

Supercritical Water Gasification of Glucose/Phenol Mixtures as Model Compounds for Ligno-Cellulosic Biomass

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Supercritical water gasification (SCWG) of biomass is one of the most promising ways to convert wet biomass into a valuable gas mainly composed of methane and/or hydrogen, according to the selected experimental conditions. A wide range of biomass can be classified as ligno-cellulosic, meaning that its main components are represented by cellulose and lignin. Such two main constituents of biomass behave in a completely different manner. It is known that lignin is much more difficult to gasify than cellulose. However, the effect of such inhibition has never been studied in great detail. In this work, glucose and phenol are used as model compounds for cellulose and lignin, respectively. Four aqueous mixtures were prepared, with a fixed organics content of 5 wt %, the remaining part being constituted by water. The organics content was represented by glucose/phenol in different relative amounts, ranging from a phenol concentration of 0 wt % (glucose only) to 30 wt %. Such mixtures underwent SCWG in a continuous tubular reactor at 400°C and 25.0 MPa, with different residence times, ranging from 10 to 240 s. Results show that phenol gives a limited contribution to gas production. On the other hand, phenol does not seem to be an inert, since it reacts in the liquid phase to form other compounds, probably tar and/or solids.

1. Introduction

In the field of renewable energy from biomass, supercritical water gasification (SCWG) has been proposed during the last few years as a valuable technology to efficiently convert biomass into energy (Matsumura et al., 2005). The reaction of biomass with water results in a fuel gas, which can be rich in methane and/or oxygen, according to the operating conditions (Castello and Fiori, 2011).

SCWG benefits of the unique properties of water at supercritical state. Indeed, supercritical water ($T > 374$ °C and $P > 22.1$ MPa) exhibits a behaviour intermediate between a liquid and a gas. Like a liquid, it has still quite high density and good solvent power; at the same time, however, it has the diffusivity and the reactivity typical of a gas. Moreover, water at supercritical state shows a very peculiar behaviour as solvent. Indeed, at high temperature and pressure, the dielectric constant of water dramatically decreases. This means that water starts behaving like a non-polar solvent, with an increased ability to dissolve many organic compounds that would not be dissolved in normal conditions (Kruse, 2009). Dealing with gasification, this translates into a great advantage: optimal mixing allows reducing the occurrence of tar formation, which is one of the factors hampering the diffusion of traditional gasification technologies (Bridgwater, 2003). Furthermore, the great advantage of SCWG is its ability to deal with wet biomass, with moisture contents even higher than 80 wt %. The energy valorisation of such class of feedstock is not commonly achievable with traditional thermochemical technologies, for which dry biomass is mandatory. SCWG opens new perspectives for the treatment of residual biomass (Myrén et al., 2011) and also algae (Freitas and Guirardello, 2013), one of the most promising energy feedstock for the future.

Many efforts have been performed in order to understand the mechanisms governing SCWG. A number of studies in the literature have been devoted to the analysis of simple organic molecules, which could be considered as model compounds for real biomass (DiLeo et al., 2008). This choice provides an effective way of studying SCWG, since it eliminates the complexity of real biomass, which is composed by a very high number of organic compounds, whose accurate characterization might even be impossible. Among the model compounds used to mimic biomass, glucose and phenol have been often used respectively for cellulose and lignin, the main constituents of ligno-cellulosic biomass. Although there are some studies which use glucose (Chuntanapum and Matsumura, 2010) and phenol (DiLeo et al., 2007) in separate tests, the gasification of glucose/phenol mixtures has been only rarely investigated. To our knowledge, the only study in this field is the one by Weiss-Hortala et al. (2010), who performed the SCWG of a glucose/phenol mixture. In their fundamental work, the authors came to the conclusion that phenol plays an inhibiting effect on glucose gasification. In other words, not only phenol was found to be refractory to gasification, but it was observed that it reduces even the gasification propensity of glucose itself. They attributed such effect to the role of phenol as a “radical scavenger”: the phenol molecule would act as a sort of barrier, limiting the course of some gasification reactions. On the other hand, the authors performed only a limited number of tests, without analyzing, for example, the effect of different concentrations of phenol.

