

TRANSFORMATION OF GLUCOSE IN HIGH ADDED VALUE COMPOUNDS IN A HYDROTHERMAL REACTION MEDIA

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Abstract. The processing and valorization of biomass for the production of biomaterials and biofuels presents an alternative to achieve a sustainable production using renewable raw materials. Glucose is considered as building block raw material that can be obtained from cellulose hydrolysis or from biomass. In this study, the chemical transformation of glucose into high added value products (lactic acid and 5-hydroxymethylfurfural) was analyzed using a hydrothermal reaction medium. A continuous pilot plant that operates up to 400°C, 30 MPa and residence times between 0.004 s and 50 s was designed and built in order to study the process. The reactions of glucose in hot pressurized water were analyzed at 300°C, 350°C, 385°C and 400°C; the pressure was fixed at 16 MPa, 23 MPa and 27 MPa for the experiments. No lactic acid was found at those conditions. A high concentration of pyruvaldehyde (80% carbon basis) was found operating at 400°C and 27 MPa with residence times of 20 s. The pyruvaldehyde is a precursor of lactic acid. Two homogeneous catalysts (H₂O₂ and NaOH) were added in different experiments to improve the lactic acid production. The maximum concentration of lactic acid was 10% carbon basis using NaOH (0.5M) as catalyst at 27 MPa and 400°C with 40 s of residence time. A model of the process kinetic was made in order to identify the main factors what influence in the selectivity. The density and pH of the medium would play an important role in the selectivity of the process.

Keywords: Biomass, Supercritical Water, Homogeneous Catalyst

1. Introduction

The processes that involve biomass valorization for the production of chemicals and fuels are growing in interest looking for sustainable production of these goods. This kind of developments can be achieved by the combination of selective and effective processes using renewable raw materials. The vegetal biomass unfit for human consumption is a massive alternative as a raw material for the production of chemicals, being cellulose one of the main component of biomass [1]. Cellulose is a polymer formed by β 1-4 linked glucose units. In a previous work a method to break these bonds was developed obtaining a solution of sugars (mainly glucose) with low degradation products formation in a supercritical water medium [2].

Glucose can be modified in a hot pressurized water medium in order to obtain high added value products like lactic acid or 5-hydroxy-methyl-furfural (5-HMF) [3-6]. The different properties that pressurized water medium can adopt could be used to choose the most selective medium. The properties of the medium can be modified by changing the pressure and the temperature of the system. The density seems to be an influential factor in the glucose degradation reactions, favoring retro-aldol reactions at low densities (lactic acid formation pathway) and favoring 5-HMF formation at high densities [3, 4].

In this study, the chemical modification of glucose into high added value products (lactic acid and 5-hydroxymethylfurfural) was analyzed using a hydrothermal reaction medium.

2. Materials and Methods

2.1 Materials

The glucose (99%) and sodium hydroxide (>98%) used in the experiments was purchased from Sigma. Distilled water was used in the experiments. The patterns 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 carbon content of the 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 SH-1011 Shodex at 50°C and a flow of 0.8mL/min using H₂SO₄ (0.01 N) as mobile phase. A Waters IR detector 2414 was used to identify the sugars and their derivatives. An UV-Vis detector was used to determine the 5-hydroxy-methyl-furfural (5-HMF) concentration at a wavelength of 254nm.

Glucose conversion was determined by equation 1, where X is the glucose conversion, C_i is the inlet glucose concentration measured in ppm, C_o is the outlet glucose concentration measured in ppm.

$$X = \frac{C_i - C_o}{C_i} \quad (1)$$

The selectivity of the determined compounds (fructose, glyceraldehyde, methyl glyoxal, lactic acid, formic acid, acrylic acid and 5-HMF) was determined by equation 2, where Y_s is the selectivity of compound 's', C_s is the concentration of the compound 's' measured in ppm, C_{c,s} is the carbon composition of the component 's' with a value between 0 and 1 and C_{c,g} is the carbon composition of glucose.

$$Y_s = \frac{C_s C_{c,s}}{C_i X C_{c,g}} \quad (2)$$

2.3 Pilot plant

The continuous pilot plant used is presented in figure 1; it is operated at temperatures of up to 400°C and pressures of up to 30 MPa. The main advantages of the pilot plant are: (a) the reactor can be considered isothermal due to the instantaneous heating and cooling; (b) the products are not diluted in the cooling; (c) the residence time of the reactor can be varied from 0.004 s to 50 s. A more detailed description and the operation procedure of the pilot plant was presented in a previous work [7].

