

# Semi-Continuous Carbonated Hot Water Pretreatment of Lignocellulosic Biomass: Use of Multiple Syringe Pumps to Produce Sugars and Carbochemicals

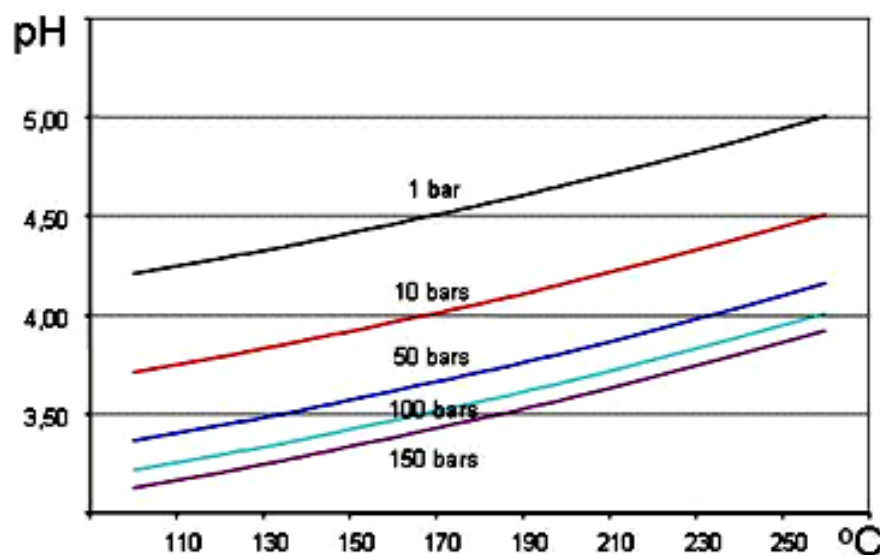
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## Introduction

Biomass substrates such as switch grass and corn stover are now commonly used in the production of biofuels. Such substrates consist of approximately 40-50% cellulose and 25-35% hemicellulose which is broken down to lower oligomeric and monomeric sugars, and further fermented to produce biofuels such as ethanol and butanol [1]. In this study, we have constructed a laboratory-based semi-continuous flow apparatus using three high precision Teledyne Isco syringe pumps and a constant temperature oven, to carbonate water as a function of temperature and pressure for use in the reactive pretreatment of switch grass. Conditions were selected to optimize the biomass pretreatment for sugar

(glucose and xylose) or carbochemical yields (furfural and 5-hydroxymethyl furfural-HMF). The latter compounds are dehydration products of the sugars at high temperatures (usually greater than 200 °C) in hot water.

Carbon dioxide, when dissolved in water (as a function of temperature and pressure), forms carbonic acid, which decreases the pH of the water below 4 (see Figure 1). Such conditions can catalyze sugar depolymerization and/or dehydration. The carbonated-water pretreatment of biomass presents a “greener” sustainable method for the production of sugars and carbochemical, as opposed to using mineral acids for pretreatment and hydrolysis of the biomass.



**Figure 1: Variation in pH of water as a function of temperature and carbon dioxide pressure [2]**

## Experimental Apparatus

Switch grass was ground using a cyclone sampling mill and sieved. The ground switch grass was then packed in a stainless steel (SS-316) cell (15.2 cm x 0.743 cm i.d.). The switch grass mass used usually varied between 0.7 to 0.9 g. Ultrapure water (18.2 MΩ) was obtained from a Milli-Q Synthesis A10 water purification unit (Millipore, Bellerica, MA, USA). The water was pumped using a Teledyne Isco 260D pump (constant flow mode) through a preheating coil and into the stainless steel cell placed in a constant temperature Hewlett-Packard Model 5890 gas chromatographic (GC)

