SELECTIVE PRODUCTION OF SUGARS AND GLYCOLALDEHYDE FROM AGRICULTURAL BIOMASS USING SUPERCRITICAL WATER AS REACTION MEDIUM

Celia M. Martínez, High Pressure Processes Group, Deparment of Chemical Engineering and Environmental Technology, University of Valladolid, Spain
celiamaria.martinez@uva.es
Danilo A. Cantero, Department of Chemical and Biomolecular Engineering, Energy Institute, Cornell University, USA
Francesc Recasens, Deparment of Chemical Engineering, Universitat Politècnica de Catalunya, Spain
MJ Cocero, High Pressure Processes Group, Deparment of Chemical Engineering and Environmental Technology, University of Valladolid, Spain

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Introduction

Biomass is a renewable and worldwide-distributed carbon resource which has the potential to produce energy, chemicals and fuels for the future sustainable industries [1]. Biobased industries, based on the use of renewable materials and energy, are still in development to success to promote a decentralized production that can be an alternative to the centralized petrochemical production plants.

Taking into account the wide range of possibilities for biomass refineries, plant biomass is considered a promising source to replace fossil fuels as feedstock for the sustainable production of fuels, materials and fine chemicals as sugars and added-value compounds as glycolaldehyde [2, 3] that can be obtained via thermochemical processes such as hydrolysis [4]. Glucose would be obtained from cellulose hydrolysis, hemicellulose would release its component sugars and lignin would produce phenolic compounds [5]. Also, glycolaldehyde is the main retro-aldol condensation product from glucose and it is a promising raw material to produce two-carbon building block molecules. For example, ethylene glycol is a widely applied polymer in the plastic and polyester industries. Apart from petroleum, it can be obtained through the hydrogenation of glycolaldehyde by a transition metal catalyst [6, 7]. Therefore, selective hydrolysis of cellulose into glucose and glycolaldehyde is a key process for the effective use of biomass [8].

In the recent years the use of sub and supercritical water (SCW) has been proposed as a promising medium to process biomass since water at around the critical point ($T_c = 374.2$ ºC, $P_c = 22.1$ MPa and $\rho_c = 0.323$ g/cm^3) shows properties that are very different from those of ambient liquid water [9]. The main variations in water properties are: (1) around the critical point the dielectric constant is decreased by increasing temperature, enhancing the solubility of small organic compounds (2) above the critical point the ionic product (Kw) decreases drastically (from 10-14 to 10-25) promoting in that way the free-radical reaction mechanisms instead of ionic reaction mechanisms (3) moreover, interphase mass transfer resistances are substantially reduced or eliminated operating at supercritical conditions, allowing faster reaction rates [10, 11]. SCW technology allows fast conversion of cellulose into sugars, being a tunable reaction medium for the synthesis of selected chemicals from biomass [12].

The main hydrolysis reaction pathway for cellulose in SCW is shown in Figure 1, based on a previous work [13]. Cellulose is firstly hydrolyzed into oligosaccharides and then into glucose. Once glucose has been produced, it can be converted into dehydrated (5-HMF) or retro-aldol condensation products (glycolaldehyde, pyruvaldehyde and glyceraldehyde). It was also demonstrated in a previous work [14] that at SCW conditions, the cellulose hydrolysis kinetics are faster than glucose hydrolysis kinetics, confirming that cellulose hydrolysis can be perform at supercritical conditions with high sugars yield.

Then, the challenging step in the conversion of cellulose is the production of glucose with high selectivity and yield. Our research group could improve the hydrolysis of cellulose suspensions in supercritical water by using a continuous micro-reactor, giving as a result a total conversion of cellulose in milliseconds and yielding a sugar production of 98% w/w [15]. Recently that continuous plant was used to perform the hydrolysis of complex biomass such as wheat bran [16], sugar beet pulp and tobacco scrap. In all cases, at reaction times around 0.2 s and it was possible to recover cellulose and hemicellulose fractions (yield up to 60% w/w) and lignin as solid residue.