The present work aims at extending the knowledge about glucose/phenol SCWG, since its understanding is crucial for the comprehension of the SCWG of ligno-cellulosic biomass. In order to observe the specific influence of the amount of phenol, four aqueous mixtures of glucose/phenol were considered, having the same organics contents (5 wt %), but increasing phenol concentrations. Tests were carried out in a continuous, tubular reactor operated at 400 °C and 25.0 MPa, with residence times ranging between 10 s to 240 s. Gaseous and liquid products were sampled and analyzed.

2. Materials and methods

The experimental activities were performed in a continuous tubular plant operated at 400 °C and 25 MPa. In this section, details concerning the experimental plant, preparation of the mixtures and analytical methods are provided.

The apparatus utilized for the research work is a continuous system for supercritical water gasification. A schematics of the plant is depicted in Figure 1.

The plant was fed by a bottle filled with the water solution to be gasified (glucose and phenol in different relative concentrations). The liquid was pumped by means of an 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 (Hz1-3 in Figure 1), which were set at the constant temperature of 250 °C.

After the pre-heater, the reacting mixture entered the reactor, constituted by a tube of stainless steel (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. 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.

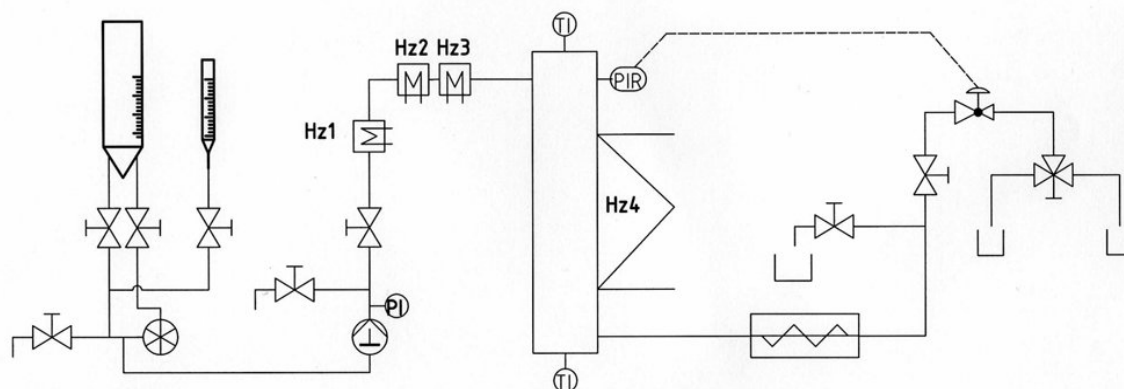


Figure 1: Process scheme of the adopted experimental device

Table 1: Composition of the mixtures (wt %)

Mixture	Water	Glucose	Phenol
Glucose	95.0	5.0	0.0
Glu/Phen 10%	95.0	4.5	0.5
Glu/Phen 20%	95.0	4.0	1.0
Glu/Phen 30%	95.0	3.5	1.5

After reaction, the products were cooled down to room temperature by means of a cooling loop. Then, a back-pressure regulator TESCOM[®] 26-1721-24A was used to expand the products to atmospheric pressure. This apparatus was used to keep the pressure at the desired value in all the units upstream the valve itself. The valve was dynamically controlled by a compressed air regulator which received the measure signal of the reactor pressure by a digital manometer and drove the head of the back-pressure valve in order to keep the pressure constant at the desired set-point (25.0 MPa). After expansion, a three-way valve allowed selecting the desired output (liquid or gaseous) for sampling.

The analyzed mixtures were represented by water-organics solutions, where water fraction was always equal to 95 wt %. The remaining 5 wt % was constituted by a mixture of glucose and phenol in variable proportions. Table 1 shows the composition of the utilized mixtures.

The tests were executed at different residence times by varying the flow rate of the HPLC pump. The residence times varied between 10 s and 240 s.

The plant was started only with water, put under pressure, and then very slowly heated up to the desired reaction temperature. This procedure was adopted in order to prevent the risk that during the heat-up phase organics could polymerize, causing rapid reactor clogging.

