

Experimental Study of Cellulose Depolymerization in Near Critical Water Using a Novel Facility. Modeling and Comparison to Literature Data

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ABSTRACT

Biorefining is the most promising alternative to replace the chemicals production from petroleum. Cellulose is the most abundant organic material in the world (34 - 50% of vegetal matter). Nevertheless most of this cellulose is not processed due to the difficulty in dissolving it. Water in the surrounding of its critical point presents unique properties for cellulose processing, being able to rapidly hydrolyze and dissolve cellulose: cellulose is dissolved in liquid water at 275°C in around 90 s, while this time reduces to 0.01s at 400°C.

The High Pressure Processes Group of the University of Valladolid built an experimental facility that works at temperatures up to 450°C and pressures up to 400 bar for the study of the cellulose depolymerization in water.

The cellulose hydrolysis in near critical water yields a high number of products comprising sugars, furfurals, aldehydes, ketones and acids.

Literature cellulose depolymerization kinetics were revised and a mathematical model consisting on an isothermal tubular reactor was developed. The model correctly predicts the cellulose decomposition rate, but at 350°C and 325°C experimental results show a slightly faster depolymerization rate than that predicted. The appearance and disappearance of glucose, erythrose and fructose is well predicted by the model but the experimental pyruvaldehyde production is faster than the model prediction.

INTRODUCTION

Biomass is an alternative as a renewable source for chemicals and fuels. Biomass can be found mainly in vegetal materials that grow worldwide and its principal constituent is lignocellulosic material (LCM). Cellulose is one of the principal components of the biomass and it is synthesized by plants capturing CO₂ and using sunlight as source of energy. The limitations of its uses is because the difficulty of its processing. An average value for the

production of biomass around the world is ~ 10 dry tons ha^{-1} year $^{-1}$ [1]. Cellulose is the principal compound of LMC material with an production of $1.5 \cdot 10^{12}$ tons year $^{-1}$ [2]. The LCM is composed of 34-50% cellulose, 19-34% hemi-cellulose and 11-30% of lignin [3].

Ragauskas and coworkers [1] point the supercritical fluids as the ideal media (solvents) for obtaining biofuels and chemicals of interest from biomass. The use of supercritical fluids (SCF) has been proposed as a clean technology for performing the integration of the depolymerization-reaction-separation processes. Particularly, high temperature pressurized water has proved to be good solvent for clean, safe and environmentally benign organic reactions[4]. Supercritical Water (SCW) has some properties, such as low dielectric constants and few and weak hydrogen bonds, that make it a good solvent for organic components [4]. The ionic product of water (K_w) reaches a maximum at temperatures around 300°C at pressure above critical point. This fact facilitates the creation of a medium with high concentrations of hydronium (H_3O^+) and hydroxyl groups (OH^-). Above critical temperature (T_C) the value of K_w decreases drastically to levels of about $1 \cdot 10^{-25}$ [4].

Cellulose hydrolysis in SCW has been investigated reporting 100% conversions at 400°C and 25 MPa with 0.01 s of residence time [5]. Also, water at temperatures between 327 and 387°C has been used to separate cellulose from lignin [6] obtaining cellulose with a high purity (89.5 to 100%) with residence times in the reactor between 0.35 s and 0.5 s.

In this work a bibliographic analysis of the kinetics involved in the process of hydrothermal reactions of cellulose was done. Using selected kinetics parameters a mathematical model of an isothermal tubular reactor has been developed. A facility was designed and built with fast heating and cooling of the reaction in order to know with precision the residence time. A comparison between literature and experimental data is shown.

MATERIALS AND METHODS

Materials. Cellulose used was micro-crystalline cellulose of particle size between 20 – 137 μM purchased from VWR. Distilled water was used in the experiments. The reagents used in HPLC analysis were: cellobiose (+98%), glucose (+99%), fructose (+99%), glyceraldehyde (95%), pyruvaldehyde (40%), erythrose (+75%), 5 hydroxy methyl furfural (99%) purchased from Sigma.

