evolution began at temperatures above 450 °C and began to decline above 700 °C. All samples had similar mass decay curves that were completed by 900−1000 °C and were independent of the amount of CO_2 injection. Improved char conversion was observed when CO_2 was present. The biomass fuels and their ash residue were analyzed using atomic absorption spectroscopy (AAS) and scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX). A significant amount of highly corrosive ash residues were observed with no CO_2, yet much smaller volumes were observed when CO_2 was present. Finally, the experimental data was compared to ASPEN simulations to understand the influence of CO_2 recycle for carbon based fuels, and they showed good agreement.

1. Introduction

The need to meet increasing energy demands, while addressing the importance of energy security and environmental impact, has resulted in renewed interest in alternatives to fossil fuels. Biomass constitutes one of the more promising carbon neutral energy sources that can be part of the solution. Since biomass fuels are globally available and do not have the intermittency associated with wind and photovoltaics, and they constitute nearly one-quarter of the fuel available from municipal solid waste, the thermal processing of biomass offers the potential to transition from a fossil fuel driven global economy.[1]

Biomass fuels currently provide 3% of the U. S. energy production, yet nearly one-third of the renewable energy sources in the United States can be attributed to woods, grasses, and agricultural forestry wastes and residues.[2] On the basis of a recent study, biomass has the capacity for supplying 5% of the nation's power by 2030, and biomass-derived fuels have the potential to provide 20% of the U. S. transportation demand.[3] With energy consumption expected to double over the next 40 years and with heightened environmental consciousness as to the need for limiting CO_2 atmospheric emissions, the feasibility of biomass-derived fuels as one of the significant carbon neutral energy solutions has emerged. Making fuels from biomass typically entails thermal treatment.

The thermal treatment of plant-derived fuels can be by either pyrolysis, gasification, or combustion. The complex lignocellulosic structure of biomass renders it more difficult to either gasify or combust. Direct combustion of biomass feedstocks results in fuel-bound nitrogen and sulfur being converted to NO_x and SO_x. Gasification offers the opportunity to control the level of gaseous and particulate emissions, leading to lower concentrations of soot particles, aerosols, NO_x, and SO_x and the production of clean fuel gas or chemical feedstock streams (e.g., H_2, CO, or CH_4). Much of the mass decay during biomass decomposition occurs at lower pyrolysis temperatures. The steam-gasification process enables thermal treatment under a reducing atmosphere that leads to fuel-bound nitrogen release as N_2 and fuel-bound sulfur conversion to H_2S that is more easily removed by means of adsorption beds. Furthermore, introduction of steam in the feed can be used to enhance the H_2 production during the gasification process. There have been numerous studies demonstrating the enhanced H_2 production from carbon based fuels through the use of steam in the gasifying medium. Most of these studies have investigated gaseous evolution from thermal treatment of coal, though several have been in-depth studies of the gasification products for other fuels such as municipal solid waste and biomass.[12−14]

Other reforming enhancements, such as adsorption-enhanced reforming (AER) in which the CO_2 is removed to push the equilibrium forward in the water gas shift (WGS) reaction,

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \Delta H = -41.2\ \text{kJ/mol} \quad (1)$$

are effective strategies to increase hydrogen concentration during steam gasification. Several studies have involved the use of H_2, O_2, Ar, He, air, CO, and CO_2 or a combination of these along with steam to enhance the gasification of the carbon based fuels. Of the several experimental investigations that have been done to study the nature of enhanced steam gasification of biomass feedstocks with CO_2, none have involved an in-depth study of the specific influence of CO_2 concentration on each of the gas species evolved. Presented below are the studies done that are closest to the present work having elements relevant to those in the current investigation.

Iyer et al.[4] studied the gas evolution from adsorption-enhanced steam reforming (AER) of syngas during coal gasification. Their "calcium looping" scheme involved CO_2 and H_2S adsorption onto a reactive proprietary mesoporous precipitated calcium carbonate sorbent (PCC) at high steam-gasification temperatures (700−900 °C). Continuous CO_2 removal resulted in lower CO levels and higher H_2 concentrations. Without regeneration of the sorbent, the higher CO_2 levels led to a reverse WGS reaction with lower H_2 concentration and higher CO concentration. In another study,[5] they observed that the level of CO_2 began to rapidly rise with decreasing adsorption for temperatures 650 and 700 °C and pressures of 1, 10, and 20 atm. This coincided with a rapid drop in the level of CO conversion. This resulted in a corresponding steep decline for all of the H_2 concentration curves as the CO levels abruptly increased.

Bretado et al.[6] performed a thermodynamic analysis for the adsorption-enhanced production of H_2 using a Na_2ZrO_3 adsorbent. A rapid rise in CO_2 levels corresponded to a rise in CO

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