Only after the temperature had been reached (usually after 1-2 h), the feeding was switched from water to glucose/phenol solution by means of a three-way valve. After that, a running time between 20 and 150 minutes, depending on the flow rate, was adopted before sampling, in order to allow the system to reach steady-state conditions.

First, gas flow rate was measured by means of a water gasometer. By using this device in combination with a chronometer, the time required to produce a fixed volume of gas was measured, thus obtaining the gas flow rate. For each experimental run, such measure was repeated at least four times in order to ensure its reproducibility.

After that, the three-way valve was switched and the liquid started dropping inside a sampling vial, allowing a straightforward sampling. The amount of residual phenol in the liquid phase was determined by means of a HPLC device (VWR-Hitachi[®]), equipped with a column Phenomenex Kinetex PFP[®] and a detector DAD. In order to obtain an overall estimate of the organics in the liquid phase, total organic carbon (TOC) was determined by means of the TOC analyzer DimaTOC[®] 2000 (Dimatec, Germany).

3. Results and discussion

In Figure 2 the trend of gas production as a function of residence time is shown. Gas production generally increases with the residence time. However, two different trends can be observed in the graph. In a first phase, corresponding to a residence time up to 60 s, a quite fast production of gas is obtained.

Subsequently, gas production rate becomes much slower. All the curves reach a sort of plateau, where only a slight increase in the production can be observed.

In Figure 2b, the same data points are plotted, but gas production is now referred not to the total amount of organics fed, but only to glucose. This elaboration was done according to the hypothesis that glucose is the only substance undergoing gasification, while the remaining phenol part can be considered substantially inert.

The results seem to confirm this approach. Now, the curves appear to be much more grouped together than in Figure 2a and mostly overlap. The curve relative to the pure glucose solution still expresses slightly higher yields.

According to these results, it would seem that phenol (and thus lignin) acts as a sort of inert in the SCWG of biomass. However, if the liquid products resulting from the plant are analyzed, phenol does not remain constant during the operations. In Figure 3, phenol conversion in the liquid phase is shown. Conversion X was calculated according to Eq (1):

$$X = \frac{C_0 - C(t)}{C_0} \quad (1)$$

where C_0 is the initial concentration of phenol and $C(t)$ is its concentration at time t .