3. Results and Discussion

Experiments for glucose reaction in pressurized water were carried out at 300°C, 350°C, 385°C and 400°C, at 16, 23 and 27 MPa. The residence times were fixed between 0.4s and 50s. The carbon balance among the inlet and outlet of the reactor was between 87% - 100%. The lower values of carbon balance were achieved at 400°C with residence times higher than 3 s. No char formation was observed at the outlet of the reactor. The main reaction products identified were glucose, fructose, glyceraldehyde, 5-HMF, pyruvaldehyde, lactic acid and acrylic acid.

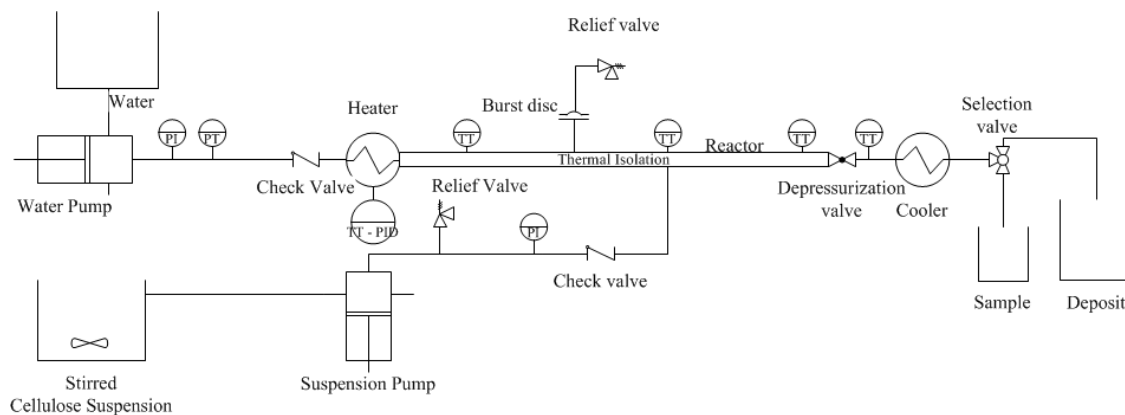


Figure 1. Pilot plant diagram.

A reaction pathway of glucose degradation in hot pressurized water is shown in figure 2. The reaction pathways were constructed using bibliography data [3-6, 8]. Glucose can be degraded mainly by a retro-aldol reaction to glyceraldehyde or via isomerization to fructose. Then, fructose can be dehydrated to 5-HMF.

In order to analyze the effect of the medium density in the reactions of glucose degradation, three sets of experiments are analyzed together in two groups. (1) The density of the medium was almost the same for two sets of experiments by using the following conditions: 400°C and 23 MPa (133 kg/m³); and 350°C and 16 MPa (102 kg/m³). (2) The temperature was kept constant and the density was varied by comparing the following conditions: 350°C and 23 MPa (616 kg/m³); and 350°C and 16 MPa (102 kg/m³). The concentration evolution of the glucose, fructose, glyceraldehyde, pyruvaldehyde and 5-HMF (from top to bottom) along residence time are shown in figure 3. Each column represents a temperature, 300°C, 350°C, 385°C and 400°C from left to right.

3.1 Glucose

The glucose total conversion was achieved at residence time of 3 s, 8 s and 30 s for temperatures of 400°C, 350°C and 300°C respectively. The medium density affects the kinetics of glucose degradation, at same density the reaction of glucose degradation is faster at 400°C than at 350°C. At same temperature the degradation of glucose is achieved faster at a low density. So, the kinetics of glucose degradation at 350°C and 16 MPa takes a value between the kinetic at 350°C and 23 MPa and the kinetic at 400°C and 23 MPa.

3.2 Fructose and Glyceraldehyde

Fructose and glyceraldehyde have a similar behavior, so their evolutions are analyzed together. The maximum selectivity was achieved at 300°C and 23 MPa, about 20% of glucose was converted into fructose in a residence time of 5 s and about 15% of glucose is converted to glyceraldehyde at the same conditions. The analyzed density and temperature effects showed the same behavior that glucose degradation. Fructose is one of the main degradation intermediates in the first reaction pathway of glucose degradation. This could explain the similar behavior find in the disappearance of glucose and appearance of fructose.

3.3 Pyruvaldehyde

The maximum concentration of pyruvaldehyde was achieved at 400 and 23 MPa with a residence time of 5 s, the pyruvaldehyde selectivity at those conditions was 60%. At 350°C and 16 Mpa with a residence time of 3 s, the maximum selectivity was (30%), subsequently in pyruvaldehyde production the temperature has a predominant effect on the selectivity and in the density range studied the density effect is not significant. So, the reaction temperature may be taken as a selectivity factor increasing the kinetic of pyruvaldehyde production more than others kinetics.

