Cellulose hydrolysis: understanding the kinetic behavior

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ABSTRACT

The use of vegetal biomass has been evaluated in the last years as a carbon resource for the production of chemicals and fuels. However, several challenges remain unsolved for the energetic and chemical supply from biomass. One of the main challenges is the production of compounds like sugars of glycolaldehyde selectively by using an efficient process. In this work, it is proposed an alternative to produce sugars from cellulose with a selectivity of 98% carbon basis or glycolaldehyde with a selectivity of 60% carbon basis. Cellulose was hydrolyzed in a pressurized water medium (300 - 400ºC and 10 - 27 MPa) with a residence time between 0.018 - 20 s. In order to analyze the product composition and the kinetic behavior, a kinetic model was developed and contrasted with the experimental data. It was observed that the kinetics of cellulose hydrolysis have a drastic change when reaction temperature is increased above the critical point of water. Sometimes, this behavior is explained due to the decrease in the medium density (water concentration) which will disfavor the formation of water transition states. However, this explanation works well only from a qualitative point of view. In this work it was proposed that the reactions of glucose in a pressurized water medium would be influenced by the ion concentration of the media due to the water molecules dissociation. The model developed was analyzed considering the density and the ion concentration as selectivity modifiers. It was observed that the density do not explain qualitatively the kinetic behavior of glucose isomerization to fructose neither fructose dehydration to produce 5-hydroxymethylfurfural. At the contrary, the hydroxyl concentration explained qualitatively these kinetic behaviors. The drastic change in the hydroxyl concentration of the water reaction medium when temperature is increased above the critical point of water would be the determining factor to avoid the production of 5-HMF. The residence time would be the key to stop the reactions for high sugars selectivity or high glycolaldehyde selectivity.

INTRODUCTION

The biomass exploitation as raw material is growing as an alternative for the sustainable production of fuels and chemicals [1]. Cellulose is one of the main compounds of biomass, representing the most abundant biopolymer [2]. An important challenge in the processing of cellulosic biomass is to hydrolyze the β1-4 glucose-glucose bond producing an output stream of sugars with low concentration of degradation products, by using an efficient process[3, 4]. The use of pressurized water is an alternative as reaction medium for the processing of cellulosic biomass in a one-step fast process.

Supercritical water (SCW) is water at temperature and pressure above its critical point (Tc=374ºC and Pc=22.1 MPa). In the surroundings of the critical point, the properties of water can be highly influenced by changing pressure and temperature. So, the identity of the medium can be modified without changing the solvent. The density of the medium represents the quantity of water per volume unit (kg/m^3); this is a measurement of water concentration, an important factor to take into account in the reactions where water participates as reagent or forming intermediate states[5]. Another important property of water as reaction medium is the ionic product (mol^2/kg^2), which represents how dissociated is water molecule (ion concentration) favoring or disfavoring acid/basis catalysis [6].

Cellulose hydrolysis in pressurized water medium was studied in different kind of reactors; batch [7], semi-continuous [8] and continuous [9-13]. Batch experiences of cellulose hydrolysis can be done obtaining as products: bio-oils; water soluble; solids and; gases. The hydrolysis of cellulose in a hydrothermal medium can be controlled in a continuous reactor by simply varying T, P and tr. Hence, the continuous process allows higher selectivity than the batch processes. Nevertheless, the maximum selectivity achieved by continuous cellulose hydrolysis was almost 70% w/w [10]. The selectivity of the process was improved by using a novel reactor obtaining sugars selectivity of 98% w/w [9]. This sugars streams could be further transformed in valuable chemical like pyruvaldehyde, glycolaldehyde [14-17], organic acids or polyalcohol [18, 19].

The aim of this work was to determine the effect of temperature, residence time and hydroxyls concentration in the selectivity of cellulose hydrolysis in pressurized water. The hydroxyl concentration was included in the reaction kinetic model in order to determine its influence.

MATERIALS AND METHODS

Sample analysis

Each sample was centrifuged and filtered in order to determine the cellulose conversion. The carbon content of the liquid samples was determined by TOC analysis with Shimadzu TOC-VCSH equipment. The composition of the samples was analyzed by HPLC (IR-UV/Vis) with a sugar column Shodex SH1011. The oligosaccharides concentration was determined following the 'Determination of Structural Carbohydrates and Lignin in Biomass' report [20].

Experimental setup

The pilot plant could be continuously operated at temperatures of up to 400ºC and pressures of up to 30 MPa. The cellulose suspension (7% w/w) was pumped to the reactor at room temperature. The heating of this stream was done at the reactor inlet by mixing it with a

supercritical water stream. The products were cooled by sudden expansion. A detailed description of the pilot plant and of the operation procedure were presented in a previous work [9, 21]. The main working advantages of the pilot plat are: (a) the reactor can be considered isothermal due to the instantaneous heating and cooling; (b), products not diluted in the cooling process; (c) the residence time is varied from 0.004 s to 40 s using tubular reactors of different lengths.