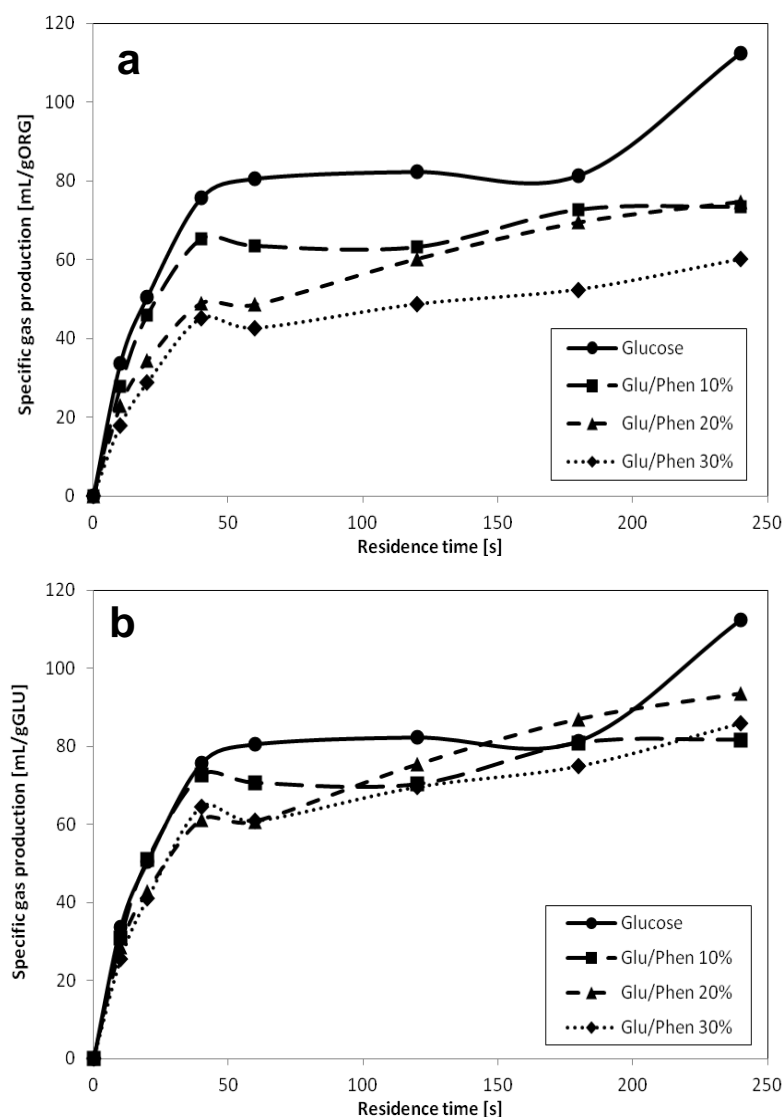


Figure 2: Specific gas production for the SCWG of glucose/phenol mixtures at 400 °C and 25 MPa. Points: experimental measures. (a) Gas production per unit feedstock; (b) Gas production per unit glucose fed

It can be clearly observed that phenol is actually consumed during SCWG. Therefore, phenol is not an inert, but it reacts in the liquid phase. Since the previous analysis showed that its contribution to gas generation is almost negligible, it could be inferred that phenol tends to form other liquid intermediates or, possibly, solid products. No evidence of solids in the sampled products was found. On the other hand, occasionally during operations, the clogging of the pre-heater occurred. This is a clue that solids are probably produced during operations, especially in the sections of the plant operated at lower temperatures.

Interestingly, all the three solutions where phenol was present exhibit approximately the same trend of phenol conversion. The points corresponding to the three considered mixtures form a sort of cloud, where the differences among the mixtures cannot be appreciated. Beyond some possible errors which could be attributed to the experimental and analytical procedures, this result can support the conclusion that phenol conversion in the liquid phase does not depend on the amount of phenol present in the mixture fed. In other words, the phenol decomposition kinetics seems to be zero-order with respect to phenol concentration.

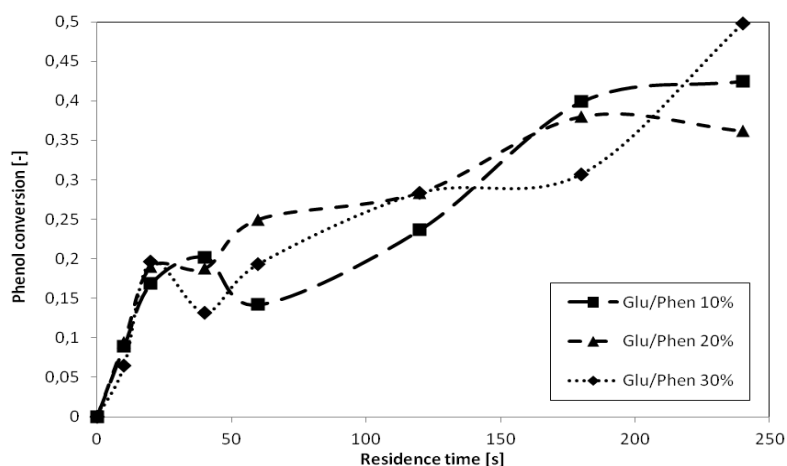


Figure 3: Phenol conversion as a function of residence time

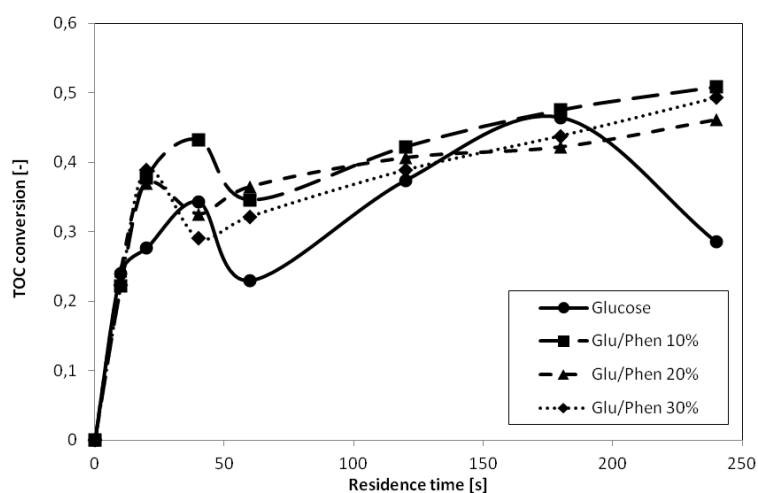


Figure 4: Total organic carbon (TOC) conversion measured in the liquid after supercritical water gasification of glucose/phenol mixtures at 400°C and 25 MPa

