Evaluating biomass reactions with cosolvents/CO_2 under subcritical and supercritical conditions

Sipho C. Ndlela, Norman K. Olson
Iowa Energy Center, Iowa State University, BECON Facility, 1521 West F Avenue, Nevada, IA 50201, USA

INTRODUCTION

Cellulose and corn stover were subjected to a reaction with polar cosolvents (methanol and water)/CO_2 at subcritical and supercritical conditions. Resulting products from a cellulose reaction at 300°C analyzed by GCMS consisted of a mixture of organic acids, sugars, and several other components. Examples of organic acids included acetic, hexanoic, heptanoic and malonic acids, whereas sugars were levoglucosan, D-Allose, and D-Galactose. Furthermore product samples from a corn stover reaction at 300°C suggested presence of ketones, aromatic hydrocarbons, and methyl esters. As evidenced by these results, reactions at high pressure are plausible although they are accompanied by a complex product composition, and an unreacted residue of cellulose and lignin.

MATERIALS & METHODS

Cellulose (20 micron) characterization: (TGA, SEM, XRD)
TGA: (a.) Non-isothermal conditions: 50 to 900°C, 5°C/min, N_2
(b.) Isothermal conditions: 200°C to 400°C, 200min., N_2
SEM: Hitachi S-2460 N variable pressure, and SEM X-ray spectrometer
XRD: Siemens D 500 x-ray diffractometer with CuK_α

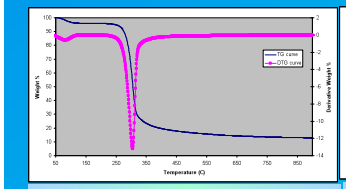

Figure 1. Cellulose thermal degradation using a TGA from 50 – 900°C under N_2 inert conditions

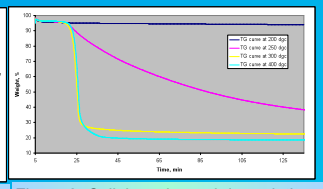

Figure 2. Cellulose thermal degradation using a TGA from at isothermal conditions

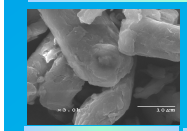

Fig. 3a Cellulose

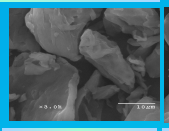

Fig. 3b Cellulose TGA at 300°C, N_2

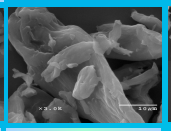

Fig.3c Cellulose TGA at 400°C, N_2

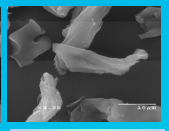

Fig.3d Cellulose TGA to 900°C, N_2

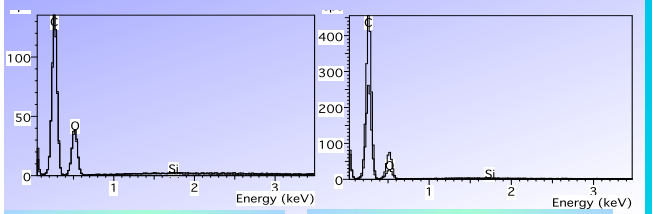

Fig. 4a SEM X-ray spectrometer 20-kx, Cellulose and TGA at 200°C

Fig. 4b SEM X-ray spectrometer 20-kx, Cellulose (dashed line) and TGA at (300,400, 900°C (full line)

Cellulose Characterization Results

- In Figure 1 weight loss at 85°C associated with loss of physisorbed water, at 305°C associate with loss of O.
- There were no significant SEM morphological changes under TGA conditions.
- In Figure 2, no weight loss at 200°C (grey/white color), gradual weight loss at 250°C (grey color), accelerated weight loss at 300 and 400 °C (black/ grey color)

SEM x-ray spectrometry data:

- TGA at 200°C looks like the reference cellulose material (Fig 4a).
- TGA at 300°C, 400°C and -900°C are similar and have lost O compared to the reference sample (Fig 4b).

MATERIALS & METHODS

Cellulose and corn stover experiments using a high pressure batch and flow reactor. Cosolvents: CO_2, Water, Methanol, Analysis instruments: SEM: Hitachi S-2460 N variable Pressure and GCMS, Agilent GC model 6890 integrated with a micromass GCT, DB5 column, Ei and Ci (NH_3 and CH_4)

High Pressure Batch Reactor system

High pressure flow reactor system

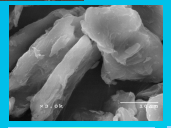

Fig.5a SCF 200°C

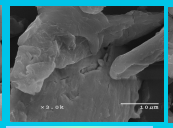

Fig.5b SCF 240°C

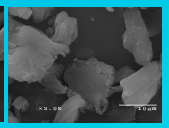

Fig.5c SCF 300°C

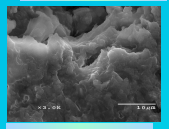

Fig.5d SCF 325°C

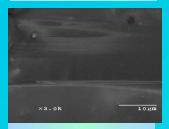

Fig.5e SCF 350°C

Fig.6a Batch reactor product (L-R): Rotavaped, Crude and recovered methanol (300°C)

Fig.6b Flow reactor product crude (L-R): at 250 °C and 300 °C

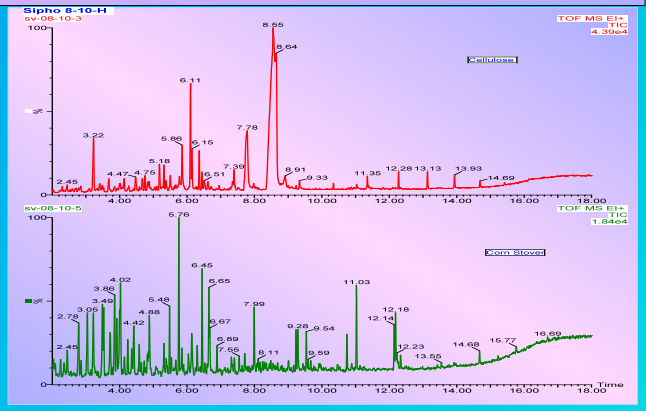

Figure 7. GC trace from analysis of RTVPcrude sample after a reaction with methanol at 300°C and 2500 psi (Top: cellulose, Bottom: corn stover)

Cellulose-Corn Stover cosolvent reaction results summary

- GCMS is a useful analytical tool for evaluating the product sample post high pressure cellulose/corn stover-methanol reactions.
- CO_2 addition during a high pressure reaction had a minimal effect in converting cellulose in the temperature range 200 to 300°C.
- Decreased amounts of cellulose residue remained after reactions above 300°C.
- Samples from batch reactor were much darker due to extended heating and cooling period when compared to corresponding conditions with a continuous flow reactor.
- Resulting products from a cellulose reaction at 300°C analyzed by GCMS consisted of a mixture of organic acids, sugars, and several other components. Examples of organic acids included acetic, hexanoic, heptanoic and malonic acids, whereas sugars were levoglucosan, D-Allose, and D-Galactose. Furthermore product samples from a corn stover reaction at 300°C suggested presence of ketones, aromatic hydrocarbons, and methyl esters. As evidenced by these results, reactions at high pressure are plausible although they are accompanied by a complex product composition, and an unreacted residue of cellulose and lignin.

ACKNOWLEDGMENTS

Iowa Energy Center, DOE Fund: DE-FG36-06GO86014

Dr. Brent Shanks, (Iowa State University Chemical and Biological Engineering Department)

Dr. Ronald Holtan, (Iowa State University Chemistry Department)

Dr. Walter Trahanovsky, (Iowa State University Chemistry Department)