



Kinetic analysis of cellulose depolymerization reactions in near critical water

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ABSTRACT

In this work, a kinetic analysis of cellulose depolymerization in hot pressurized water is presented. An experimental facility that works with temperatures up to 400 °C, pressures of up to 25 MPa and residence times of between 0.004 s and 10 s was used for the experimental study. A mathematical model was developed in order to predict the evolution of the cellulose concentration and its derivatives. To do so, a reaction scheme was proposed, and kinetic parameters currently unavailable in literature were adjusted, using the experimental data obtained in this work. The kinetics for cellulose hydrolysis showed a change around the critical point of water, the activation energy being 154.4 ± 9.5 kJ/mol and 430.3 ± 6.3 kJ/mol below and above the critical point, respectively. The activation energy for oligosaccharide hydrolysis was 135.2 ± 9.2 kJ/mol and 111.5 ± 9.1 kJ/mol for the glucose to fructose reaction. The kinetics of 5-hydroxyl-methyl-furfural formation showed a drastic change at 330 °C. The activation energy for 5-HMF formation is 285 ± 34 kJ/mol and -61.3 ± 15.7 kJ/mol at temperatures below and above 330 °C, respectively. Above 330 °C the low density and ionic product of the medium would disfavor the 5-HMF formation.

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1. Introduction

Biomass unfit for human consumption is a viable alternative as a renewable source of chemicals and energy. Cellulose is one of the principal components of this biomass. In order to reach an appropriate sustainability level, new policies have been initiated to promote the use of renewable energy and the rational use of raw materials. This environmental philosophy imposes substantial changes in production, moving from centralized large scale plants to decentralized plants on a scale according to the biomass availability in each neighborhood [1]. To fit this new conception, the development of energy efficient processes using renewable raw materials is highly necessary.

The main goals for achieving a decentralized production may be the reduction of the equipment cost and the development of environmental friendly processes. The reduction in equipment cost can be achieved by using compact apparatus, simplified production steps and reactions in one step. These kinds of processes can be achieved by using ultra-fast processes with high yield and selectivity from alternative raw materials. The environmental compatibility can be achieved using 'green solvents' like water or carbon dioxide.

The supercritical fluids are a promising media for obtaining bio-fuels and useful chemicals from biomass. Supercritical water (SCW) presents a low dielectric constants and few, weak hydrogen bonds,

making it a good solvent for organic components [2]. The properties of water may vary considerably when changing the conditions from subcritical to supercritical. Just by changing pressure and temperature, the identity of the medium may be altered to favor different kinds of reactions. Pressurized water (e.g. 25 MPa) has a density of between 800 kg/m^3 and 1000 kg/m^3 and an ionic product between 11 and 14; at temperatures below 300 °C. In these conditions, the media may favor ionic reactions, and reactions favored by high densities [2–4]. If the temperature is increased up to 400 °C, the density is almost 150 kg/m^3 and the ionic product is near 21. Under these conditions, the media favors radical reactions [5], but the reactions enhanced by high densities will be disfavored.

In literature, the hydrolysis and processing of biomass in hot pressurized water for the production of glucose and its derivatives has been analyzed [1–3,6–9]. Water at temperatures between 327 °C and 387 °C was used to separate cellulose from lignin [10]. Under these conditions, secondary components were degraded and cellulose with a high purity (89.5–100%) was obtained with residence times in the reactor between 0.35 s and 0.5 s. Cellulose hydrolysis was completed in pressurized water at subcritical temperatures, obtaining a high concentration of glucose and oligosaccharides. Nevertheless, the reaction presented a low selectivity, and indicated the need for bigger reactors and higher residence times than those achieved at higher temperatures. Rogalinski et al. [11] analyzed the cellulose hydrolysis between 240 °C and 310 °C obtaining Arrhenius parameters of $\ln A = 32$ (pre-exponential factor) and $E_a = 163.9$ kJ/mol (activation energy). The influence of the CO₂ catalysis was analyzed using a temperature range of 240–280 °C. It was observed that the use of CO₂ as a