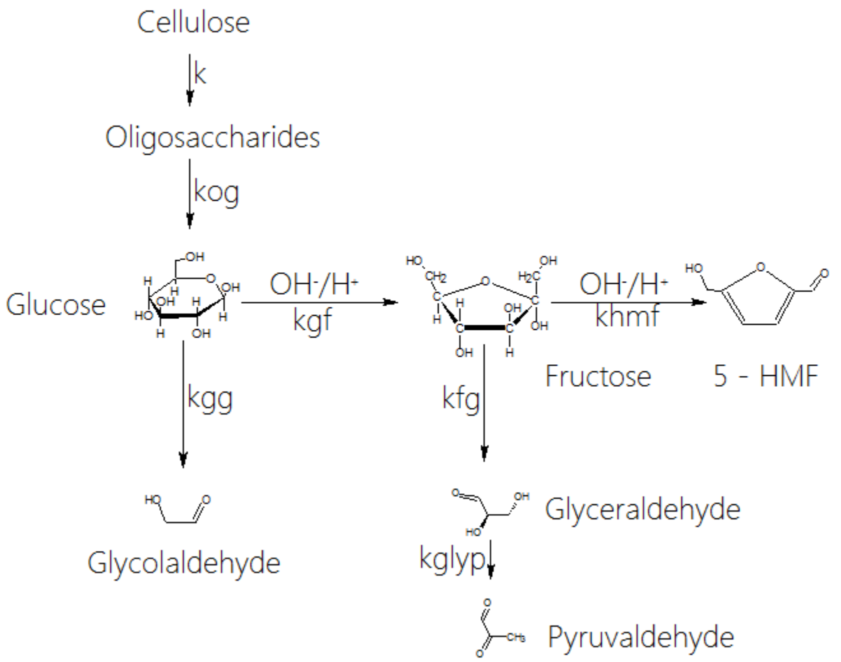

Figure 1. Reaction pathway for cellulose hydrolysis [13, 17].

Materials and methods

For complex biomass the first step was to determine the composition of the raw material. For that purpose, a Laboratory Analytical Procedure (LAP) from NREL was used to determine the structural carbohydrates and lignin in the biomass [18]. In that way cellulose, hemicellulose, soluble and insoluble lignin, ash and moisture fractions were quantified for each biomass.

The reaction product was characterized using different techniques. The composition of the liquid product was determined by high-performance liquid chromatography (HPLC). The column used for the separation of the compounds was Shodex SH-1011 at 50 ºC, using sulfuric acid (0.01 N) as mobile phase with a flow rate of 0.8 mL/min. The soluble oligosaccharide concentration in the liquid sample was determined by acid hydrolysis to glucose and HPLC determination. For cellulose hydrolysis the total carbon content (TOC) of the product was also determined with a Shimadzu TOC-VCSH equipment [17].

The solid product obtained from biomass hydrolysis, was separated by centrifugation and dried at 60 ºC for 24 h. Then, following the same NREL procedure, the total lignin content was determined. The separated solids obtained were also analyzed by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) [16].

Experimental set-up

The experiments were performed in the continuous plant of the FASTSUGARS process, able to hydrolyze biomass in SCW at temperatures up to 400 ºC and pressures up to 30 MPa. A scheme of the experimental set-up designed by the High Pressure Processes Group is shown in Figure 2.

Briefly, water and a biomass suspension were continuously pumped to the reactor at the operating pressure (25 MPa). At the inlet of the reactor (as a tee junction-M-) the biomass was instantaneously heated up by mixing it with a SCW stream, reaching in that way the operating temperature (400 ºC). After the desired reaction time was achieved, the reactor effluent was suddenly depressurized through a high temperature valve (V-1) obtaining an instantaneous cooling and therefore, stopping the reactions. The cooling method was an important part of the FASTSUGARS process, because it was the mechanism used to effectively stop the reactions, avoiding uncontrolled reactions and the dilution of the products, which would occur if they were cooled down by quenching.

An electric heater was used to control the temperature of the water stream with an adjustable power up to 10 kW. Also, a heat exchanger (HE-1) was used to both preheat the water stream and cool down the product, introducing in that way a heat integration system. SCW was supplied up to a maximum flow rate of 5 kg/h by pump P-2 and biomass suspension was fed to a maximum flow rate of 3 kg/h by pump P-1.

Finally, a flash chamber separator was installed after the reactor, allowing the separation of the products into two phases: a vapor phase mainly composed of water and a liquid phase with the concentrated product. After this stage, two heat exchangers were used to cool down the sample to room temperature (HE-2 and HE-3).

