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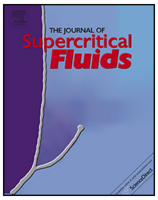

Transformation of glucose into added value compounds in a hydrothermal reaction media

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ABSTRACT

In this study, the chemical transformation of glucose into 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 used 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 23 MPa and 27 MPa for the experiments. No lactic acid was found at those conditions. High yield of glycolaldehyde (80%, w/w) was found operating at 400 °C and 27 MPa with reaction times of 20 s. Two additives (H_2O_2 and NaOH) were added in different experiments to improve the lactic acid production. The maximum yield of lactic acid was 57% (w/w) carbon basis using NaOH (0.5 M) as catalyst at 27 MPa and 400 °C with 20 s of residence time. It was observed that the pH of the medium plays an important role in the selectivity of the process.

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 [1,2]. This kind of developments can be achieved by the combination of clean, selective and effective processes using renewable raw materials. Plant biomass unfit for human consumption is a massive and worldwide available source of carbon material which is an alternative as renewable raw material for the production of bio-chemicals, bio-fuels and bio-energy. Cellulose (glucose resource) is one of the main component of biomass [3]. One of the main challenges that should be achieved to the development of the Biorefinery concept is the conversion of the biopolymers (cellulose, hemicellulose and lignin) into its monomer [4]. In this way, a method to selectively break cellulose into sugars was developed obtaining a solution of sugars with a low concentration of degraded products in a supercritical water medium [4,5]. In that process, cellulose is hydrolyzed in supercritical water obtaining a sugars (mainly glucose) production yield of around 98% (w/w). The key point to obtain this yield was the effective control in the reaction temperature and reaction time.

Glucose is a promising molecule that can be used as starting material for many productive processes. For example, glucose can be used as feed in biological processes for the production of bio-fuels or bio-chemicals [6,7]. Also, glucose can be modified in chemical processes to produce building blocks like 5-hydroxymethylfurfural (5-HMF), glycolaldehyde or lactic acid among others. Lactic acid is a product of interest for many industries such as food, chemical, pharmaceutical and cosmetic. Nowadays, the major use of lactic acid would be the production of the biodegradable lactic acid polymer [6]. So far, most lactic acid is produced by chemical synthesis or by carbohydrates fermentation. This last method being the most used in industry [6]. The 5-HMF can be used as starting material for a number of applications, including; polymer productions by monomer modification and polymerization, use as fine chemicals (pharmaceutical, agrochemical, etc.), and the production of fuels [8]. 5-HMF production is mainly achieved by carbohydrates dehydration. The different method of 5-HMF synthesis can be classified by the characteristics of the reaction medium as: single phase systems; biphasic systems and; ionic liquids systems [8].

The use of hot pressurized water medium has been proposed and proved to be a good reaction medium to perform the modification of glucose to produce lactic acid or 5-HMF [9–12]. One of the main reasons that make the use of supercritical water as reaction medium an attractive alternative for producing added value products is the possibility of changing the physic-chemical properties

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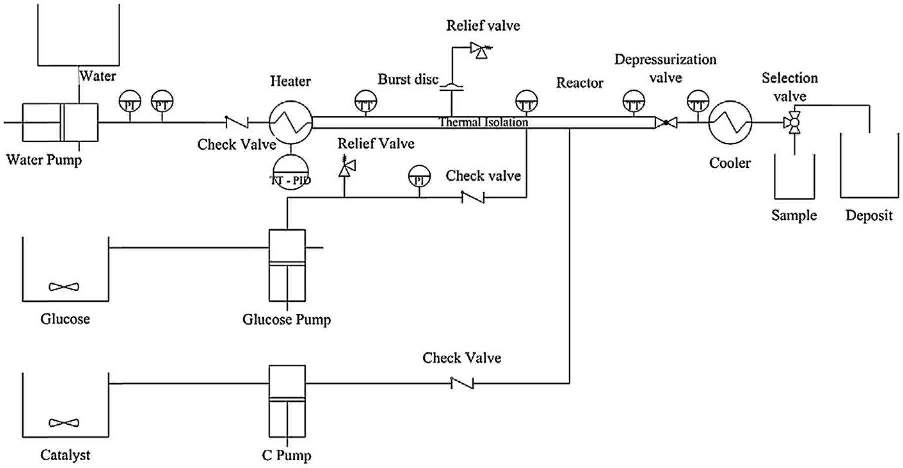