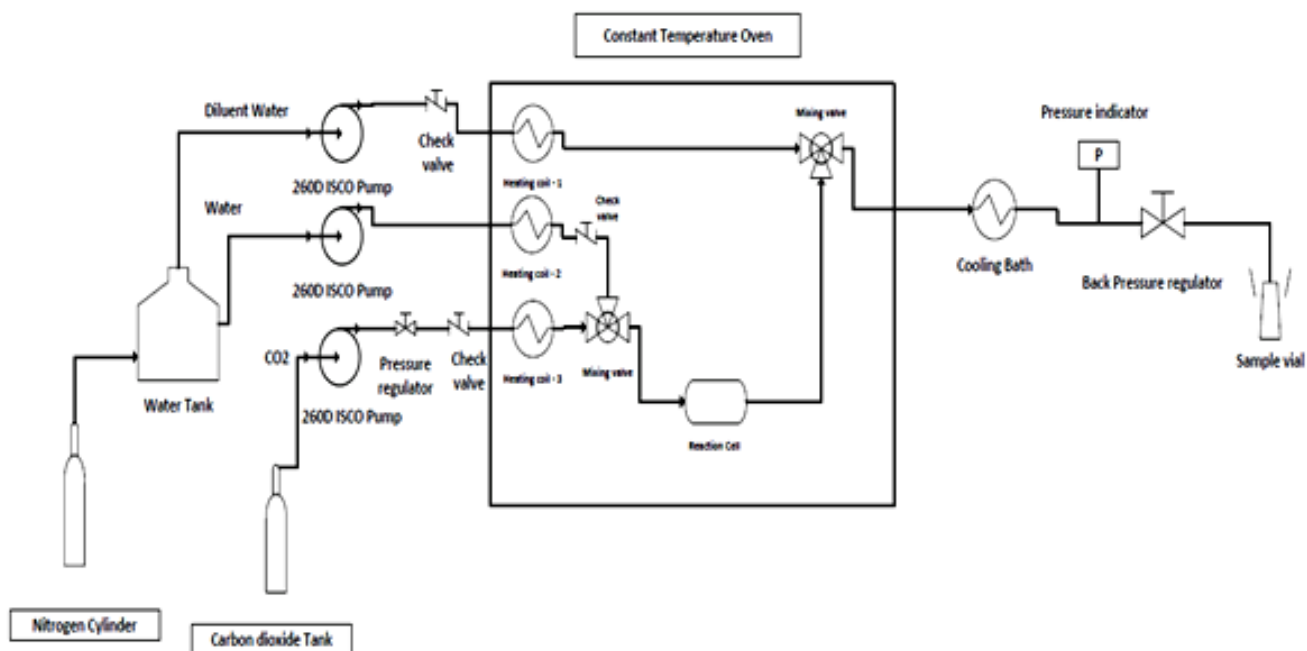
oven (see Figure 2).

Initially, the water was allowed to flow at a rate of 2-3 mL/min through the cell before increasing the oven temperature and starting the carbonation of the water. This was done to prevent thermal degradation and dehydration of the switch grass. After ascertaining the flow of solvent into a beaker outside the oven, the oven temperature was increased to the desired setpoint.

The oven temperature was measured using a J-type thermocouple coupled to an Omega Model DP703 thermocouple microcomputer (Stamford, CT, USA). After the oven reached the set experimental temperature, carbon dioxide was pumped using another 260D pump (constant pressure mode) and contacted the water in a mixing tee placed inside the (GC) oven just before the

reaction cell. The CO<sub>2</sub> – water, after flowing through the reaction cell, contacted another stream of water delivered by another 260D syringe pump (constant flow mode) at the designated tee. In Figure 2, this water was used to dilute the stream containing the products from biomass treatment in order to prevent precipitation of the components in the resultant mixture as it exits the oven. The aqueous reactant mixture then flowed through a cooling coil and into a sample vial for analysis.

The back pressure regulator, a GO Model BP66-1A11QEN151 (GO, Inc., Spartanburg, SC, 0-4000 psi) was placed in-line between the cooling bath and the sample collection vial, and was used for maintaining the system pressure to prevent flashing of the water to steam. The pump pressure and solvent flow rates were set using an Isco SFX 200 controller module. Depending on the set temperatures and pressures, the delivered carbon dioxide flow rate was typically set between 0.03 and 0.08 mL/min.



**Figure 2: Schematic of the semi-continuous carbonated hot water pretreatment system**

The pretreatment conditions were found to be different for maximizing either the sugar or carbochemical yields (see Table 1). The higher temperatures listed in Table 1 are required to produce carbochemicals rather than sugars.