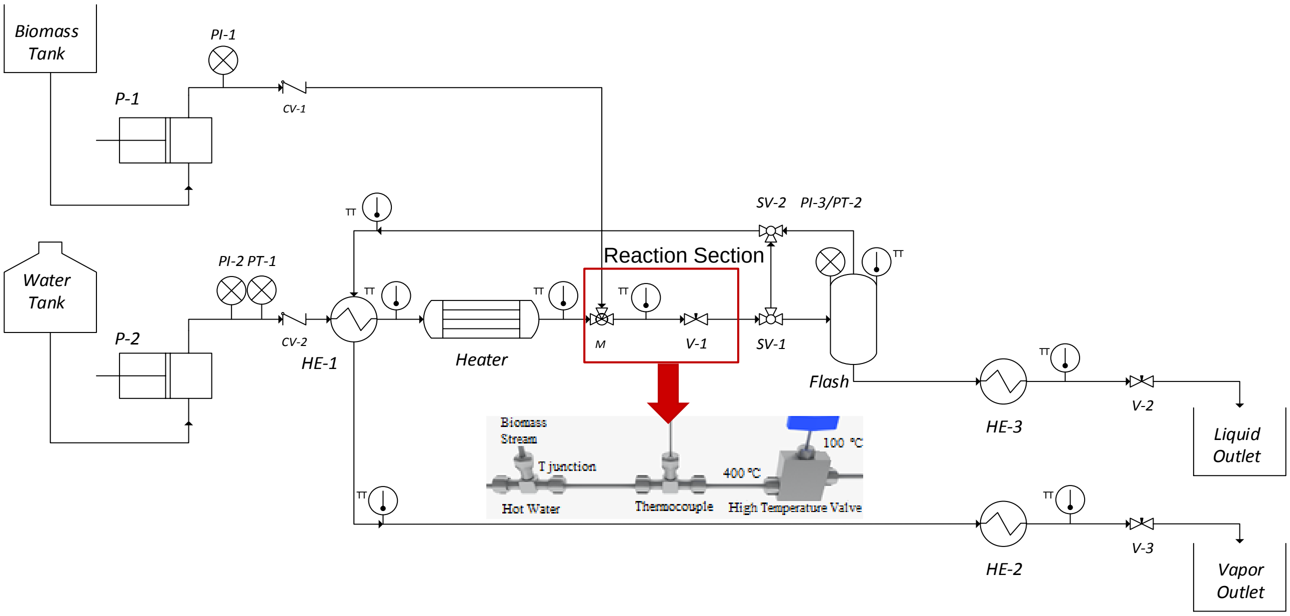

Figure 1. Experimental set-up with a flash chamber and heat integration. Detailed scheme of the reaction section [17].

Results and discussion

Different biomass resources were hydrolyzed in this experimental set-up. Not only pure biomass components as cellulose, but also agricultural biomass as wheat bran and sugar beet pulp were hydrolyzed in that plant. Some of the more relevant results are presented here.

Effect of cellulose concentration on SCW hydrolysis [17]

In order to study the influence of the cellulose concentration on the hydrolysis yield a set of experiments was carried out at different reaction times and feeding concentrations, working at the best experimental conditions found in a previous work (400 ºC and 25 MPa) [15]. The concentration at the inlet of the reactor was varied by changing the concentration of cellulose in the pumped suspension. The cellulose concentrations used were 5, 10, 15 and 20 % w/w, thus obtaining a cellulose concentration at the inlet reactor between 1.5 and 6 % w/w.

Existing models to describe the conversion rate of cellulose hydrolysis in SCW assumed that hydrolysis of cellulose particles mainly takes place at their surface [13, 19] and implied the use of a nonconventional kinetic equation. In this work, a conventional first order kinetic was assumed to describe the conversion rate of cellulose hydrolysis in SCW. Using experimental results obtained with feeding concentrations of 5, 15 and 20 % w/w of cellulose suspension (1.5, 4.5 and 6 % w/w at the reactor inlet), it was possible to calculate the kinetic constant. In Figure 3, the logarithm was plotted against the reaction time and a linear dependence was found where the slope represented the kinetic constant. It can be observed a different behavior depending on the inlet concentration. In fact, it was assumed that below 3.8 % w/w, the cellulose was completely solubilized in SCW and therefore it can be considered that hydrolysis of cellulose occurred in a homogeneous phase giving as a result a higher conversion rate (higher slope). On the contrary, if the concentration was above 3.8 % w/w the cellulose behaved as if it had been hydrolyzed at subcritical conditions. Under these conditions, the cellulose was not totally dissolved and the reaction occurred in a heterogeneous phase. This fact can be explained assuming that a decrease in the solubility of cellulose in SCW implied a heterogeneous reaction where the mass transfer resistances could limit the reaction rate.

Therefore, it was demonstrated that not only is the particle size a key parameter in the conversion rate of cellulose hydrolysis in SCW, but also the cellulose concentration and interphase mass transfer limitation must be taken into account.