In Figure 4, the conversion of the total organic carbon (TOC) of the liquid phase is shown. Its value was calculated applying Eq (1) to TOC. In all the tests, an increasing trend is observed. This implies that the amount of organics in the liquid phase is steadily decreasing. The only exception is represented by the test with glucose at 240 s, where a sudden decrease of TOC conversion can be noticed. Further experiments are needed to better understand such different behaviour. Actually, the occurrence of some experimental error may not be excluded.

The general trend substantially replicates the one found for gas production. Indeed, there is an initial phase, up to around 50 s, where a steep decrease in TOC is observed. It can be reasonably stated that, in this phase, the organics are converted into gases. The trend then becomes different for longer residence times. A slight TOC consumption can still be observed. This is in good agreement with the situation observed for the gas, where a sort of plateau was reached (see Figure 2). However, while gas production tended to a sort of plateau, now TOC conversion is still increasing, though in a slower way. One explanation to this experimental result is that the organics could have been converted into a non-polar phase (tar), which could have stick inside the pipes of the experimental apparatus. Another possibility is the formation of a solid phase, as it was previously hypothesized. Further work is needed to provide a more punctual explanation for such phenomenon. However, it can be noticed that, while gas production is significantly lower as phenol content increases in the fed, TOC conversion remains the same. As a consequence, it must be concluded that higher amounts of phenol translate into a potentially higher production of tars or solids.

Based on all the obtained results, it can be stated that, at the considered experimental conditions, phenol appears to be inactive in gas production. Differently from Weiss-Hortala et al. (2010), a real inhibition effect played by phenol cannot be observed or, at least, it is not so evident. It could be inferred that, at 400 °C, glucose and phenol follow quite different kinetics pathways: the former is widely converted into gases, while the latter mostly tend to form other soluble organics or to polymerize to tar or char. A possible interpretation of such result could be formulated considering that, at the investigated reaction temperature, the ionic reaction pathway is still significant. On the other hand, at higher temperatures, like the ones considered by Weiss-Hortala et al. (2010), the radical pathway becomes the prevailing one (Bühler et al., 2002). Therefore, the “radical scavenger effect” of phenol could be not significant at lower temperatures, where ionic reactions are still very important. This would cause glucose and phenol to react almost independently from each other.

4. Conclusions

In the present work, different water/glucose mixtures were gasified in a continuous bench-scale tubular reactor at supercritical conditions ($T = 400\text{ °C}$, $P = 25.0\text{ MPa}$). Glucose and phenol are considered as model compounds for ligno-cellulosic biomass. All the analyzed mixtures had the same amount of organics concentration (5 wt %), but a different phenol content, ranging from 0 wt % to 30 wt %. This choice allowed testing the effective contribution of phenol in the supercritical gasification process, whereas other studies in the literature (Weiss-Hortala et al., 2010) only considered a reduced number of cases.

The results clearly show that phenol has a refractory attitude towards SCWG. Considering the outputs of the experimental tests, the impression is that phenol mostly acts as an inert in SCWG for what concerns gas production. On the other hand, the experimental results show that phenol in the liquid phase is actually depleted. It must be therefore concluded that phenol (and thus lignin), rather than being a real inert, is more probably converted into other liquid or solid products.

Further studies should be devoted to the understanding of the nature of such products, as well as to the strategies to increase the amount of lignin converted into gases. To this purpose, it would be of great use to concentrate the research efforts on the determination of the reaction mechanisms involved (Castello and Fiori, 2012) and to the development of an effective catalyst able to overcome these limitations.

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