Following the experimental run, the contents of the reaction cell were removed and vacuum filtered, and the lignin residue determined using weight difference before and after pretreatment.

The collected samples were initially centrifuged using a Thermo Scientific Speed-Vac system (Model SC210A), and then the supernatant was re-filtered using a 5µm nylon membrane before HPLC analysis. The pH of the collected samples was measured using a Mettler Toledo Seven-Easy pH meter system.

Carbohydrate analysis was done using a Dionex HPLC module (Dionex Corporation, Sunnyvale, CA, USA) utilizing a Biorad Aminex HPX-87P column and Shodex RI-101 refractive index detector, with water as eluent at 85 °C flowing at 0.6 mL/min. The carbochemical analysis was done using a Waters Alliance (Model 2695) system using a Bio-Rad Aminex HPX-87H column and a Waters photodiode array detector (Model 2998) with dilute acid (0.005M sulfuric acid in water) as eluent at 60 °C flowing at 0.6 mL/min.

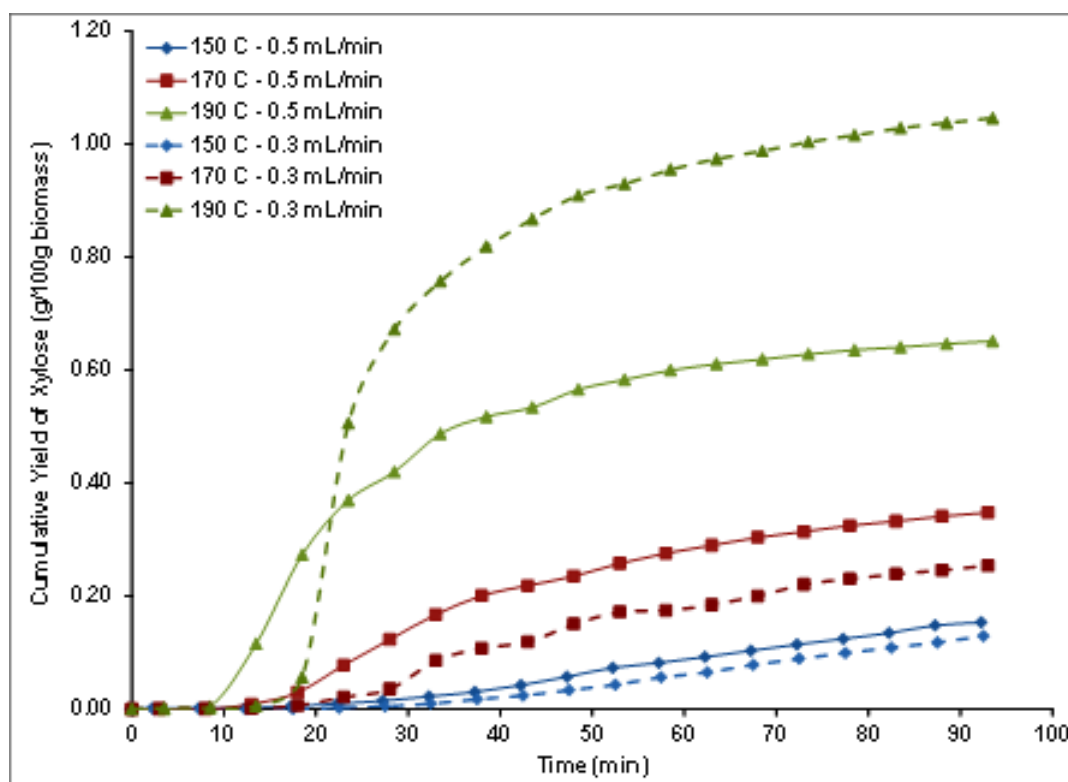
**Table 1: Experimental conditions for carbonated water pretreatment of switch grass to produce sugars and carbochemicals**

Experimental Conditions	Reactive Pretreatment to produce sugars	Reactive Pretreatment to produce carbochemicals
Particle size (switch grass)	75-106 $\mu\text{m}$	180-250 $\mu\text{m}$
Solvent flow rate	0.3, 0.5 and 0.7 mL/min	3 mL/min
Diluent flow rate	0.3, 0.5 and 0.7 mL/min (1:1 dilution)	2 mL/min
Temperature	150, 170 and 190 C	210, 250, 280 and 310 C
Carbon dioxide pressure	0, 1000 and 2000 psia	0 and 1000 psia
Reaction time	90 min	60 min

