



# Selective transformation of fructose and high fructose content biomass into lactic acid in supercritical water



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## ABSTRACT

The reactions of fructose in sub- and supercritical water were analyzed changing the chemical properties of the reaction medium ( $K_w$ ,  $\epsilon$ , pH and free radical kidnapers). The reactions were performed in a continuous reactor at 260 °C, 330 °C and 400 °C, at 23 MPa and 27 MPa using water as reaction medium. The pH of the medium was modified using oxalic acid and sodium hydroxide. Also, scavengers (TEMPO and BHT) were tested in order to determine its influences in the radical reactions. The main product of fructose hydrolysis in supercritical water was pyruvaldehyde (>80%, w·w<sup>-1</sup>) at 400 °C and 23 MPa with a reaction time of 0.7 s. Furthermore, the reactions of fructose were analyzed in combination with glucose. It was determined that different retro-aldol condensation products can be obtained depending on the starting material. Fructose produced mainly C-3 molecules (pyruvaldehyde) and glucose produced mainly C-2 molecules (glycolaldehyde). The isomerization of fructose to glucose was negligible and so was the production of C-2 when the starting material was fructose. The yield of 5-HMF was negligible when the starting material was glucose. Three different biomass enriched in fructose (sugar cane molasses, beet molasses and inulin) were tested as starting material for the hydrolysis process. It was determined that lactic acid (50%, w·w<sup>-1</sup>) was the main product of molasses and inulin hydrolysis in a supercritical water medium modified with basic catalysts.

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## 1. Introduction

Processes that involve the use of biomass as raw material have been intensively studied in the near past looking for new processes capable of producing biocompounds, biofuels and bioenergy using “green” solvents. One way to achieve these processes is by using selective and efficient reaction mediums. The vegetal biomass is an alternative as raw material, being cellulose (glucose resource) one of the main component of biomass [1,2]. A method to break cellulose into sugars (mainly glucose and fructose) was developed in a previous work obtaining as product a solution of sugars with low formation of derived products, such as 5-hydroxymethylfurfural (5-HMF) in a supercritical water medium [3]. Another interesting raw materials for the production of chemicals are the by-products

of the food and agriculture industry with high amounts of carbohydrates, such as the sugar cane and beetroot molasses produced in the sugar manufacturing process. These by-product streams are composed mainly of sucrose, glucose and fructose.

Lactic acid is a product of interest of many industries; it is used in food, chemical, pharmaceutical and cosmetic industries. Nowadays, the most valuable alternative for the use of lactic acid would be the production of the biodegradable lactic acid polymer [4]. The lactic acid can be produced by chemical synthesis or by carbohydrates fermentation. However, lactic acid is industrially produced mainly by fermentation [4]. Glucose can be modified in a hot pressurized water medium in order to obtain added value products like lactic acid [5–10]. The production of lactic acid was achieved in a previous work of our group by using NaOH as medium modifier [9]. The production of lactic acid was also studied using by-products streams like sugar cane molasses [11,12]; paper sludge [13] or other cellulosic biomass [14,15] as raw materials. Also the production of lactic acid was studied using fructose as raw material [16]. However, several works in literature attempt to produce

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5-hydroxymethylfurfural (5-HMF) from fructose because this product is considered as a building block in the production of chemicals [17]. The production of 5-HMF was studied using ionic liquids with acid catalysts [18–20]; biphasic reactors with solid catalyst [21] and; hydrothermal reactor with catalyst [22,23].

Pressurized water at temperature between 300 °C and 400 °C can adopt different identities depending on the temperature and pressure. This behavior of compressed water could be used to change the medium identity and choose the most appropriate one to the desired reactions. Thus, only using water could set a selective medium. The density and the ionic product of water are the two key factors in the hydrolysis reactions of glucose and fructose, favoring retro-aldol reactions at low densities (lactic acid formation pathway) and favoring 5-HMF and ionic products formation at high densities [5,6,24–26]. Additionally, the use of supercritical water as reaction medium allows the intensification of the process by reducing the required reaction time of the reactions. Typical reaction times of glucose and fructose reactions at supercritical conditions are between 0 s and 5 s [6,9]. These reaction times are substantially lower than the required for the low temperature catalyzed processes (from seconds to hours) or microorganism processes (from seconds to days).

In this study, the influence of the reaction medium in the chemical modification of fructose into pyruvaldehyde, considered as a lactic acid precursor [27,28], was analyzed using a hydrothermal reaction medium. The reaction pathway was analyzed to understand the driving factors to obtain high selectivity of the desired products. The production of lactic acids in a hydrothermal medium was analyzed using sugar cane molasses, beetroot molasses and inulin as starting material.