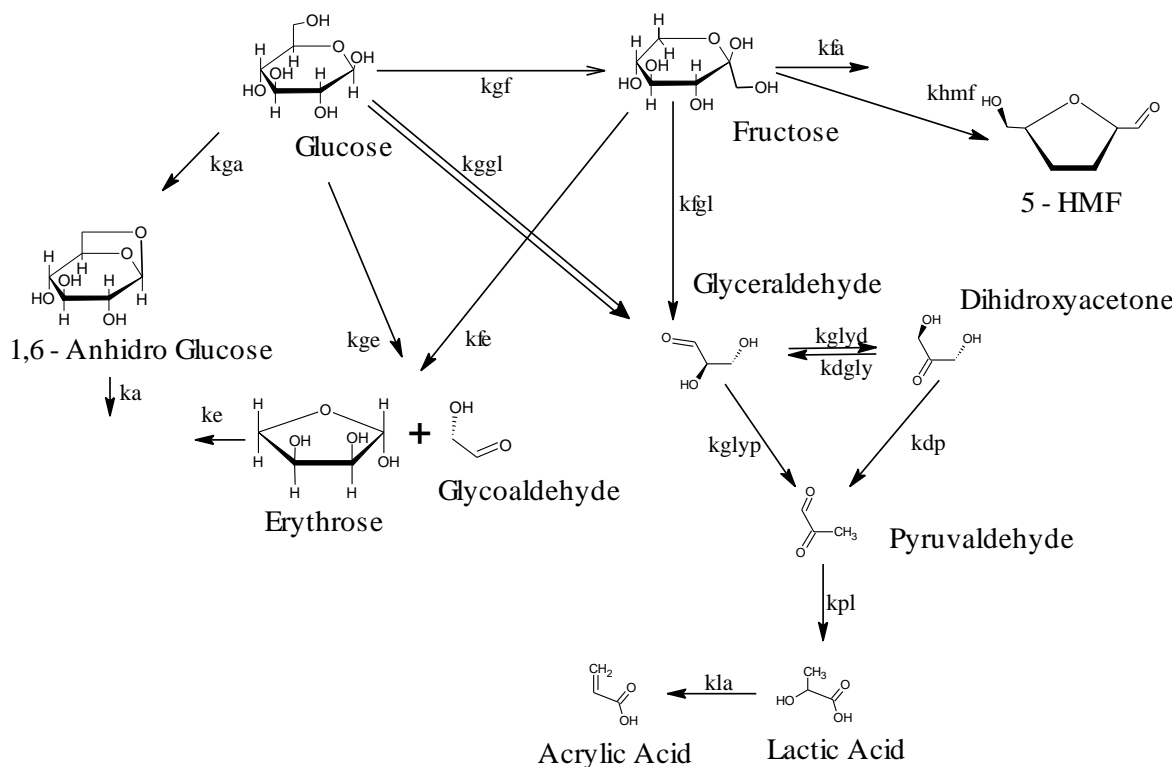


Figure 2. Reaction pathway of glucose degradation in sub and supercritical water [3-5, 8].

3.4 5-HMF

The maximum concentration of 5-HMF was achieved at the lowest temperature, 300°C. The maximum selectivity of 5-HMF was 30% at 30 s of residence time. Like pyruvaldehyde analysis previously presented, the density variation has not a significant influence in 5-HMF formation, while the temperature decreasing improve the 5-HMF formation. At same density, by increasing the reaction temperature (and decreasing reaction pressure) the production of 5-HMF is highly avoided.

3.5 Medium selectivity

The properties of the reaction medium are shown in Table 1. These properties were calculated according a bibliography method [9]. The density change from 350°C/23 MPa (616 kg/m³) to 400°C/23 MPa (133 kg/m³) implies that that density decreased almost 5 times, while ionic product (K_w) is increased 2 times and the dielectric constant (ε) is decreased 7 times. Although, the change from 400°C/23 MPa to 350°C/16 MPa does not imply a significant change in the reaction medium conditions.

Table 1. Reaction medium properties at reactions conditions.

