Chemical Conversion of Biomass under Subcritical/ Supercritical - Solvent Conditions Using a Pilot Scale Flow Reactor: An Overview of the Iowa Energy Center-BECON Supercritical Fluids Program

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Abstract

The first phase of this project evaluated the reaction pathways for biomass feedstock in the presence of various cosolvents including acetone, methanol, CO_2, and water using a 1 liter (di: 7.6cm, l: 23.1cm) high pressure batch reactor. Additionally, the effect of temperature on the extent of the reaction was assessed at 200 to 350 ^oC. In both instances biomass conversion rates compared to the starting material ranged from 70 to 90 %, with the remaining portion being the unreacted fraction and lignin. The resulting products consisted of complex chemical fractions: organic acids, organic ester derivatives, sugars, sugar-alcohols, thermal degradation products and more. Although the impact of using various cosolvents was noticeable at lower temperatures, at higher temperatures the extent thermal degradation products increased due to longer heating times to reach the target temperature (2 to 8 hrs.). Despite the challenges with longer residence time when using the batch reactor, results from this study gave an important understanding of the reaction behavior and interaction of the solvent and biomass.

To have better control of the reaction extent at pilot scale, a flow reactor was assembled. The system consisted of a 250 ml/min slurry pump with reactor chamber that is 212 cm longer by 3 cm diameter, a maximum system working pressure up to 69 Mpa, electrical heating jackets and a condenser. Biomass slurry of 5 to 10% was fed into the reactor at varying temperatures from 200 to 350 ^oC and at residence times of 5 to 30 minutes. Analysis results from the flow reactor study will be main focus for this discussion.

Summary

The Iowa Energy Center at the Biomass Energy Conversion Facility (BECON) is known for its incubation of a variety of pilot scale projects for reactions of biomass to biofuels including biodiesel, thermal gasification, conversion of plastics to fuels, microwave dryers, and MycoMax Fungal Process. These projects are mostly financed by industries in the private sector, but some are run by Iowa State faculty through independent grant programs. Although the BECON facility accommodates these startup programs, we also fund work on Supercritical Fluids (SCF) biomass reactions. Of interest in the SCF area is bench scale work by Walt Trahanovsky [1] and Gary A. Aurand [2]. Trahanovsky's work was tailored towards the synthesis of value added compounds from biomass using solvents at sub/supercritical conditions. On the other hand, Aurand continued to explore hydrolysis reactions and biomass gasification projects. Additionally, through a DOE funded project, the endeavor to tackle these fundamental issues using sub/supercritical fluid reactions with biomass (cellulose, hemicellulose, switchgrass, and cornstover) has now been extended to include pilot scale high pressure batch and flow reactor systems. A few examples of projects in progress using both of these reactors under sub/supercritical conditions include:

a. Solvent-biomass reaction with and without cosolvents
b. Oil-protein extraction from oilseeds, Ndlela et. al. [3]
c. Algae and other biomass hydrolysis
d. Catalyst free biodiesel synthesis (esterification and transesterification)

Figure 1. High pressure batch reactor system (Digital and Astra gauge, heat control unit for main reactor and pre-heater, HPLC solvent pump, modular mixer speed control, HPLC CO_2 pump)

Shown in Figure 1 is a high-pressure, 316 stainless-steel batch reactor (Supercritical Fluid Technologies, Inc., One Innovation Way, Newark, Delaware 19711, USA). The reactor, pressure rated for 241 MPa, consists of 1 L internal volume (7.6 cm internal diameter and 23.1 cm length) heated by an electrical jacket, two J thermocouples, an analog pressure Astra gauge, digital pressure gauge, and a MagneDrive stirring assembly (Autoclave Engineers, Supercritical Fluid Technologies Inc., Newark, DE, USA).

A high pressure pilot scale flow reactor (Figure 2) is being tested simultaneously to replicate parameters that were initially evaluated using the batch reactor. One major challenge experienced with the batch system is the longer reactor heating and cooling times, which typically results in thermal product degradation, especially when testing at high temperatures. With the flow reactor, short residence times are attainable, better temperature control is achieved, and the system pressure can be varied by a control valve. At ISSF 2012, the focus of our talk will be on the solvent-biomass reactions completed so far using the flow reactor as compared to the batch reactor system.

Figure 2 illustrates the 316 stainless-steel flow reactor (Supercritical Fluid Technologies, Inc., One Innovation Way, Newark, DE 19711, USA). System pressure is rated for 69 MPa. The system consists of a vertical tube reactor of 1.7 L internal volume (3.2 cm internal diameter and 211.7 cm length), heated by three separate electrical jackets, J thermocouples, an analog pressure gauge, digital pressure gauge, control valve, process monitoring panel, HPLC solvent pump rated at 250 ml/min, and the Milton Roy “C” pump: 100 micron, 250 ml/min.

Figure 2. Pilot Scale high pressure flow reactor at the Iowa Energy Center-BECON facility

Acknowledgements

1. Walter S. Trahanovsky, “Use of Supercritical Fluids and Other Novel Methodologies for the Production of High –Value Compounds from Biomass”, http://www.energy.iastate.edu/Renewable/biomass/cs/supercritical.htm, 2009-2010.

2. Gary A. Aurand, “Supercritical Water Gasification of Biomass”, http://www.energy.iastate.edu/Renewable/biomass/cs/supercriticalwater.htm, 2009-2010.

3. S. C. Ndlela, J. M. L. N. de Moura, N. K. Olson, L. A. Johnson, “Aqueous Extraction of Oil and Protein from Soybeans with Subcritical Water”, J Am Oil Chem Soc, 1993-7, 2012.

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