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 concentrations of

5 wt. %, where the relative phenol content ranged from 0 wt. % (pure glucose) to 30 wt. %. 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_2. 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.

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 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. Among the works showing the interactions among different biomass

constituents, a first example is provided by the work 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 1 wt. % 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]. 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 concentration (5 wt. %). 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.

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 Figure 1.

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 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 (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 expansion, a three-way valve allowed selecting the desired output (liquid or gaseous) for sampling (see Section 2.2).

Four different aqueous glucose/phenol mixtures were considered for the experiments. All of them were characterized by a constant concentration in organics of 5 wt. %, the remaining part being Milli-Q water. The composition in organics of each mixture was varied, with the relative fraction of phenol ranging from 0% to 30%: Table 1. Glucose monohydrate (Merck KGaA, Germany) and phenol for synthesis with purity higher than 99% (Merck-Schuchardt, Germany) were utilized for preparing the mixtures.

Table 1

5

The tests were executed at different residence times (10, 20, 40, 60, 120, 180, 240 s) by varying the flow rate of the HPLC pump. The residence time τ was calculated as the ratio between the mass of the mixture inside the reactor, and the mass flow fed to the reactor:

$$\tau = \frac{\rho V}{W} \tag{1}$$

Where ρ is the density of water at 400 °C and 25.0 MPa (166.5 kg m^{-3} [22]), V is the reactor volume and W is the mass flow delivered by the pump. For sake of simplicity, the residence time was calculated as that of pure water. Such simplification is reasonable, since the investigated mixtures are considerably diluted.

During the start-up phase, the plant was run with pure 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 of organics polymerization during the heat-up phase, which could cause rapid reactor clogging.

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

2.2 Sampling and measuring procedures

Product sampling at ambient temperature and pressure was performed by means of a three-way valve placed at the end of the outlet pipe. If the gaseous products were required, the outlet pipe was directed into a bottle filled of water, with a cylinder inside. The gaseous products were then bubbled inside such cylinder, where they gathered and then they were sampled by means of a gas trap. When liquid products were required, the outlet pipe was simply allowed pouring inside the sampling vials, where around 20 ml of liquid products were sampled.

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. The determination of the residual glucose and fructose was

made by using an enzymatic test (R-Biopharm®), according to DIN 10381. Organic acids, alcohols

and aldehydes were measured through HPLC Rezex®, while furfurals were characterized through

HPLC Merck-Hitachi®, with a column Merck LiChroCART® 250-4, equipped with a UV detector.

HPLC measures were characterized by a confidence level of ±5%. 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

The results of the SCWG tests are shown in the present section. Section 3.1 presents the results

relative to the gaseous phase, while Section 3.2 shows the results concerning the analysis of the

liquid products. In Section 3.3 a simplified reaction mechanism is reported.

3.1 Gaseous products

The results concerning the production of gases are reported in Figure 2.

Figure 2

Gas production generally increases with residence time. This is the result of the ongoing conversion of liquid substances into gaseous products, due to the gasification reactions. Although the overall trend is always increasing, two different trends can be clearly individuated for all the four mixtures. In a first stage, that is up to a residence time of 40 s, the rate of gas production is very high. The production of gas is maximum in the case of glucose alone and it diminishes as the phenol content of the mixture increases. Mixture M0 provides a specific gas production of approximately 80 mL/g, while the mixture M30 reaches a value which is around the half (about 40 mL/g). A second stage is then observed, for residence times above 40 s. In the case of glucose, gas production remains practically stable at around 80 mL/g. For all the other mixtures, a moderate increase occurs. Such increase is slight for M10 (from 63.5 to 73.4 mL/g), and it is more relevant for the other mixtures: for M30, gas production increases from 42.6 mL/g to 60.0 mL/g.

The effect of phenol addition on gas production is evident. A higher phenol content results in a reduced gas production (Figure 2a).

Therefore, does phenol simply not yield significant amounts of gases, and therefore it can be considered as a sort of inert, or does it play a real inhibitory effect on glucose gasification?

In order to obtain such information, in Figure 2b the production of gases is referred to the sole amount of glucose fed: the trends look very different from those of Figure 2a. The four curves are indeed much more grouped and sometimes they also overlap. The experimental points relevant to the mixture with only glucose testify a slightly higher initial gas production with respect to the others. From 120 s onward, the experimental points almost overlap.