Temperature °C	Pressure MPa	Density kg/m ³	Ionic Product K _w	Dielectric Constant ε
350	23	616	11.9	14.7
400	23	133	20.8	2.0
350	16	102	22.9	1.7
400	27	219	17.8	3.2

At 300°C, the selectivity of 5-HMF is higher than the pyruvaldehyde selectivity (28% vs 18%). By rising temperature the selectivity of pyruvaldehyde is increased while 5-HMF selectivity is decreased. When the effect of density and temperature are analyzed for both products (pyruvaldehyde and 5-HMF) at the same time, it can be concluded that the medium conditions would has not effect in the selectivity at the analyzed

conditions. The temperature would have a predominant effect in the selectivity. The kinetic of pyruvaldehyde production is faster than the kinetic of 5-HMF production when the temperature is increased. Kinetics data of pyruvaldehyde and 5-HMF from a previous work and bibliography were plotted to confirm this idea (Figure 4).

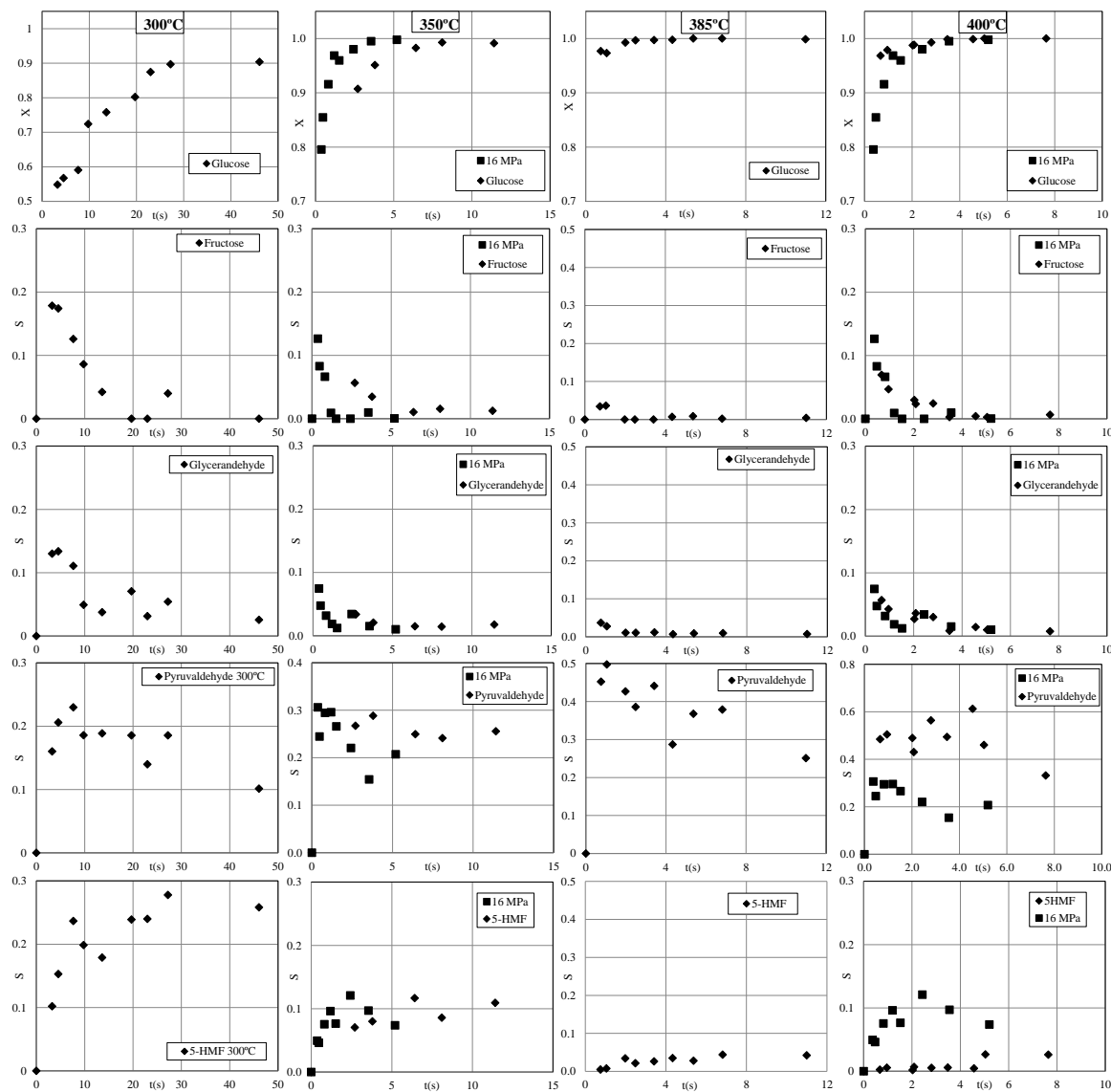


Figure 3. Glucose conversion along residence time at 300°, 350°C, 385°C and 400°C. Selectivity evolution along residence time of fructose, glycerandehyde, pyruvaldehyde and 5-HMF at 300°, 350°C, 385°C and 400°C .