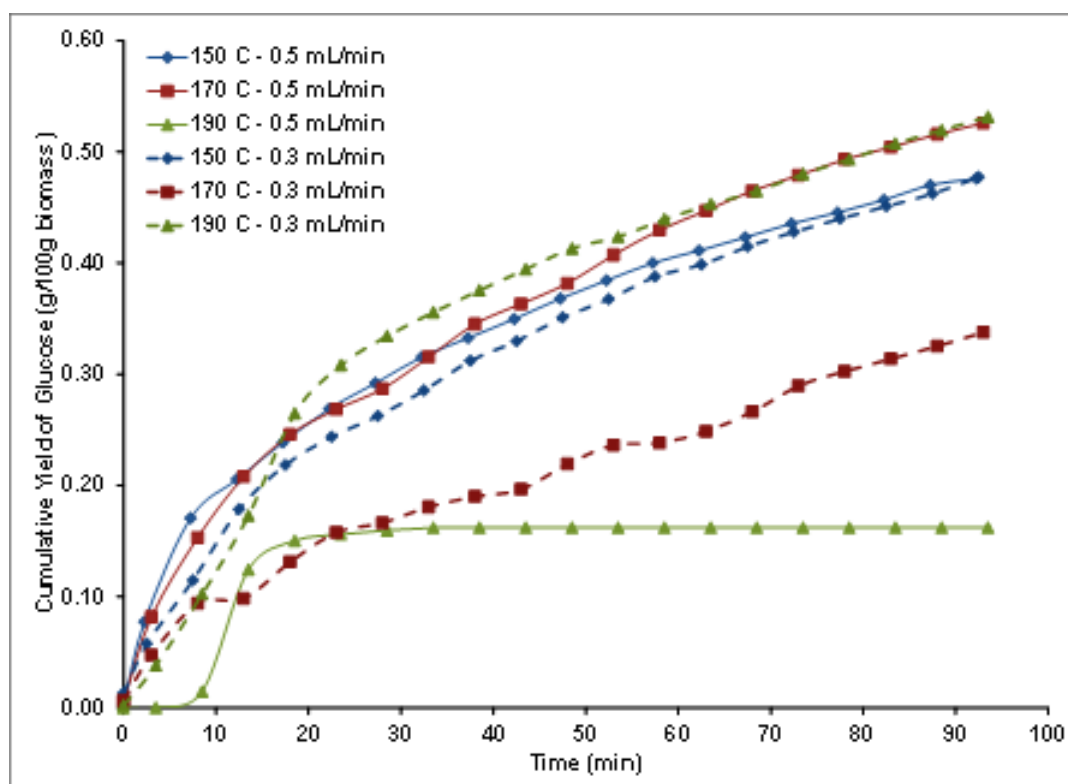
## Results and Discussion

The results obtained from the semi-continuous apparatus indicated that there was a significant effect of temperature, pressure and solvent flow rate on the sugar and carbochemical yield from switch grass. Preliminary experiments in the absence of carbon dioxide pressure indicated that the xylose yield increased with an increase in temperature (Figure 3). It was also found that at the higher temperature ( $T = 190^\circ\text{C}$ ) there was significant increase in the glucose yield at flow rate of 0.5 mL/min (solid line) over that at 0.3 mL/min (dotted line). However, an opposite trend was seen at the lower temperatures where lower flow rate was found to be more effective. Similar trends were also observed for the

pretreatment of switch grass to yield glucose (Figure 4). However, it was found that there was no significant difference between the glucose yield at  $170^\circ\text{C}$ , 0.3 mL/min and  $190^\circ\text{C}$ , 0.5 mL/min. The decrease in the glucose and xylose yield at lower flow rates can be attributed to the onset of thermally initiated dehydration, etc., which results in the formation of furfural and HMF. However, these compounds are intermediate intermediates which on further rehydration produce levulinic, formic and acetic acids [3]. Hence, the optimization of the flow rate is very important to selectively obtain the desired products (sugars and/or carbochemicals).