Experimental facility. A schematic diagram of the experimental setup is shown in figure 1. Cellulose-water suspension (7.5% w/w) was continuously stirred during the experiments in order to obtain homogeneity. The suspension was fed to the reactor by a 305 Gilson Piston pump at a flow rate of 20 mL/min. To control accurately the residence time a high temperature vapour was injected to cellulose suspension stream at the inlet of the reactor to instantaneously heat the suspension. The inlet of the reactor is a ‘tee’ union where the cellulose suspension is mixed with preheated water. Cellulose concentration in the

experiments at the inlet of the reactor was 1.5% w/w. Temperature of each experiment was achieved by mixing of the streams with different temperatures of the preheated water. The reactor used for the experiments were tubes of ¼” and different lengths depending on the residence times. The reactor was thermally isolated. An instantaneously cooling at the end of the reactor was achieved by sudden decompression, using an Autoclave valve 30VRMM4812. After the decompression valve a jacket cooler was set to get the sample at room temperature.

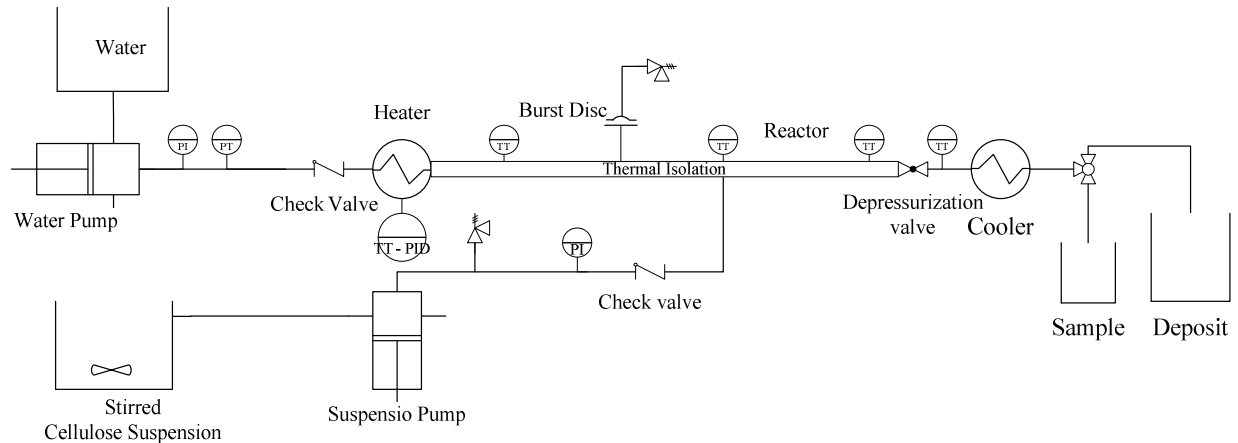


Figure 1. Schematic diagram of the experimental facility.

The residence time was evaluated by equation 1, where V is the volume of the reactor (m^3), ρ ($kg.m^{-3}$) is the density of the media (considered as water due to the low concentration of cellulose) and F_m is the mass flow ($kg.s^{-1}$).

$$\tau = \frac{V\rho}{F_m} \quad (1)$$

Analysis. The solids in the products were separated by centrifugation and filtration and dry at 60°C during 24 hours. The conversion of cellulose was determined by equation 2.

$$X = \frac{W_o - W}{W_o} \quad (2)$$

The carbon content of the liquid products was determined by TOC analysis with Shimadzu TOC-VCSH equipment. The composition of the products were determined with an HPLC equipment composed of an isocratic pump 1515 Waters, 717plus autosampler Waters, 2412 RI detector Waters, 2487 absorbance detector Waters. The HPLC column used for the separation of the soluble compounds was SUGAR KS-802 Shodex at 80°C and a flow of 0.8mL/min.