Model

The considered reaction pathway for cellulose hydrolysis is shown in Scheme 1. The concentration of each component was calculated along residence time considering a continuous tubular reactor. More detail of the model resolution were published in a previous work [21].
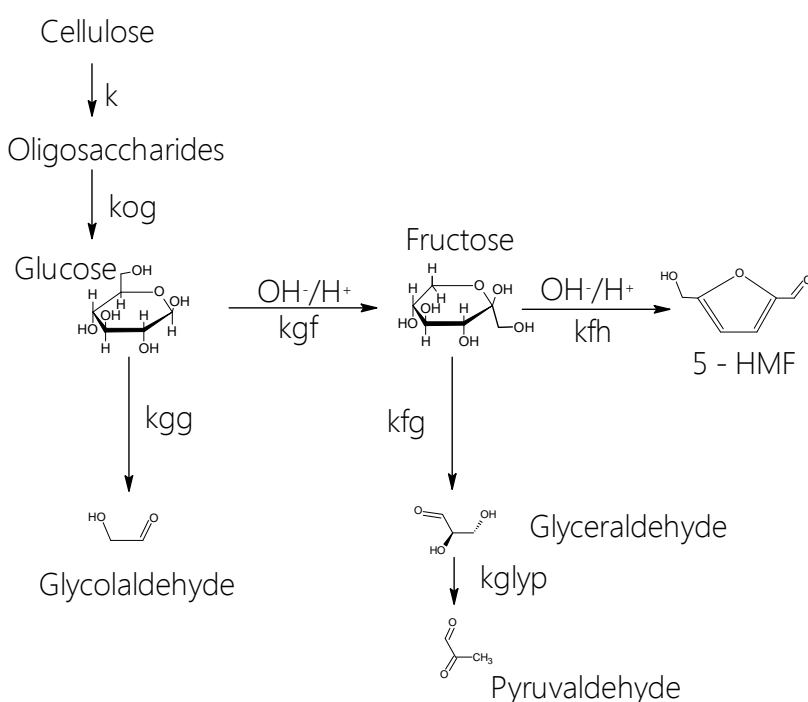
Scheme 1. Reaction pathway of cellulose hydrolysis.

Selectivity

The selectivity of each compound (*Si*) was calculated according equation 1. Where, Xc is compound carbon composition (*Xc*); *Ci* is the compound concentration and *TC* is total carbon at the reactor inlet.

$$Si = Ci \, Xc/TC. \tag{1}$$

RESULTS

The reactions of cellulose in hot pressurized water were analyzed at 300ºC (10 MPa, 18 MPa, 23 MPa and 27 MPa), 350ºC (10 MPa, 18 MPa and 23 MPa) and 400ºC (23 MPa, 25

MPa and 27 MPa). The experiments were carried out isothermally in a continuous pilot plant. Water density was calculated according the IAPWS industrial formulation[22], while the molal ionic product of water was calculated following 'International Formulation of Ionic Product of Water Substance'[23].

Important changes in the identity of the medium can be obtained if temperature and pressure are changed at the same time. For example, the density of water at 300ºC and 27 MPa is around 750 kg/m^3; this value can be decreased to 130 kg/m^3 if the conditions are modified to 400ºC and 23MPa. The OH concentration at 300ºC and 23 MPa is around 2.10^{-6} mol/L which means that the medium has high concentration of ions ($[H^+]$ and $[OH^-]$) favoring the ionic reactions [14, 24]. The hydroxyls concentration will take a value of $5.5.10^{-12}$ mol/L if the temperature and pressure are changed to 400ºC and 23 MPa; this reaction medium would favor radical reactions [25].

The effect of temperature on the soluble sugars selectivity along residence time is shown in Figure 1. It is observed that the selectivity was maximized at 400ºC and extremely low residence times. This results are in agreement with previous results works [9].
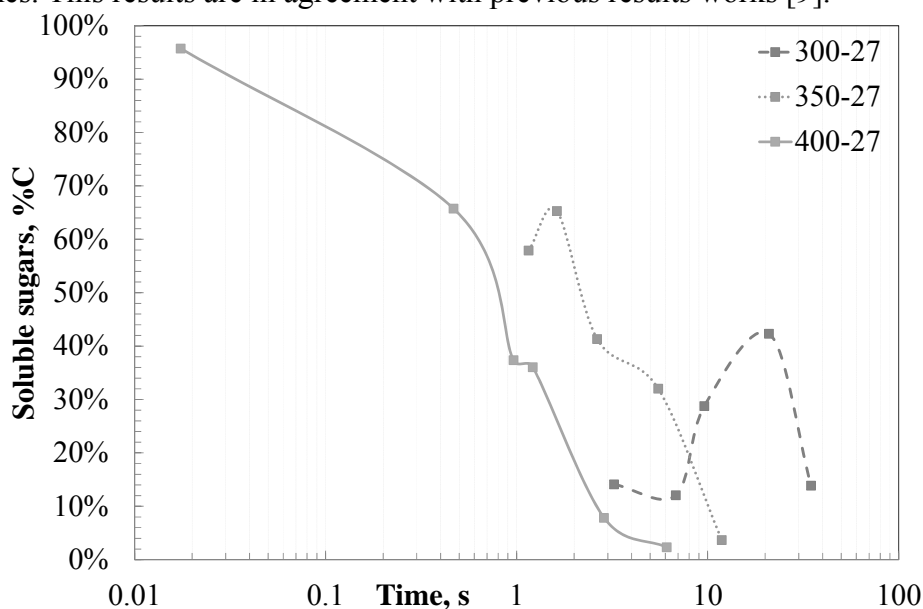

Figure 1. Soluble sugars selectivity of cellulose hydrolysis at 27 MPa. Effect of temperature and residence time.