Thus, phenol seems to behave as a sort of inert in terms of syngas production. More precisely, without excluding the possibility that some reactions involving phenol could produce gases, phenol is preferably converted into other liquid intermediates (see Section 3.2 and [16]).

In Figure 3, the production of the most representative gaseous species, that is H_2, CH_4, CO and CO_2, is presented. Data are expressed as moles of gas per unit glucose fed and are based on total gas production and gas composition.

Figure 3

In all the plots of Figure 3, the two stages of gasification are evident: one characterized by high production rates and the other where gas production is more contained. All the four gaseous molecules analyzed reflect such behavior, though with some significant differences.

The H_2 trend exhibits some peculiar aspects (Figure 3a). Here, the four investigated mixtures behave in a considerably different way. Mixture M0 yields all H_2 in the first stage of gasification. The H_2 production is much higher for M0 than the other mixtures. After 60 s, pure glucose yields around 440 $mmol_{H_2}/kg_{glucose}$, while the other three mixtures yield around 200 $mmol_{H_2}/kg_{glucose}$. Nevertheless, in the second stage H_2 yields are almost constant for M0, while they increase for the mixtures containing phenol. As a whole, the higher is the concentration of phenol in the feed, the lower the H_2 yield. Figure 3a thus clearly shows that phenol plays an inhibitory effect on H_2 production or leads to H_2 consumption, in a way similar to that observed for lignin [18].

Such inhibitory effect can be hardly noticed for the other gaseous species. When observing the production of CH_4 (Figure 3b), the four curves mostly overlap, especially in the first stage. For longer residence times, a higher content of phenol in the mixture causes a higher CH_4 production: such preference for CH_4 formation was also previously observed [23]. The molar production of CH_4 is lower than that of H_2: maximum values are in the range 100-140 $mmol_{CH_4}/kg_{glucose}$.

The highest molar yields are obtained for CO and CO_2. On a molar basis, more than 80% of the gas produced consists of CO and CO_2. CO trends (Figure 3c) practically do not depend on phenol concentration. On the other hand, CO_2 (Figure 3d) shows a particular trend. At the end of the first stage of gasification, the lower is the phenol concentration in the feed, the higher the CO_2 production. Afterwards, CO_2 is still produced for M20 and M30, while for M0 and M10 the CO_2 production remains stable at approximately 1200 $mmol_{CO_2}/kg_{glucose}$.

It is interesting to compare the data about gas production with equilibrium forecasts. To this

purpose, the thermodynamic equilibrium model presented in [24] was utilized to calculate the

equilibrium composition of the gas. The values are presented in Table 2, where they are compared

with the experimental results obtained at 240 s residence time.

Table 2

The thermodynamic equilibrium model foresees that the whole mixture fed is converted into

permanent gases. The experimental data obtained are very far from such prediction, since the

measured gas production after 240 s is around 10 wt. % of the organics fed.

As far as the gas composition is concerned, relevant differences can be pointed out. No CO is

foreseen at equilibrium. Conversely, CO is the most relevant gaseous compound found

experimentally. A specular situation occurs for CH_4. According to equilibrium, its percentage

should be very relevant, always above 40 vol. %. Measured data reveal a concentration only slightly

above 3 vol. %. However, for CH_4, the results of the thermodynamic equilibrium model correctly

foresee the dependence on phenol content: increasing the concentration of phenol in the feed

enhances CH_4 production. The molar fraction of H_2 and CO_2 experimentally measured and

predicted at equilibrium are extremely similar. The experimental H_2 volume percentage shows

approximately the same dependence on phenol content as that predicted by the model: higher

phenol concentrations disfavor H_2 production. As far as CO_2 is concerned, model data tend to

slightly overestimate its production: they expect a concentration in the range 47.6 - 49.6 %, while

measured data oscillate from 35.9 to 44.5%.

The comparison with equilibrium data reveals that equilibrium is very far from being reached. Such

conclusion is evident (Table 2), and reinforced by the fact that a large part of the original feedstock

is actually converted into liquid products (see Section 3.2). The amount of CO represents the main

difference between experimental and model data. CO is practically not found at equilibrium, and this can be explained by key reactions taking place during the process.