3.6 Catalyst

In a water medium, the reactions of glucose degradations did not produce lactic acid. In order to obtain lactic acid several catalyst combinations were experimented. The different experiments carried out are shown in Table 2.

Sodium hydroxide and hydrogen peroxide were used as catalyst in the experiments in order to produce lactic acid. The experiments using sodium hydroxide produce lactic acid with a selectivity of 8% in a residence time of 43 s. When hydrogen peroxide was used as catalyst, the pyruvaldehyde production was lower than without catalyst but no lactic acid was produced. The maximum selectivity (40%) of lactic acid

was achieved using both catalyst at a pressure of 27 MPa and a residence time of 40 s. The lactic acid selectivity was increased from 5% to 40% when the residence time was increased from 30 s to 40 s.

The concentration of acrylic acid was also analyzed in the experiments using catalyst. Acrylic acid is a degradation product of lactic acid dehydration reaction [10]. The maximum selectivity of acrylic acid was obtained when H₂O₂ was used as catalyst with a residence time of 12 s.

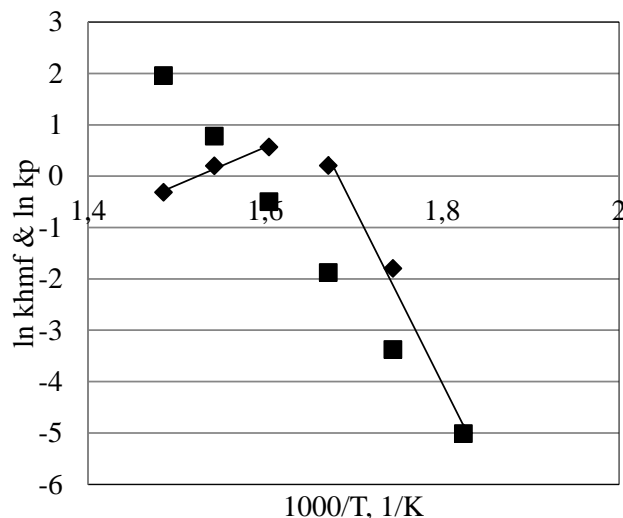


Figure 4. Diamonds (♦), kinetics of 5-HMF formation [7]. Squares (■), kinetics of pyruvaldehyde formation [8].

Table 2. Different catalyst combinations used in the experimentation. The temperature of the experiments was kept constant at 400°C. NaOH was used with a concentration of 0.5 M. H₂O₂ was used in a stoichiometric concentration.

P	Res time	Catalysts	Selectivity			Concentration, ppm		
			Pyruv.	Lactic Acid	Acrylic Acid	Pyruv.	Lactic Acid	Acrylic Acid
230	20.0±0.3	-	0.85	0	0.01	7600	0	170
230	43.5±1.7	NaOH	0	0.08	0.03	0	2100	390
270	12.1±0.1	H ₂ O ₂	0.26	0	0.14	2100	0	1400
270	10.0±0.1	H ₂ O ₂	0.2	0	0.01	1600	0	170
270	10.2±0.1	H ₂ O ₂	0.11	0	0.03	870	0	420
270	10.2±0.2	H ₂ O ₂ + NaOH	0.09	0	0.02	700	0	360
270	40.1±0.5	H ₂ O ₂ + NaOH	0	0.4	0.05	0	3300	700
270	30.0±0.5	NaOH	0	0.05	0.01	0	380	280
270	33.2±0.5	H ₂ O ₂ + NaOH	0	0.06	0.03	0	440	460

4. Conclusions

A lactic acid selectivity of 40% was achieved using a continuous reactor at 400°C and 27 MPa. The maximum lactic acid production was reached using NaOH and H₂O₂ as catalyst. The selectivity of the reactions of glucose degradation could be driven by managing the temperature and the density of the medium. The temperature would play an important role in the intensification of one of the following parallel reactions: production of 5-HMF via fructose dehydration; or pyruvaldehyde formation via retro-aldol condensation of glucose and fructose. At low temperatures 5-HMF formation reactions are favored; at high temperatures the

pyruvaldehyde reactions are favored. The density would play an important role favoring the reactions of dehydration.

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