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# Low temperature supercritical water gasification of biomass constituents: Glucose/phenol mixtures



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## ABSTRACT

Supercritical water gasification (SCWG) is an interesting technology for the production of energy from wet and residual biomass. To date, the complete understanding of the fundamental phenomena involved in SCWG is still an open issue. An interesting aspect to be investigated is represented by the interactions among the single constituents of biomass, such as cellulose and lignin. This can be accomplished by using glucose and phenol as model compounds. In the present study, four glucose/phenol mixtures were utilized. All mixtures presented a constant organics mass fraction of 5%, where the relative fraction of phenol ranged from 0% (pure glucose) to 30%. The mixtures were gasified at 400 °C and 25.0 MPa in a continuous tubular reactor, with a residence time between 10 and 240 s. Results showed that, at the considered reaction conditions, phenol mostly behaves as a sort of inert in terms of total gas production, although it plays an inhibitory action towards H<sub>2</sub>. The analysis of the liquid phase revealed that phenol likely inhibits Cannizzaro and de-carbonylation reactions and it advantages the pathways involving de-hydration reactions.

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## 1. Introduction

Biomass, that is every material resulting from a living being, is an interesting feedstock which can be used for the chemistry of tomorrow. A large part of world's available biomass is wet, with a moisture content even higher than 70% [1]. This is the case, for example, of many residual materials deriving from agriculture and agro-industry. Traditional thermochemical technologies, such as combustion, gasification and pyrolysis,

are not suitable for such kind of feedstock. Indeed, they require a dry material in order to reduce the energy needs of the operations and, thus, to ensure the economic sustainability of the whole process [2]. The only possibility for the energy conversion of wet biomass is currently represented by biochemical processes (e.g. anaerobic digestion), relying on microorganisms to produce biogas. Although biochemical technologies are quite popular, their efficiency is limited, since they are only effective for the fraction of bio-materials that can be degraded by bacteria.

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A possible solution for the energy valorization of wet biomass is offered by supercritical water gasification (SCWG) [3]. SCWG involves the reaction of biomass with water at supercritical state, that is at a temperature higher than 374.1 °C and at a pressure above 22.1 MPa. Under these conditions, water exhibits a very peculiar behavior, with properties intermediate between those of liquids and gases. Moreover, the dielectric constant of water reduces significantly [4], thus enabling it to dissolve also non-polar compounds. A very homogeneous reaction environment can thus be established, with chemical processes taking place in a single, supercritical phase. This is highly beneficial for reaction rates, and it ensures high gas yields, avoiding the formation of unwanted compounds like char and tar [5].

In the literature, a number of studies have been presented, concerning several different biomass feedstock [6–10]. One difficulty of conducting experimental studies with biomass is represented by the high heterogeneity of such material. Indeed, biomass composition is potentially highly variable, including an exceptionally large number of organic compounds. Such aspect represents a strong limitation for the study of the fundamentals of the process. In order to overcome such an issue, a common approach is to utilize standardized model compounds, able to mimic the constituents of real biomass. In this way, it is possible to achieve a fixed and controlled composition, allowing for an easier observation of the basic phenomena involved in SCWG. Cellulose and lignin, that is the main constituents of ligno-cellulosic biomass, have been often schematized through glucose [11–15] and phenol [16], respectively. Indeed, glucose is the monomer of cellulose, while phenol represents one of the constituting building blocks of lignin. Other sugars were also adopted, especially as model compounds of hemicelluloses [17,18]. Protein-containing biomass (e.g. animal residues or algae) has been modeled through amino acids, like glycine [19].

Glucose and phenol could be thus considered as model compounds for the main constituents of ligno-cellulosic biomass. Through such schematization, it is also possible to investigate the mutual effects played by the different biomass constituents. This is a fundamental issue: indeed, since biomass is an agglomerate of several compounds, it is useful to understand the interactions taking place among such constituents. A first example of work showing the interactions among different biomass constituents was provided by Goodwin and Rorrer: the authors gasified xylose and phenol in a micro-structured device [17]. Another example is represented by the work by Yoshida and Matsumura [18], where ternary mixtures of cellulose, xylan and lignin were gasified. As far as glucose/phenol mixtures are concerned, a fundamental work is represented by the experimental tests by Weiss-Hortala et al. [20]. In this work, the authors gasified water solutions of glucose and phenol at a mass fraction of 1% at different temperatures, ranging from 450 °C to 550 °C, in the presence of  $K_2CO_3$  catalyst. They observed that, compared to the single compounds, the SCWG of their mixture gave a gas yield lower than their sum: in other words, phenol was observed to play an inhibitory effect on glucose gasification, which was attributed to the activity of phenol as a free radical scavenger. Some issues are still open. First of all, it is interesting to observe how the same system would behave at lower

SCWG temperatures, where radical pathways are competing with ionic ones [21]. Low temperature SCWG is also interesting for technological reasons. By lowering the process temperature, lower capital and operating costs could be achieved in view of a future industrial implementation, still obtaining a valuable fuel gas. Furthermore, it would be important to evaluate the effect of increasing phenol concentrations on the gasification yields. Finally, a systematic analysis of both gaseous and liquid products at varying residence times would give precious information about the reaction pathways involved.

In the present work, the gasification of glucose/phenol mixtures was carried out in a continuous tubular reactor. Four different glucose/phenol mixtures were adopted, with increasing phenol content but with the same overall organics mass fraction (5%). The tests were conducted at 400 °C, at a pressure of 25.0 MPa, with residence times ranging from 10 to 240 s. Gaseous and liquid products were sampled and then characterized by means of analytical chemistry techniques. Possible reaction schemes were sketched on the basis of the analytical results.

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## 2. Materials and methods

In the present section, details are given about the experimental apparatus (Section 2.1) and the analytic procedures utilized to characterize the reaction products (Section 2.2).

### 2.1. The experimental apparatus

The apparatus utilized is a continuous system for SCWG, based on a heated pressurized tubular reactor. A scheme of the plant is depicted in Fig. 1.

The plant was fed by a bottle filled with the water solution to be gasified (glucose and phenol in different relative amounts). The liquid was pumped by means of a HPLC (high performance liquid chromatography) pump to the desired pressure of 25.0 MPa and passed through a pre-heater, constituted by three electrical resistors of 250 W each. Control loops, involving thermocouples and PID controllers, allowed holding the temperature of each resistor at the constant value of 250 °C.

After the pre-heater, the reacting mixture entered the reactor, constituted by a tube of stainless steel 1.4571/316Ti (length: 320 mm; internal diameter: 8.2 mm). The reactor was placed inside a heater constituted by a ceramic shell with four electrical resistors of 500 W each. This heating element was able to increase the temperature of the fluid up to the reaction conditions (400 °C). Inside the tube, a K-type thermocouple, located at approximately 150 mm along the axis of the reactor, was used to read the inner temperature.

After reaction, the products were cooled down to room temperature by means of a cooling loop. Then, a back-pressure valve (TESCOM® 26-1721-24A) expanded the products to atmospheric pressure. The whole pressure control loop consisted of a digital manometer reading the reactor pressure, a controller, and the back-pressure valve driven by compressed air at a variable pressure. The loop allowed to keep the reactor pressure at the desired set point value (25.0 MPa). After

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