Water-gas shift (WGS) has been reported to be one of the most important reactions of SCWG:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$
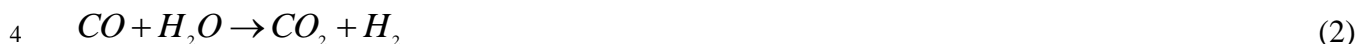
It has been also stated that most H_2 obtained in SCWG is actually produced by such reaction [25]. The occurrence of WGS is evidently not observed in the experimental tests carried out in the present work. The reason should be found in the intrinsic kinetics of such reaction. Indeed, at the considered reaction conditions, the rate of WGS is very low. This was also observed in a previous study by our group, where complete removal of CO among the SCWG reaction products was observed only after a few hours of reaction [14]. The slow kinetics of WGS could thus explain why CO is present in high amounts at the considered residence time.

Another reaction through which CO can be consumed is represented by CO-methanation (Eq. 3):

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (3)$$

By looking at the equilibrium values displayed in Table 2, where CH_4 is reported as one of the most significant products at equilibrium, it can be hypothesized that such reaction could play an important role, possibly in strong relationship with WGS. However, the data of Table 2 testify that CO-methanation does not occurs to a significant extent, due to the short residence time of the experimental tests.

3.2 Liquid products

The liquid products include those molecules which are dissolved in the liquid phase after condensation of the products from SCWG. In this treatise, they are referred as "liquid compounds" even though, at reaction conditions, they are most likely found in the supercritical phase.

The spectrum of compounds arising from SCWG is very wide and it is practically impossible to characterize each of them. Glucose and phenol, indeed, undergo reactions transforming them into

several other organic compounds, whose number is extremely high. However, it is possible to

quantify the overall amount of organics present in the liquid phase by resorting to TOC, which

provides the concentration of organic carbon present in that phase. In Figure 4 the TOC values are

reported. Since the analyses also involved the measure of some organic compounds (see Section

2.2), the contribution of the single compounds to the TOC is reported in Figure 4. Such operation

was performed by calculating, for each compound measured through the HPLC technique, its

contribution in terms of carbon. The part of TOC that was not possible to attribute to any of the

measured compounds was labeled as "unknown".

Figure 4

For all the four mixtures, the trend of TOC decreases at increasing residence time. Time $t = 0$ refers

to the initial mixtures, where all the organic compounds are in the liquid phase, since the feedstock

is perfectly dissolved. After then, a fraction of carbon is transferred to the gaseous phase, in the

form of the gaseous products shown in Section 3.1. The trend of TOC mirrors that of gas

production: TOC removal is maximum in the first phase of SCWG, while it becomes less

significant as the reaction goes on. The four mixtures do not present any relevant difference, as the

relative conversion of TOC is approximately the same.

The analysis of the single species contributing to the TOC values provides interesting information.

Looking at Figure 4, glucose and its isomer fructose are practically never found among the reaction

products. The only occurrence is with M0 after 10 s of reaction time. Because of that, it is not

possible to draw any conclusion about the kinetics of glucose degradation, which takes place in the

very first seconds of reaction, as also reported in the literature [26].

Conversely, when phenol is utilized, it is largely found among the reaction products. Averaging all

the measures at different residence times ($0 < \tau \le 240$ s), phenol represents 22% of TOC for M10,

39% for M20, and 54% for M30. As a matter of fact, phenol converts very slowly.

In Figure 5, the conversion of phenol for the three phenol-containing mixtures is reported.

Conversion values were calculated by means of Eq. 4:

$$X = \frac{C_0 - C(t)}{C_0}$$
(4)

Figure 5

Phenol conversion increases approximately from 0.1 to 0.5 at increasing residence times. Even after 240 s, more than half of the phenol fed to the SCWG reactor is still found among the reaction products. Phenol is very stable at the considered reaction conditions. Assuming first-order kinetics, phenol conversion data can be described by the relation:

$$X = 1 - \exp(-k\tau)$$
(5)

where k represents the kinetic constant of phenol degradation. The optimization of the value of k in best fitting the experimental data allowed to obtain $k = 2.72 \times 10^{-3}$ s^{-1}: the relevant fitting curve is reported in Figure 5. Such value is in quite good agreement with those by Weiss-Hortala et al. ($k = 5.48 \times 10^{-3}$ s^{-1}) [20] and by Yong and Matsumura ($k = 5.89 \times 10^{-3}$ s^{-1}) [27]. In other experimental works, significantly different values were obtained: it is the case of Goodwin and Rorrer ($k = 6.21 \times 10^{-8}$ s^{-1}) [17] and Huelsman and Savage ($k = 3.83 \times 10^{5}$ s^{-1}) [28]. However, in such works the reaction conditions were much different from those adopted in the present study.