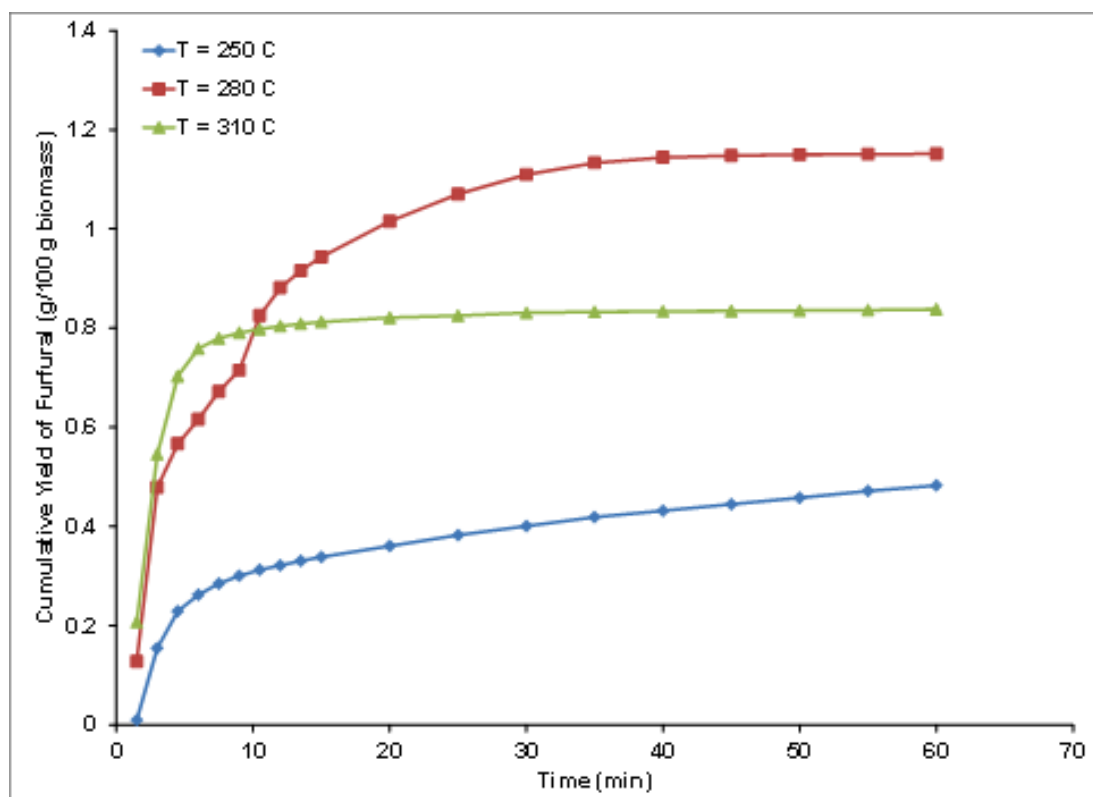
**Figure 3: Cumulative yield of xylose obtained from hot water pretreatment of switch grass as a function of temperature, flow rate and residence time.**



