Pressure and temperature effect on cellulose hydrolysis in pressurized water

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HIGHLIGHTS

- Cellulose hydrolysis was modeled and analyzed in pressurized water changing P and T.
- Overall cellulose hydrolysis kinetic was not affected by pressure.
- Glucose and fructose reaction kinetic were highly modified by changing P and T.
- The selectivity of biomass hydrolysis can be set to the desired value by choosing P and T.

GRAPHICAL ABSTRACT
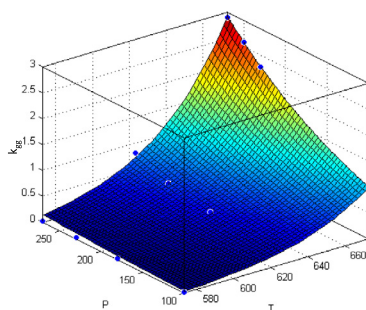
ABSTRACT

In this study, the effect of temperature and pressure on cellulose and glucose hydrolysis in a hydrothermal media was analyzed. To do so, cellulose hydrolysis experiments were carried out in a continuous pilot plant capable of operating up to 400 °C and 27 MPa. The reaction times were varied between 0.004 and 40 s. The main products of cellulose hydrolysis were oligosaccharides, cellobiose, glucose and fructose. The concentration profiles of each component followed a similar behavior at a fixed temperature changing pressure. Nevertheless, glucose and fructose hydrolysis reaction to give dehydration of retro aldol condensation products were strongly affected by pressure and temperature. When increasing temperature in the studied range, the reaction of glucose isomerization to fructose and the production of 5-hydroxymethylfurfural (5-HMF) obtained through fructose dehydration were inhibited. On the other hand, 5-HMF production was favored by high proton concentrations due to water dissociation. Thus, at a constant temperature, the production of 5-HMF was increased by rising the ionic product of water (increasing pressure). The production of glycolaldehyde (retro-aldol condensation of glucose) was increased by rising temperature and pressure. The kinetic constants of the cellulose hydrolysis reactions were determined at the experimented conditions using the experimental results. The kinetic constants were plotted against temperature and pressure to determine the activation energy and the activation volume for each reaction, respectively. Pressure seems to have no effect on the cellulose hydrolysis kinetic to simple sugars. However, at supercritical water temperatures the increment in pressure disfavored the glucose isomerization and dehydration reactions.

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1. Introduction

The chemical transformations of vegetal biomass have been intensively studied in the last years looking for renewable sources

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Notation

A	pre-exponential factor of Arrhenius equation
CW_{og}	carbon weight of the oligosaccharide monomer molecule (g mol^{-1})
CW_g	carbon weight of glucose molecule (g mol^{-1})
E_a	activation energy of Arrhenius equation (kJ mol^{-1})
k	reaction rate constant of cellulose hydrolysis (s^{-1})
k_{fa}	reaction rate constant of fructose to organics acids (s^{-1})
k_{fg}	reaction rate constant of fructose to glyceraldehyde (s^{-1})
k_{fh}	reaction rate constant of 5-HMF production (L mol^{-1} s^{-1})
k_{ga}	reaction rate constant of glucose to 1,6 anhydroglucose (s^{-1})
k_{gf}	reaction rate constant of glucose to fructose (L mol^{-1} s^{-1})
k_{gg}	reaction rate constant of glucose to glycolaldehyde (s^{-1})
k_{glyp}	reaction rate constant of glyceraldehyde to pyruvaldehyde (s^{-1})
k_h	reaction rate constant of cellobiose hydrolysis (s^{-1})
k_p	reaction rate constant of pyruvaldehyde degradation (s^{-1})
K_w	ionic product of water
$\dot{M}$	mass flow (kg h^{-1})
MW_g	molecular weight of glucose molecule (g mol^{-1}).
n_i	concentration of component 'i' (mol L^{-1})
P	pressure (MPa)
R	gas constant (kJ K^{-1} mol^{-1})
S	cross area of the tubular reactor (m^2)
T	temperature (K)
t	time (s)
t_r	residence time (s)
W	mass of cellulose (g)
X	conversion
z	length (m)
ρ	density (kg m^{-3})
ε	dielectric constant
$\Delta v^{\neq}$	Activation volume (cm^3 mol^{-1})

