

Investigation of Supercritical Fluids for Use in Biomass Processing & Carbon Recycling

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ABSTRACT

An apparatus was built in the Mizzou Carbon Recycling Center to explore the continuous thermochemical conversion of biomass and model compounds in supercritical water. The apparatus was used to investigate gasification of biomass and other organics in supercritical water to produce fuel gases. It proved to be superior to other designs in that the apparatus was capable of achieving both high gasification efficiencies and high gasification rates. The apparatus is also amenable other thermochemical conversion processes including SCW oxidation (combustion), hydrolysis in super and subcritical water, or combinations thereof.

The continuous supercritical water gasification apparatus is used to investigate glucose gasification in supercritical water at high temperatures and low residence times. A 2³ full factorial experiment was performed to determine the effects of feed concentration, temperature, and residence time on glucose gasification. Glucose is a good representative of cellulosic biomass. Additionally, supercritical water gasification of ethanol and butanol as biomass model compounds was explored over a range of residence times from 0.7 to 34 s. Residence time was decreased until turbulence was achieved ($\tau \leq 1.2$ s). As fluid transitioned from laminar to turbulent flow, gasification rate was maximized while gasification efficiency was reduced. Gasification rates up to 107 g/L-s were observed; this is nearly an order of magnitude higher than previously reported. Arrhenius parameters were estimated to model the intrinsic kinetics of gasification of model compounds in supercritical water operating in plug flow without any transport limitations in the radial direction; this technique has never before been applied to supercritical water gasification.

Separations relevant to operation the continuous supercritical water gasification apparatus, and thus a biorefinery, are explored with the motivation to increase purity and energy density of gasification products. The separation of a supercritical mixture of nitrogen and carbon dioxide is investigated at pressures from 10 to 31 MPa and temperatures of -5° and 23°C. Nitrogen is used as a model compound for valuable fuel gases (H₂, CH₄) produced during SCWG. Nitrogen mole fraction increases in the positive vertical direction near the top of the pressure vessel leading to an effective separation. The separation effectiveness is increased with increased pressure and decreased temperature. Preliminary experiments were also performed with additional binary systems: CO₂/H₂, CO₂/CH₄, and CO₂/Air, all of which behave similarly to the CO₂/N₂ system. This kind of high pressure separation has applications in continuous processing of pressurized gasification products, other biomass refinery operations, and in the natural gas industry.

Solid feeding is an important issue during biorefinery operation. One of the largest delays with the implementation of SCWG technology on a large scale is the lack a reliable feeding mechanism for a variety of biomass and waste feeds. A novel feeder was developed to meet this need and is detailed. Finally, a complete mass and energy balance is performed on the supercritical water gasification apparatus. The final energy balance results in an energy density of the products that is 4-10 times higher than the required energy input suggesting that supercritical water gasification is a viable process. The energy balance also presents opportunities for water and heat recycle for added energy balance advantages.