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A	pre-exponential factor of Arrhenius equation
E_a	activation energy of Arrhenius equation (kJ/mol)
k	reaction constant rate of cellulose hydrolysis (s^{-1})
k_1	reaction constant rate of cellobiose pyrolysis to glucosyl erythrose (s^{-1})
k_2	reaction constant rate of cellobiose pyrolysis to glucosyl glycoaldehyde (s^{-1})
k_a	reaction constant rate of glucose to organics acids (s^{-1})
k_{cello}	reaction constant rate of cellobiose decomposition (s^{-1})
k_{dgly}	reaction constant rate of dihydroxyacetone to glycoaldehyde (s^{-1})
k_{dp}	reaction constant rate of dihydroxyacetone to pyruvaldehyde (s^{-1})
k_{ge}	reaction constant rate of glucose to erythrose (s^{-1})
k_{glyd}	reaction constant rate of glycoaldehyde to dihydroxyacetone (s^{-1})
k_{glyp}	reaction constant rate of glycoaldehyde to pyruvaldehyde (s^{-1})
k_e	reaction constant rate of erythrose to organics acids (s^{-1})
k_f	reaction constant rate of fructose decomposition (s^{-1})
k_{fa}	reaction constant rate of fructose to organics acids (s^{-1})
k_{fe}	reaction constant rate of fructose to erythrose (s^{-1})
k_{fgl}	reaction constant rate of fructose to glycoaldehyde (s^{-1})
k_g	reaction constant rate of glucose decomposition (s^{-1})
k_{ga}	reaction constant rate of glucose to 1,6-anhydroglucose (s^{-1})
k_{gf}	reaction constant rate of glucose to fructose (s^{-1})
k_{ggg}	reaction constant rate of glucosyl glycoaldehyde to glucose (s^{-1})
k_{geg}	reaction constant rate of glucosyl erythrose to glucose (s^{-1})
k_h	reaction constant rate of cellobiose hydrolysis (s^{-1})
k_p	reaction constant rate of pyruvaldehyde to organics acids (s^{-1})
k_s	reaction constant rate of superficial decrease (s^{-1})
K_w	ionic product of water
S	area of cellulose grain (m^2)
t	time (s)
T_c	critical temperature (K)
t_R	residence time (s)
V	volume of cellulose (m^3)
W	mass of cellulose (g)
X	conversion
ε	dielectric constant
φ	mass factor for cellobiose formation

catalyst enhanced the reaction rate of cellulose hydrolysis at sub-critical temperatures. At temperatures above 260 °C the catalysis effect is negligible [12]. Cellulose hydrolysis in supercritical water (SCW) was investigated, reporting 100% conversions at 400 °C and 25 MPa with 0.5 s of residence time [13]. Up to 370 °C the activation energy and pre-exponential factor of cellulose hydrolysis were found to be 145.9 kJ/mol and 27.4, respectively. At temperatures higher than 370 °C the reaction rate of cellulose hydrolysis was found to increase; the activation energy and pre-exponential factor being 547.9 and 102.7, respectively [9]. The change in the

properties of the medium around the critical point of water is expected to modify the mechanism of the hydrolysis and thus increase the reaction rate. The authors explained that near critical water would be able to swell or dissolve the cellulose, since the hydrolysis reaction took place in a homogeneous phase [9].

The objective of the present work is to identify the kinetic pathway of cellulose hydrolysis, and its intermediate production and decomposition reactions in both, sub and supercritical water media, as well as adjusting the kinetic parameters of these reactions. To do so, a novel facility was designed and built for the study of cellulose hydrolysis. A mathematical model of an isothermal tubular reactor was developed. The kinetic reaction parameters of cellulose hydrolysis, oligosaccharides degradation, glucose to fructose reaction and 5-hydroxymethylfurfural (5-HMF) production were fitted.

2. Materials and methods

2.1. Materials

The cellulose used in the experiments was micro-crystalline cellulose with a particle size between 20 μ M and 130 μ M, purchased from VWR chemical company. Distilled water was used in the experiments. The reagents used in HPLC (high performance liquid chromatography) analysis were: cellobiose (+98%), glucose (+99%), fructose (+99%), glyceraldehyde (95%), pyruvaldehyde (40%), erythrose (+75%), 5-hydroxymethylfurfural (99%) purchased from Sigma.

2.2. Analysis

The solids in the products were separated by centrifugation and filtration, and dried at 60 °C for 24 h. The conversion of cellulose (X) was determined by Eq. (1), where ' W_0 ' is the concentration of cellulose at the inlet of the reactor and ' W ' is the concentration of cellulose after the hydrolysis, at the outlet of the reactor.

$$X = \frac{W_0 - W}{W_0} \quad (1)$$

The carbon content of the liquid products was determined by total organic carbon (TOC) analysis with Shimadzu TOC-VCSH equipment. The composition of the liquid products was determined with an HPLC. The HPLC column used for the separation of the compounds was SUGAR KS-802 Shodex at 80 °C and a flow of 0.8 mL/min using water Milli-Q as mobile phase. A Waters IR detector 2414 was used to identify the sugars and their derivatives.

2.3. Pilot plant concept

To analyze the kinetics of cellulose hydrolysis, it is necessary to know the residence times of the reactions with accuracy, that is, to know when the reaction starts and ends. At temperatures higher than 350 °C, the hydrothermal reactions are extremely fast, so heating and cooling ramps can lead to inaccurate results. In order to avoid this problem, instantaneous heating and cooling systems were designed and installed. A schematic diagram of the experimental setup is shown in Fig. 1. A cellulose–water suspension (7.5%, w/w) was continuously stirred during the experiments in order to ensure the homogeneity of the slurry. The cellulose suspension was fed into the reactor by a HPLC pump with a maximum flow rate of 1.5 kg/h. The heating of the process was achieved by the injection of supercritical water into a tee junction working as the reactor's inlet. This stream was generated by an electric heater which provided adjustable power of up to 10 kW, in order to control the temperature of the stream. Supercritical water was supplied up to a maximum flow rate of 5 kg/h. A plan of the reactor is shown

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