MODEL

Among the various kinetics available in literature, the kinetic model for cellulose decomposition of cellulose in high temperature pressurized water developed by Sasaki et al was used in the model [7]. Cellulose is considered as a cylindrical grain. Only the cellulose of

the surface of the grain is considered to react. The kinetics of cellulose is shown in equation 3 where 'x' is conversion, 't' is time in seconds and 'k' is the kinetic constant for cellulose hydrolysis (s⁻¹).

$$\frac{dx}{dt} = 2k(1 - x)^{1/2} \quad (3)$$

The model considers a stationary isothermal tubular reactor with plug flow. The reaction is considered to start at the beginning of the reactor where the hot water and the cellulose mix and the reaction finish at the end of the reactor connected to the valve. In figure 2 a schema of the reactor is shown.

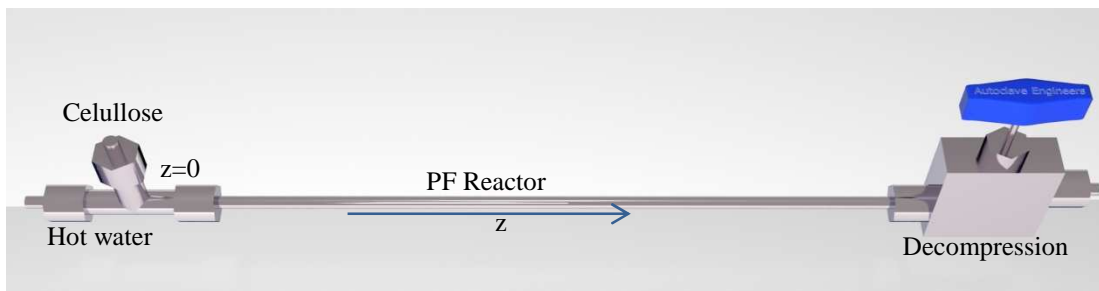
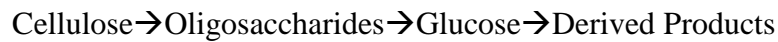


Figure 2. Reactor considered for the model.

The model was solved along the reactor (z) considering four groups of reactions, as follows;



The model was executed with the kinetic parameters found in literature [7-10]. The flow in the reactor was set at 6 kg/h with a composition of 16.7 grams of cellulose per kilogram of total flow (obtained after mixing the streams. The pressure was fixed at 25 MPa and the model was executed between 250°C and 400°C.

With equation 3 developed for length of reactor, equation 4 is achieved. ' ρ_w ' is the density of the media assumed as water (kg.m⁻³), ' D ' is the diameter of the reactor (m), ' \dot{M} ' is mass flow (kg/s) and ' z ' is the length of the reactor (m).

$$\frac{dx}{dz} = \frac{\rho_w \left(\frac{\pi D^2}{4} \right)}{\dot{M}} 2k(1 - x)^{1/2} \quad (4)$$

The production of the derived products is developed for each compound according equation 5. ' n_i ' is mole of compound i, ' c_i ' is the stoichiometric coefficient being positive for production and negative for consumption and ' k_i ' is the kinetic constant for the reaction.

$$\frac{dn_i}{dz} = \frac{\rho_w \left(\frac{\pi D^2}{4} \right)}{\dot{M}} \sum c_i k_i n_i \quad (5)$$

The residence time was calculated along the reactor according equation 6.

$$\frac{dt}{dz} = \frac{\rho_w}{\dot{M}} \left(\frac{\pi D^2}{4} \right) \quad (6)$$

EXPERIMENTAL RESULTS

Experiments for cellulose depolymerization were carried out between 250°C and 400°C, at 25 MPa. The residence time were between 0.01s and 30s. Main compounds identified were cellobiose, glucose, fructose, glyceraldehyde, 5 hydroxy methyl furfural (5-HMF), pyruvaldehyde and erythrose in different concentration depending on reaction temperature and residence time; at 400°C cellulose is completed hydrolysed in 0.07s with high production of glucose and cellobiose as products. When residence time is increased (1s) the concentration of glucose and cellobiose decrease and high production of pyruvaldehyde is obtained. At 300°C the concentration of glucose, fructose and pyruvaldehyde is lower than at 400°C but the concentration of 5-HMF is higher with a maximum concentration at 5 second of residence time. The coincidence between literature cellulose kinetic and experimental data is good at high (400°C and 375°C) and at low temperature (250°C – 300°C), nevertheless, at 350°C and 325°C experimental data show a slightly faster reaction rate. In general, the model correctly predicts cellulose conversion and cellobiose, glucose and fructose concentration (see figure 3). Pyruvaldehyde concentration is higher than predicted. The results for pyruvaldehyde are analogous for all temperatures.