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of chemicals and fuels [1]. Cellulose is generally the major compound of vegetal biomass representing the most abundant biopolymer in nature [2]. Cellulose depolymerization was studied following different methods in order to obtain valuable compounds like soluble sugars [3–6], lactic acid [7] or 5-hydroxymethylfurfural (5-HMF) [8,9] among others. The conversion of cellulose into these valuable products depends on the reaction medium and the reactions conditions [10]. The use of supercritical fluids as reaction medium is a promising alternative for the biomass upgrading due to the possibility of tuning the medium properties by changing pressure and/or temperature. Supercritical water (SCW) is water at a temperature and pressure above its critical point (Tc = 374 °C and Pc = 22.1 MPa). The properties of water can be drastically modified by changing pressure and/or temperature in the neighborhood of its critical point. Changing the properties of water by changing its temperature and pressure can selectively inhibit or accelerate reactions. Three important properties of water as reaction medium are density, dielectric constant and ionic product. The density (ρ) of the medium is a measurement of the water molecules population per unit of volume. The water concentration is an important factor to take into account in the reactions where water participates, both as reagent or forming intermediate states [11]. The dielectric constant (ε) also increases sharply with pressure in the compressible region, and this behavior parallels to some extent the change in density. In the vicinity of the critical point, SCW behaves like a moderately polar organic liquid. The dielectric constant is reduced to the point where organic materials are readily soluble while the solubility of inorganic species is greatly reduced. The ionic product of water (K_w) represents how dissociated are water molecules (ion concentration). This property could be manipulated in order to favor or disfavor the acid/basis catalysis. The variations of these two properties of water in the surroundings of the critical point are shown in Fig. 1 [12,13]. Drastic variations in density and ionic product can be found at 400 °C by increasing pressure in the range 150–300 bar. However, the changes in water properties with pressure are less pronounced (less than 10%) at subcritical temperatures than at 400 °C. The changes in the property of the medium can be significant if temperature and pressure are changed at the same time. For example, density of water at 300 °C 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 400 °C and 23 MPa. Ion product of water at 300 °C and 27 MPa is around 10^{-11} mol^2/l^2, which means that medium has high concentration of ions ([H$^+$] and [OH$^-$]) favoring the ionic reactions [14–16]. The ionic product of water will take a value of 10^{-21} mol^2/l^2 if the temperature and pressure are changed to 400 °C and 23 MPa favoring radical reactions [17]. Having low dielectric constant and high ionic product, water under near-critical conditions become a suitable solvent for hydrolysis of organic compounds.

Cellulose hydrolysis in pressurized water medium was studied in different kind of reactors; batch [18–20], semi-continuous [21] and continuous [3,22–28]. Batch experiments can be done with simple equipment allowing fast and non-expensive results. This problem, the process control (t_r, T) is poor, making it difficult to obtain products with high selectivity. The main difficulty of the continuous process is the steady supply of cellulose (solid, non-soluble in water) to the reactor due to the possible pump clogging.
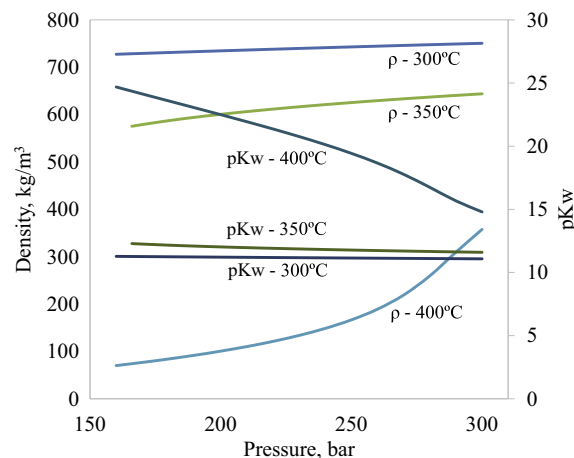

Fig. 1. Density and ionic product of water at different temperatures along pressure. Black lines: minus logarithmic of ionic product; gray lines: density. Continuous lines refer to 400 °C; dashed lines refer to 350 °C and spaced dashed lines refer to 300 °C.