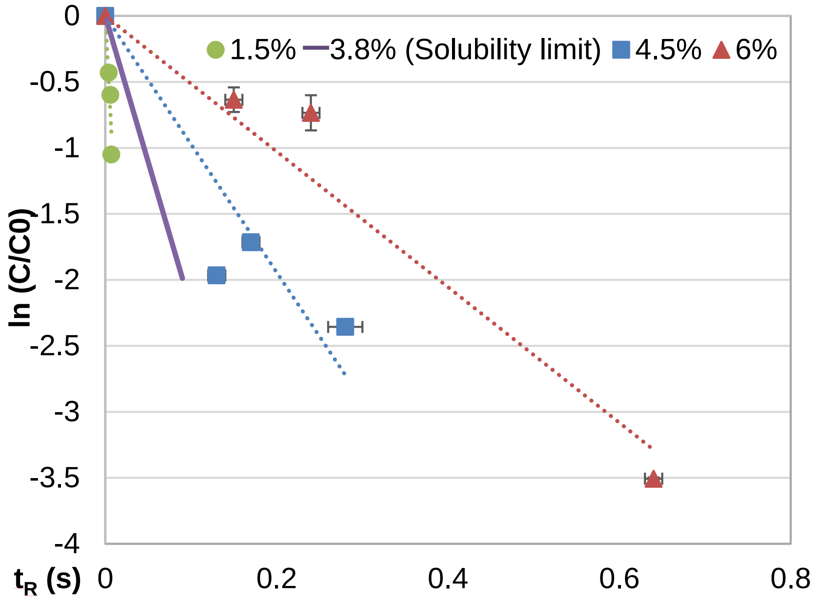

Figure 3. Kinetic analysis for cellulose concentrations of 5, 15 and 20 % w/w [17].

Recovery of cellulose & hemicellulose fractions from wheat bran by SCW hydrolysis [16]

The conversion of wheat bran into soluble saccharides such as glucose, xylose and arabinose was studied at 400 ºC and 25 MPa with reaction times between 0.2 and 1 second. The process yield was evaluated for two target products: C-6 (sugars derived from cellulose: cellobiose, glucose and fructose) and C-5 sugars (saccharide derived from hemicellulose hydrolysis: xylose, mannose, galactose and arabinose). On the other hand, the production of glycolaldehyde, organic acids (acetic and formic acid), glyceraldehyde and 5-HMF was analyzed as by-product formation.

First step was the determination of the composition of this biomass, which results are shown in Table 1.

Table 1. Chemical composition of wheat bran [16].

Component	% dry basis
Moisture	8.2
Extractives	10.6
Cellulose	31.4
Hemicellulose	20.3
Insoluble lignin	2.7
Soluble lignin	19.6
Ash	0.5

Performing the hydrolysis of wheat bran it was observed that the recovery of soluble sugars from liquid products decreased when the reaction time was increased from 0.19 to 0.69 s. The yield of C-5 and C-6 obtained as soluble sugars is shown in Figure 4. It can be seen that the maximum recovery of soluble sugars was 73 % w/w at 0.19 s. Also, a total recovery of C-5 sugars was achieved at the same reaction time. Regarding the solid composition after hydrolysis, it was found that increasing the reaction time the lignin content in the solid increased from 22 % up to 85 % w/w.

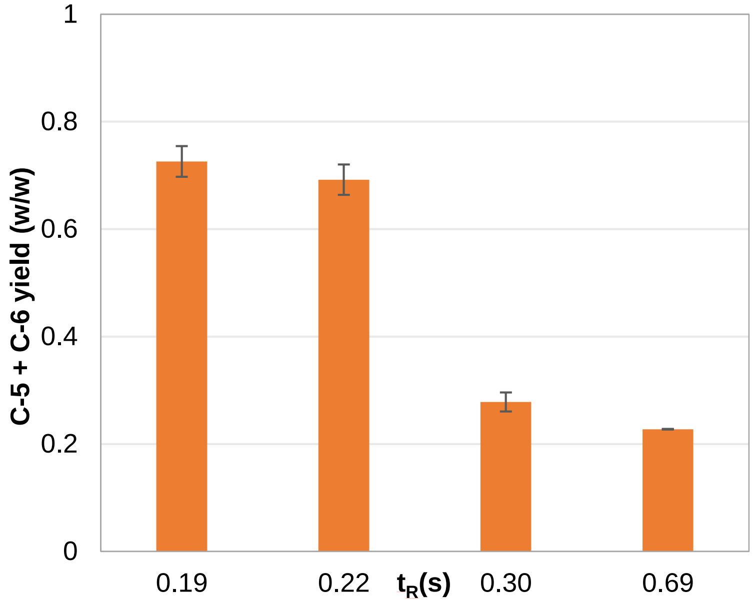

Figure 4. Yield of cellulose and hemicellulose sugars recovered at different reaction times after SCW hydrolysis of wheat bran [16].

