

CO₂ as a Carbon Neutral Fuel Source via Enhanced Biomass Gasification

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The gas evolution, mass decay behavior and energy content of several woods, grasses, and agricultural residues were examined with steam and CO₂ gasification using thermogravimetric analysis and gas chromatography. CO₂ concentrations were varied between 0 and 100% with steam as a coreactant. Carbon conversion was complete with 25% CO₂/75% steam compared to 90% conversion with pure steam in the temperature range of 800–1000 °C. The largest effect was from 0–5% CO₂ introduction where CO concentration increased by a factor of 10 and H₂ decreased by a factor of 3.3 at 900 °C. Increasing CO₂ from 5 to 50% resulted in continued CO increases and H₂ decrease by a factor of 3 at 900 °C. This yielded a H₂/CO ratio that could be adjusted from 5.5 at a 0% CO₂ to 0.25 at a 50% CO₂ concentration. Selection of the gasification parameters, such as heating rate, also enabled greater control in the separation of cellulose from lignin via thermal treatment. 100% CO₂ concentration enabled near complete separation of cellulose from lignin at 380 °C using a 1 °C min⁻¹ heating rate. Similar trends were observed with coal and municipal solid waste (MSW) as feedstock. The likely mechanism is the ability for CO₂ to enhance the pore structure, particularly the micropores, of the residual carbon skeleton after drying and devolatilization providing access for CO₂ to efficiently gasify the solid.

Introduction

Increasing energy demands coupled with a heightened awareness of the influence of various pollutant species on the global climate system, particularly that due to the production of greenhouse gases, have resulted in incentives to develop alternative sources of energy and chemicals to address energy security in an environmentally responsible manner. Biomass fuels constitute promising renewable resources for meeting a significant portion of the demand for energy and transportation fuel production. By suitable control of the gasification process, the gasification medium, and the type of feedstock, the possibility exists for the production of a spectrum of liquid hydrocarbons. An important attribute of biomass, along with its carbon neutral status, is its versatility from a dual polysaccharide (cellulose/hemicellulose) and aromatic (lignin) structure.

While one method of dealing with commercial scale release of CO₂ has been through the development of carbon capture and sequestration technologies, we are investigating

an alternative strategy for dealing with the large CO₂ streams produced as a result of industrial processes. This beneficial use for CO₂ involves its recycling by incorporation into the fuel making process. A potential market for these applications can be created that can globally process tens to hundreds of megatons of CO₂ per year (1, 2). Additionally, thermal processing through CO₂ rather than steam avoids the use of large quantities of water. CO₂ gasification of biomass offers a distinct advantage in enabling a more complete conversion to volatiles at a lower temperature. An immediate reduction of greenhouse gases can be realized in the production of hydrocarbon liquid fuels from renewable resources. If 20% of liquid fuels were produced from carbon neutral sources, such as biomass, the resulting CO₂ emissions reduction would be 15%. Total global CO₂ emissions amount to nearly 29.5 billion metric tons with nearly one-third arising from the transportation sector (3). With the use of 20% biofuels, 15% of this CO₂ production or 1.4 billion metric tons, can be averted through fuel replacement alone. For low temperature gasification of beachgrass we found that incorporation of CO₂ into the fuel making process to satisfy 20% of the 1.07 × 10²⁰ kJ estimated 2008 total transportation energy demand (4), could create a beneficial use for an additional 437 million metric tons of CO₂. For a typical automobile producing 6 t of CO₂/year this would be equivalent to removing 308 million vehicles from the road.

The mass decay curves for both CO₂ and steam gasification of grasses, woods and agricultural and forestry residues all showed gasification behavior intermediate between the extremes of low conversion lignin and high conversion cellulose. Actual feedstocks high in cellulose showed pyrolytic mass decomposition characterized by thermal processing at lower temperatures with smaller quantities of pyrolytic char. Feedstocks high in lignin showed more significant levels of residual pyrolytic char with significant mass decomposition occurring into the gasification range, behavior characteristic of the thermally resistant lignin structural component. However, pyrolysis behavior was not framed by the two extreme decay rates of the cellulose and lignin structural surrogates due to the impurities inherent in any natural lignocellulosic feedstock. Many of the biomass fuels, particularly the herbaceous feedstocks, underwent significant depolymerization much earlier than the pure structural components indicating a possible coupling of the degradation mechanisms and the presence of a catalytic effect similar to that observed by Ye et al. (5). They found catalytic effects to be significant in the CO₂ gasification of coal chars, where the mineral components were chemically bound to the functional groups of the hydrocarbon feedstock.

Research using CO₂ as a gasification medium has been done with biomass and coal samples. The main performance comparison was with those results using steam to understand the impact on the kinetics and reactivity. Ye et al. (5) found that CO₂ gasification had a lower activation energy than steam but overall reactivity was higher using steam for low-rank coal samples. Zhang et al. (6) also found similar performance for anthracite coal. They determined that char reactivity with steam gasification was significantly higher than with CO₂ and concluded that CO₂ gasification was more dependent on catalytic effects from the mineral content in the coal. Marquez-Montesinos et al. (7) reported similar trends in activation energy and char reactivity for gasification of grapefruit skin char. They also attributed CO₂ gasification reactivity to a catalytic effect of minerals from the biomass.

It should be noted that these studies examined char that was produced via heat-treatment in a nitrogen atmosphere

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