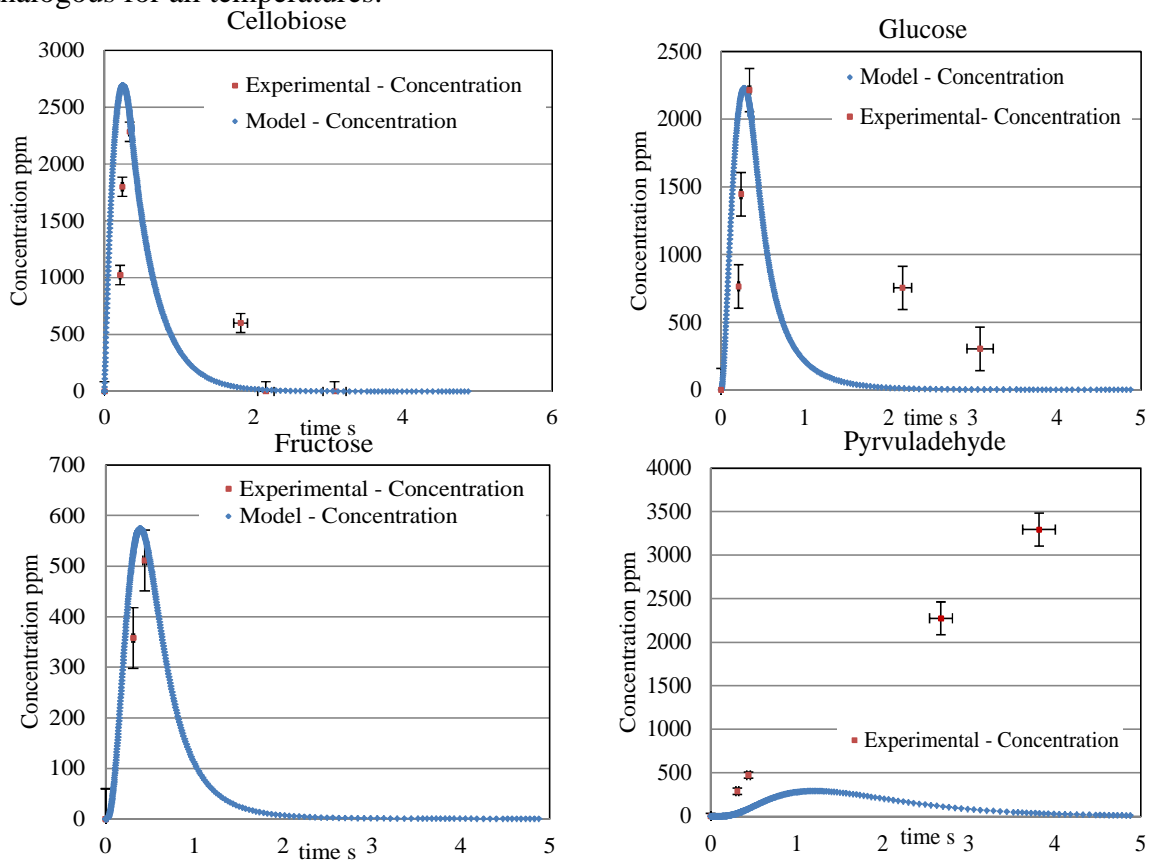


Figure 3. Comparison of the model predictions with experimental data

CONCLUSION

Cellulose decomposition in near critical water was analysed experimentally. It was found that the kinetics of the reactions depends strongly of temperature. Concentrations of the products vary greatly with temperature and residence time.

A mathematical model was developed using kinetic constant from literature data. The match between experimental and model prediction is good for the kinetic of cellulose hydrolysis.

The model correctly predicts the evolution of the derived products, except pyruvaldehyde at high residence times. Pyruvaldehyde experimental concentration is higher than the model prediction.

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