Recovery of sugars from sugar beet pulp via SCW hydrolysis

Based on previous results, sugar beet pulp was hydrolyzed at 390 ºC and 25 MPa with reaction times between 0.16 and 1.12 s in order to analyze the yields of sugars (C-5 and C-6 saccharides), retro-aldol (RA) condensation products and other compounds such as acetic and formic acid and 5-HMF. As it was done for wheat bran, the first step was the characterization of the raw material, shown in Table 2.

Table 1. Chemical composition of sugar beet pulp.

Component	% dry basis
Moisture	14.1
Extractives	2.2
Cellulose	13.2
Hemicellulose	16.8
Insoluble lignin	3.8
Soluble lignin	15.2
Proteins	7.9
Ash	1.1

The yield of C-5 and C-6 sugars is shown in Figure 5, where it can be seen that the maximum yield of sugars was 60 % w/w achieved at 0.19 s. Specifically, at 0.19 s, 70 % of cellulose was recovered as C-6 sugars and 55% of hemicelluloses were recovered as C-5 sugars. The sugars yield increased up to a maximum when increasing the reaction time. Above 0.19 s, the sugars produced started to yield degradation products. The yield of those degradation products such as RA, organic acids and 5-HMF followed the same trend, showing their maximum production at 0.19 s. At higher reaction times (around 1 s), the main hydrolysis products were glycolaldehyde and organic acids.

It is important to notice that the optimum reaction time for sugar beet pulp was 0.19 s, same as it was for wheat bran. In both cases, the insoluble lignin content was lower than 4 %, so that the maximum liquefaction would be around 95 % w/w. Once it would be reached that conversion, the production of sugars would reach its maximum. So that as for both biomass at 0.19 s it was achieved the highest liquefaction ratio, the yield of sugars reached its maximum at the same reaction time.

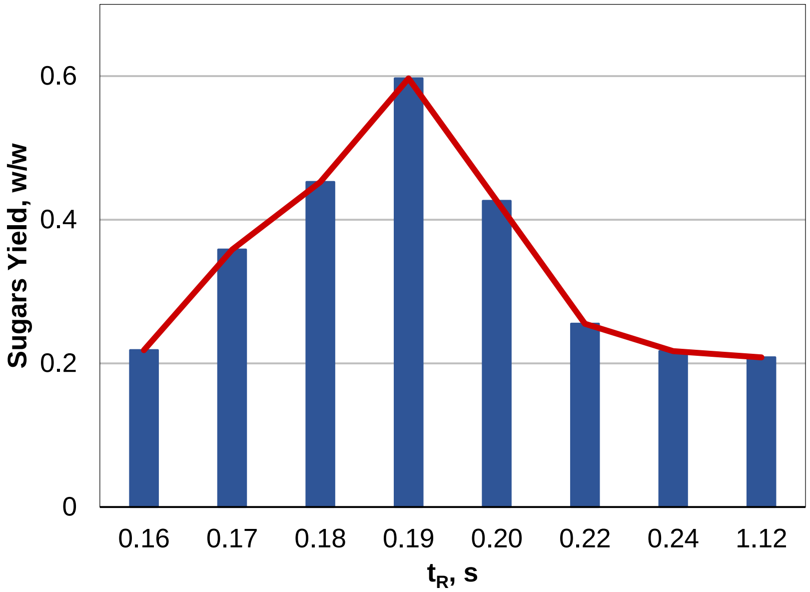

Figure 2. Yield of cellulose and hemicellulose sugars recovered at different reaction times after SCW hydrolysis of sugar beet pulp.

Concluding remarks

Supercritical water hydrolysis showed to be an effective technology to hydrolyze biomass to selectively transform biomass into sugars and chemicals with reaction times below 1 second.

The major goals of this work were:

(1) The effective control of reaction time in order to stop the reaction after the total hydrolysis and before the sugars degradation reactions, giving as a result a very high recovery of sugars from biomass.

(2) Development of a unique pumping system in order to improve the pumping of concentrated biomass suspensions (up to 20 % w/w) at high flow rates.

(3) Versatile production of building block molecules from biomass, just by changing the reaction time it was possible to obtain either sugar monomers or retro-aldol condensation products such as glycolaldehyde, which are key compounds to produce fine chemicals as sorbitol, xylitol and ethylene glycol. Also, lignin was recovered as solid residue after the reaction. All these products are promising feedstock for the future Biorefinery industry.

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