



## Energetic approach of biomass hydrolysis in supercritical water



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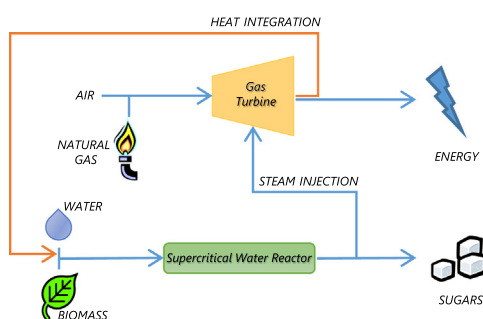
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### HIGHLIGHTS

- Synergy between supercritical water hydrolysis and combined heat and power systems.
- Production of sugars selectively with low energy demand.
- Yield improvement of the combined heat and power systems by vapor injection.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Cellulose hydrolysis can be performed in supercritical water with a high selectivity of soluble sugars. The process produces high-pressure steam that can be integrated, from an energy point of view, with the whole biomass treating process. This work investigates the integration of biomass hydrolysis reactors with commercial combined heat and power (CHP) schemes, with special attention to reactor outlet streams. The innovation developed in this work allows adequate energy integration possibilities for heating and compression by using high temperature of the flue gases and direct shaft work from the turbine. The integration of biomass hydrolysis with a CHP process allows the selective conversion of biomass into sugars with low heat requirements. Integrating these two processes, the CHP scheme yield is enhanced around 10% by injecting water in the gas turbine. Furthermore, the hydrolysis reactor can be held at 400 °C and 23 MPa using only the gas turbine outlet streams.

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### 1. Introduction

In the last years a general tendency to the production of fuels, energy and chemical products from sustainable methods has been motivated for the development of a society supported in the bioeconomy (BECOTEPS, 2013). This goal would be reached by using energy efficient processes treating renewable raw materials.

Plant biomass is probably the most useful and widely available renewable raw material. For example, lignocellulosic biomass that

cannot be used for human consumption, represents a viable alternative source of chemicals and energy (Ragauskas et al., 2006; Tollefson, 2008). The annual biomass growth on land areas is estimated to be 10,000 dry tons ha<sup>-1</sup> (Ragauskas et al., 2006). Taking into account the crude oil production and the carbon-energy equivalence between biomass and oil (2.5 times higher for oil), less than 10% of the annual growth of plant biomass is needed to replace current carbon from petroleum production (Bobleter, 1994). Biomass is composed of 34–50% cellulose, 16–34% hemicellulose and 11–29% lignin (Bobleter, 1994). As the most important skeletal component in plants, cellulose is an almost inexhaustible polymeric raw material (Klemm et al., 2005). The challenging step in the processing of the cellulose fraction of biomass is the

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production of sugars such as glucose (Tollefson, 2008). Usually, a pretreatment process is required to fractionate biomass into its fractions previous cellulose hydrolysis. However, the supercritical water medium showed to be a promising technology to hydrolyze cellulose and hemicellulose simultaneously and selectively without pretreatments (Cantero et al., 2015). Glucose is a target product because it can be used as a raw material in the production of chemicals, materials and bio-fuels (Corma et al., 2007; Huber and Corma, 2007; Huber et al., 2006; van Putten et al., 2013). Hydrolysis leads to cleavage of ether and ester bonds by the addition of one molecule of water for every broken linkage which results in the production of simpler sugars as glucose (Brunner, 2009). The current manufacturing philosophy is based on the massive production of throwaway products with large requirements of raw materials and energy. On the other hand, for a biomass chemical industry, the philosophy may be moved to a local production of renewable products from low energy density sources taking into account the distributed nature of biomass resource. 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 region (Arai et al., 2009).

The reduction in equipment cost, environmental compatibility and the hydrolysis at high temperatures can be achieved using supercritical fluids, mainly supercritical CO<sub>2</sub> and H<sub>2</sub>O (Peterson et al., 2008). The properties of water at conditions near and above its critical point (374 °C, 22.1 MPa) constitute new ways of byproducts valorization from industry wastes, for example the waste of food industry (Arai et al., 2009). The main reasons that make the hydrothermal medium a promising alternative for biomass processing are as follows (Peterson et al., 2008): (1) it is not necessary to reduce the water content in the raw material, thus avoiding energy losses expenses linked to evaporation or drying; (2) the reaction media permits the transformation of the different biomass fractions; (3) the mass transfer limitations are reduced or avoided, thus allowing faster reaction rates. Furthermore, it is possible to control the reaction selectivity adjusting the conditions of the reaction media simply by changing pressure and temperature, which is useful to avoid the generation of by-products. In addition, biofuels and chemical products produced would be free of biologically active organism and compounds, including bacteria, viruses and even prion proteins (Peterson et al., 2008) because of the high temperatures involved. For these reasons, the use of supercritical fluids has been proposed as a clean technology to integrate the depolymerization-reaction-separation processes. Also, the reactions of biomass hydrolysis in supercritical water are extremely fast (Cantero et al., 2013b), which allows the processing of high amounts of biomass in small reactors. Because of the aforementioned advantages, this technology can be considered as promising for decentralizing chemical processes.