In can be observed that an increase in the residence time at 300ºC and 350ºC, increased the selectivity of soluble sugars until a peak yield was achieved. After this peak concentration, the selectivity decreased. However, at 400ºC the increment of residence time decreased the selectivity of soluble sugars. The main product of sugars hydrolysis is glycolaldehyde. The effect of temperature and residence time on glycolaldehyde selectivity at 27 MPa is shown in Figure 2. The experiments at 400ºC showed the highest selectivity of glycolaldehyde (around 60% w/w) at 1 s of residence time. At lower temperatures than 400ºC, the selectivity of glycolaldehyde was lower.
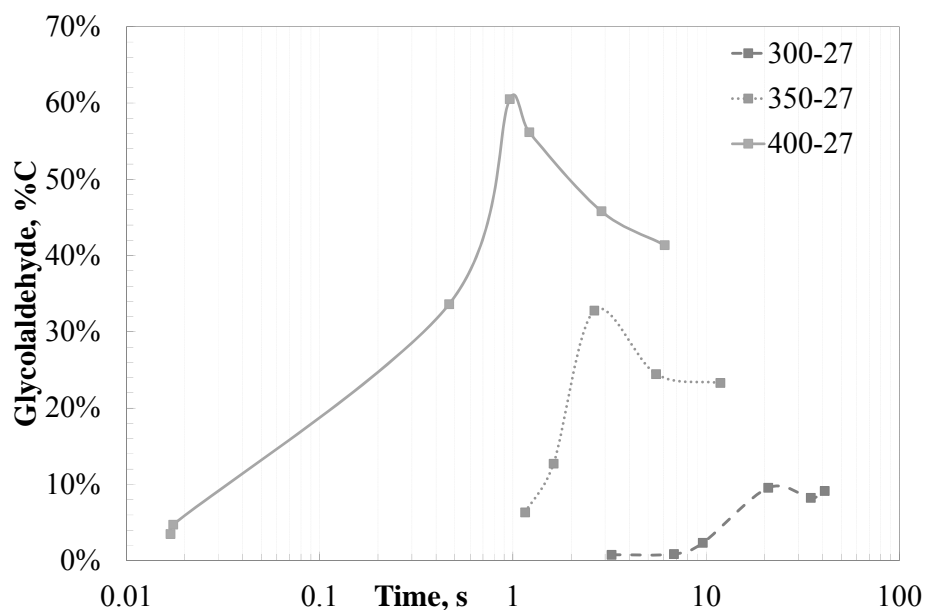
Figure 2. Glycolaldehyde selectivity of cellulose hydrolysis at 27 MPa. Effect of temperature and residence time.

The kinetic constants of glycolaldehyde production are shown in Figures 3. It can be observed that glycolaldehyde kinetic constant is enhanced by rising temperature. An increase in pressure seems to have an enhancing effect on the reaction of glycolaldehyde.
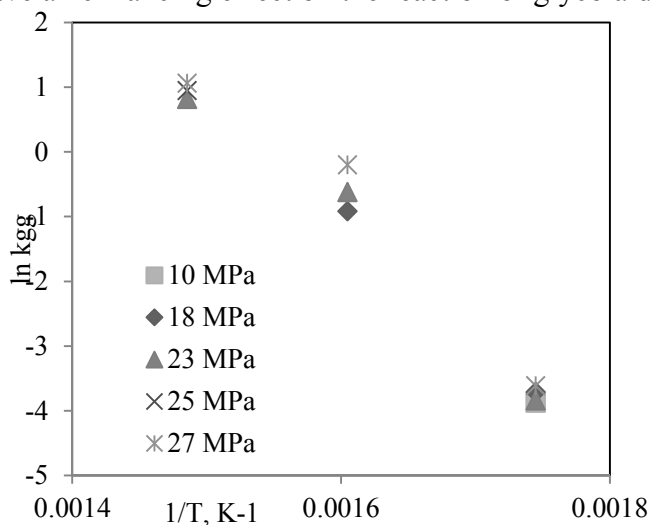

Figure 2. Kinetics constant of glucose retro-aldol condensation reaction along temperature at 10 MPa (■), 18 MPa (♦), 23 MPa (▲), 25 MPa (x) and 27MPa (*).

CONCLUSION

The process presented in this work shows an efficient alternative to hydrolyze cellulose selectively. The control of the residence time is the key for obtain a selectivity higher than 95% w/w of soluble sugars or 60% w/w of glycolaldehyde. From the viewpoint of chemistry, the selectivity of the process would be governed by the hydroxyls concentration.

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