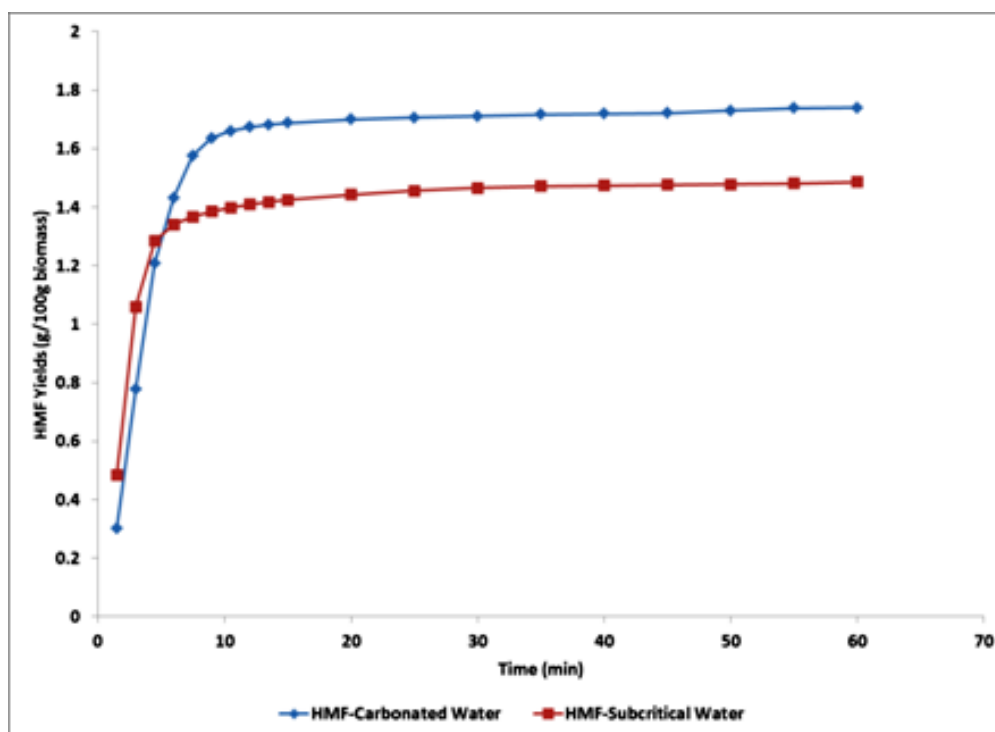
**Figure 4: Cumulative yield of glucose obtained from hot water pretreatment of switch grass as a function of temperature, flow rate and residence time.**

The thermal degradation of the sugars obtained from pretreatment of switch grass to furfural and HMF was more pronounced at higher temperatures when the water flow rate was optimized at 3 mL/min. Our studies indicated that there was maximum furfural yield at  $T = 280\text{ }^{\circ}\text{C}$  (see Figure 5).

Further reaction studies in the presence of carbon dioxide indicated a significant increase in the reaction rate and the yield of sugars and carbochemicals. Figure 5 shows the effect of carbon dioxide pressure of 1000 psi on the yield of HMF from reactive pretreatment of switch grass at  $310\text{ }^{\circ}\text{C}$ . It can be seen from Figure 5 that carbonating the water increased the yield of HMF by 20% [4]. However, our studies indicated that in some cases the total yield remained the same but the reaction rate was higher, suggesting that a smaller residence time was sufficient to obtain optimized pretreatment in the presence of carbonation [5]. Such an effect can be better understood using the semi-continuous flow apparatus using a multi-syringe pump system (as reported in this application note), rather than in a batch scale process. In addition,  $\text{CO}_2$  for use in the above reaction can be obtained from the fermentation step to produce alcohols from sugars, lessening its environmental impact, as well as promoting an environmentally benign catalysis of carbochemicals and sugars from naturally renewable resources.



**Figure 5: Cumulative yield of furfural obtained from hot water pretreatment of switch grass as a function of temperature and residence time.**



**Figure 6: Cumulative yield of HMF from the semi-continuous flow pretreatment of switch grass at 310 °C with and without carbonation.**

References

1. Yat, S. C., Berger, A., Shonnard, D. R. 2008. Kinetic characterization of dilute sulfuric acid hydrolysis of timber varieties and switchgrass. *Bioreour. Technol.* 99, 3855-3863.
2. van Walsum, P. 2001. Severity function describing the hydrolysis of xylan using carbonic acid. *Appl. Biochem. Biotechnol.*, 91-93, 317-329.
3. Chheda, J. N., Roman-Leshkov, Y. and Dumesic, J. A. 2007. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem.*, 9, 342-350.
4. Dhamdere, R. T., Lu, Y-W., Srinivas, K. and King, J. W. 2011. Catalytic conversion of lignocellulosic biomass to carbohydrates in carbonated water. Abstracts of the 2011 AIChE Annual Meeting, Minneapolis, MN, October 16-21.
5. van Walsum, P. and Shi, H. 2004. Carbonic acid enhancement of hydrolysis in aqueous pretreatment of corn stover. *Bioresour. Technol.*, 93, 217-226.

*Last modified January 31, 2012*

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