The aim of this work was to evaluate alternatives for obtaining an efficient supercritical water hydrolysis process with low demand of energy. In this kind of processes, the reactor should be operated at high pressure (23 MPa) and temperature (400 °C), which makes necessary the use of high quality energy flows. Also, the supercritical water hydrolysis process involves a rapid cooling of the reaction products in order to avoid their degradation obtaining in this way a considerable loss of energy quality. However, the cooling method presented in this article (flashing of the products from 23 MPa to 1.3 MPa) has the advantage of producing two streams: saturated water vapor at 200 °C and concentrated sugar solution. Considering the restriction of the process, the focus of the energy integration studied here was concentrated in the use of the steam produced after the reactor. The steam composed almost exclusively of water (>99.9%) is susceptible of being injected in the traditional system of combined heat and power

schemes. The CHP schemes use natural gas as fuel, which is burned and expanded in a turbine producing high temperature flue gases and shaft work (Koivu, 2007). These processes could be enhanced by injected steam to the combustor, obtaining higher yields and decreasing the NO<sub>x</sub> emissions (Nishida et al., 2005). Considering the needs and requirements of the supercritical water process and the combined heat and power scheme, there have been studied three energetic alternatives to develop the process of biomass hydrolysis in an energy efficient way. Two of them deal with the integration of the supercritical water hydrolysis process with a process of energy production using a gas turbine with or without steam injection. The third alternative was fossil fuel independent, using a biomass burner to obtain the heat requirements.

The objective of this work is the thermodynamic analysis of the processes integration between: (1) cellulose hydrolysis in supercritical water and; (2) gas turbine with steam injection. The thermal energy contained in the gas turbine flue gases is used to heat up a pressurized stream of water, which will reach supercritical conditions to carry out the hydrolysis process. Moreover, vapor fraction produced after the hydrolysis reactor is used to enhance the shaft work production of the gas turbine.

## 2. Methods

### 2.1. SCW cellulose hydrolysis: process description

The hydrolysis of cellulosic biomass in supercritical water can be analyzed in different stages as it is shown in Fig. 1. As starting point, cellulose and water should be pressurized up to the reactor pressure. For this purpose, a positive displacement pump can be used to increase the pressure from atmospheric until 25 MPa (or desired pressure). Special attention should be devoted in the biomass pumping. Biomass is composed of diverse materials and is not soluble in water. Because of this, a suspension of biomass should be able to be pumped. Although this issue would produce troubles of clogging at lab scale, this problem can be overcome in the scaling up (Peterson et al., 2008).

In a previous work of our research group (Cantero et al., 2013b), a pilot plant was designed and built in order to perform biomass hydrolysis. In the aforementioned setup (see Fig. 1), two pumps were used to impulse water and a biomass suspension (5% w w<sup>-1</sup>). The second stage in the process is the heating of the biomass stream, which coincides with the start of the reactions. In order to avoid uncontrolled reactions, it is important to heat up the cellulose stream as fast as possible avoiding heating ramps. The heating of biomass stream was achieved by mixing it with supercritical water in a tee junction. This heating method is almost instantaneous. The biomass stream pumped by P-1 reaches the reactor at room temperature. On the other hand, water pumped by P-2 is heated up to 450 °C in a furnace to be finally mixed with biomass. The third important stage is the reaction. After the desired temperature is reached, the residence time of biomass at reaction conditions is critical for the selectivity of the process. Supercritical water hydrolysis is fast, so reaction times higher than 0.3 s would lead to a product with high rate of degradation products (Cantero et al., 2013c). The residence time was changed in the designed setup by modifying the flows and the reactor volumes (length in tubular reactors). Finally, after the desired residence time is achieved, the products should be rapidly cooled in order to stop the hydrolysis reactions. The cooling of the products was achieved by sudden decompression of the reactor products. With this method it is possible to decrease the temperature of the stream from 400 °C to 150 °C between the inlet and outlet of the valve. After this, the products were cooled down to room temperature in a heat exchanger. See the Supporting information for further details about the experimental setup.

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