Fig. 1. Pilot plant diagram.

of the solvent by simply changing the pressure and temperature of the reactor. These properties can be modified in order to choose and adequate medium where highest selectivity of chosen compounds is obtained. The ion concentration of the medium seems to be a key factor in the glucose degradations reactions, favoring retro-aldol reactions at low ion concentrations (lactic acid formation pathway) and favoring 5-HMF formation at high ion concentrations [13]. For example, the production of lactic acid was maximized in a batch reactor using NaOH and $Ca(OH)_2$ as catalysts obtaining yields of between 20 and 40% at temperatures of 300 °C and residence time of 1000 s [14,15].

In this study, the influence of the reaction medium in the chemical modification of glucose into added value products (lactic acid) was analyzed using a hydrothermal reaction medium.

2. Materials and methods

2.1. Materials

The glucose (99%), sodium hydroxide (>98%) and hydrogen peroxide (30%) used as reagents in the experiments were purchased from Sigma. Distilled water was used as solvent to feed the reactor in the experiments. The standards used in HPLC (High Performance Liquid Chromatography) analysis were: glucose (>99%), fructose (>99%), glyceraldehyde (95%), glycolaldehyde dimer (99%), 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 by HPLC. The HPLC column used for the separation of the compounds was Sugar SH-1011 Shodex at 50 °C and a flow of 0.8 mL/min using H_2SO_4 (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.

Glucose conversion was determined by Eq. (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.

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

The yield of the determined compounds (fructose, glyceraldehyde, methyl glyoxal, lactic acid, formic acid, acrylic acid and 5-HMF) was determined by Eq. (2), where Y_s is the yield 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 (g carbon/molecular weight); and $C_{c,g}$ is the carbon composition of glucose.

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

2.3. Experimental setup

The pilot plant used in this work is presented in Fig. 1. The reactor of the hydrolysis pilot plant could operate at temperatures up to 400 °C and pressures of up to 30 MPa. All the hot parts of the setup were constructed with Inconel alloy 625 in order to avoid corrosion in the materials. The reactor was continuously operated and it was fed with three different streams: glucose solution (up to 6 kg/h), water (up to 2 kg/h) and additives (up to 1 kg/h). The glucose solution (7%, w/w) was chemically stable at room temperature (any degradation was observed). The starting of the hydrolysis reactions was achieved by heating the glucose stream at the inlet of the reactor.

In order to avoid heating ramps that can lead to undesired reactions, the heating and the cooling of the reactor was designed and built in an instantaneous way as it was schematized in Fig. 2. The glucose stream (cold) was pumped up to the operation pressure at room temperature and then it was mixed in a tee junction (beginning of the reactor) with supercritical water (hot). In this way, the temperature of glucose was modified from room temperature to the reaction temperature very fast. The hydrolysis reactions start when the temperature is increased, so in this setup the starting of the reactions was achieved almost instantaneously. The original facility was developed in a previous work [5], however, it was modified in order to make possible the feeding the reactor 10 cm after the inlet. The aim of this modification was to feed an additive to the reactor in an independent stream. So, the reactor was fed with a hot stream of water, a cold glucose stream and an additive stream (Fig. 2). The reaction time was varied changing the length of the reactor (volume) and the flows fed to the reactor. In order to make the reactor as thermal stable as possible it was insulated with Rockwool.

The other important development of the experimental setup is the cooling method. The temperature governs the beginning and ending of the reactions, so the cooling method was designed