## 2. Materials and methods

### 2.1. Materials

Glucose (99%), fructose (99%), sucrose (99%), sodium hydroxide (>98%) and oxalic acid (98%) used in the experiments were purchased from Sigma. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-tert-butyl-4-methylphenol (BHT) were supplied by Sigma. A local supplier provided sugar cane and beetroot molasses. The company Boneo Orafit provided inulin. Distilled water was used as reaction medium in the experiments. The chemicals used as reagents in HPLC (High Performance Liquid Chromatography) analysis were: cellobiose (>98%), glucose (>99%), fructose (>99%), glyceraldehyde (95%), pyruvaldehyde (40%), erythrose (>75%), glycolaldehyde dimer (>99%), 5-hydroxymethylfurfural (99%), lactic acid (85%), levulinic acid (98%), formic acid (96%) and acetic acid 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 pH of the samples was measured with a pH meter Nahita model 903. The composition of the liquid products was determined with a HPLC. The HPLC column used for the separation of the sample compounds was SH-1011 from Shodex® at 50 °C and a flow of 0.8 mL min<sup>-1</sup> using H<sub>2</sub>SO<sub>4</sub> (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-HMF concentration at a wavelength of 254 nm. In order to identify the main peaks and calculate the areas of the complex mixture that we obtained during the experiments we have used a band-analysis via Fast Fourier Transform (fft) and band-adjustment by Gaussian functions. The adjustment was done by minimizing the quadratic error using a Nelder–Mead algorithm.

The yield of the determined compounds (fructose, glucose, glyceraldehyde, pyruvaldehyde, lactic acid, formic acid, acrylic acid and 5-HMF) was determined by equation 1, where  $Y_s$  is the yield of the compound 's',  $C_s$  is the concentration of the compound 's' measured in ppm,  $F_{c,s}$  is the carbon composition of the component 's' with a value between 0 and 1; TOC is the total organic carbon content in the sample in ppm:

$$Y_s = \frac{C_s F_{c,s}}{\text{TOC}} \quad (1)$$

### 2.3. Experimental setup

To perform the experiments presented here a continuous sub- and supercritical continuous hydrolysis plant able to work at conditions up to 400 °C and 30 MPa was used. The solution of biomass (fructose, glucose/fructose mixture, molasses or inulin) was continuously pumped up to the operation pressure and instantaneously heated by injecting a stream of supercritical water at the inlet of the reactor. The effluent was suddenly depressurized at the outlet of the reactor without previous cooling in order to instantaneously stop the reaction, reducing in this way its temperature down to 150 °C. A scheme of the pilot plant is shown in Fig. 1.

The main advantages of the pilot plant design 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 reaction time can be varied from 0.01 s to 50 s by using different reactor volumes and flows. A more detailed description of the facility and the operation procedure of the pilot plant was presented in a previous work [29]. However, two improvements were added to the used experimental setup in this work in comparison with the previous one. Firstly, an extra pipeline was added to the reactor. The catalyst or medium modifier (if used) was fed directly to the reactor in a separate stream. At the beginning of the experimentation, the catalyst was pumped to the reactor together with the biomass stream. At that moment, it was observed that the biomass was degraded before reaching the reactor because of the interaction with the catalyst. Considering that, the catalyst and the biomass were fed to the reactor separately as it is shown in Fig. 1. The cooling method used in this work was the sudden decompression of the reactor outlet. As it was mentioned above, this method allows the rapid cooling of the reagents which stops the reactions very fast. Moreover, this cooling method presents some opportunities in the post processing of the sample. The drop in the pressure, from 250 bar to atmospheric is a flash operation that can be used as a purification process if a separator is installed after the decompression valve. In order to test this effect, a flash chamber was installed in the experimental setup for evaluating its benefits.

## 3. Results and discussion

The experiments of fructose hydrolysis in pressurized water were carried out at 260 °C, 330 °C and 400 °C, at 23 MPa and 27 MPa. The reaction time was varied between 0.1 s and 6 s. In order to evaluate the effect of pH, oxalic acid [30] or NaOH [31] were added to the medium. The carbon balance of the samples was determined by the TOC concentration between the inlet and outlet of the reactor. The obtained values were between 93% (w·w<sup>-1</sup>) and 100% (w·w<sup>-1</sup>). The reaction products identified were glucose, glycolaldehyde, glyceraldehyde, 5-HMF, pyruvaldehyde, lactic acid and acrylic acid.

A reaction pathway of glucose hydrolysis in hot pressurized water is shown in Fig. 2. The reaction pathways were constructed following the reaction pathways developed in literature [32]. Fructose can be degraded mainly by (1) retro-aldol condensation reaction to produce glyceraldehyde or (2) via dehydration to 5-HMF, being the isomerization of fructose to glucose a minor

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