It is worth noticing that phenol can be a product of glucose degradation: phenol may indeed be produced from furfurals, which are intermediates in glucose degradation reactions [29]. Such behavior was actually observed here during the SCWG of pure glucose. However, the amount of phenol produced was very small. In the experiments with pure glucose, the maximum concentration of phenol found among the products was of approximately 57 mg/l, value which does not contribute enough to the TOC to be visible in Fig. 4a. It is therefore reasonable not to consider glucose-derived phenol, as it contributes in a negligible way to the total amount of phenol found after reaction.

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Among the other gasification products, it can be observed a decrease in the aldehydes (formed in the first instants of reaction), and a production of both organic acids and alcohols as the residence time increases (Figure 4). It is noteworthy the occurrence of methanol, which is produced in relevant amounts. Methanol alone represents 39% of TOC in the case of pure glucose. Such percentage lowers when glucose/phenol mixtures are considered: 28%, 21% and 19%, for M10, M20 and M30, respectively.

Importantly, the extent of the so-called "unknown" compounds is relatively low (Figure 4). The only significant occurrence of such compounds is for reaction times from 120 s ahead, where the value of "unknown" is around 20% on an average basis. Such result highlights that the choice of the organic compounds to be measured (see Section 2.2) is effective, as they represent a significant part of the total amount of organics found in the liquid after SCWG.

As far as the liquid products are concerned, it is interesting to analyze the yields of some of the typical products associated with the degradation of glucose in supercritical water: Figure 6. As it was done for the production of gases (Figure 3), in Figure 6 the amount of the liquid species is reported in terms of moles produced per unit glucose fed.

Figure 6

Glucose degradation in supercritical water takes place by means of several pathways. According to Kabyemela et al. [30], among the other reactions, glucose can undergo dehydration into 5-HMF or conversion into two molecules of glyceraldehyde. In Figure 6a and 6b, 5-HMF and glyceraldehyde are shown, respectively. During the first stage of gasification, 5-HMF shows a trend specular to that of gas formation. At first, its concentration decreases quite fast, down to a value of approximately 400 mmol/kg$_{glucose}$. After that, it continues diminishing, but in a much slower way. A slightly higher relative 5-HMF production is obtained from the mixtures where a higher phenol content is present. Glyceraldehyde exhibits a quite complicated trend. Its value is maximum for pure glucose. Then,

when phenol is added (M10), a strong diminution of glyceraldehyde is observed. However, a further

increase in phenol content results in a higher glyceraldehyde production.

The differences in trend become more evident in the case of glycolic acid (Figure 6c). When pure

glucose is utilized, the trend strongly increases, showing a maximum point of 2000 mmol/kg$_{glucose}$

occurring at 120 s; after then, it decreases to a value of approximately 1000 mmol/kg$_{glucose}$. The

trend of the curves relevant to the phenol containing mixtures is completely different. In the first

phase, glycolic acid shows a first apparent maximum point at around 20 s and then a minimum at 40

s. In this phase, the three curves are practically superposed. After then, the three curves start

increasing in an almost linear way. The higher is the phenol content, the lower is the rate of glycolic

acid production, even though the differences among the three mixtures are rather reduced.

The production of methanol is really remarkable: Figure 6d. Methanol is the product yielded in the

highest amount. Its concentrations are impressive: with M0, methanol concentration reaches 22.6

g/L, corresponding to around 45% of the feedstock loaded. The curve exhibits the clear trend of a

reaction intermediate. Tre trend increases in the first phase, it reaches a maximum, and then it starts

decreasing. The mixtures with phenol generate quite similar trends, though methanol concentrations

are lower.

In Figures 6e and 6f the trends of two different organic acids are reported. Acetic acid (Figure 6e)

shows a trend similar to that of gas production, with a first production stage followed by a sort of

plateau. Acetic acid could be produced by several organic reactions and, once formed, it is quite

stable at 400 °C [31]. In Figure 6f, formic acid is shown. Here, the behavior is opposite to that of

gas production. Formic acid is produced in the earlier phase of the reaction, before 10 s, and it is

consumed as far as new gases are formed. It can be inferred that formic acid has an active role in

gas production. Actually, as it was reported by Akiya and Savage [32], at the considered

temperature and in the presence of water the de-carboxylation reaction is favored. Therefore, formic

acid decomposes mainly into H_2 and CO_2. Interestingly, the number of moles of H_2 produced

(Figure 3a) is comparable with the number of moles of formic acid depleted (Figure 6f), especially

1 for the mixtures with higher phenol content. This is a clue that formic acid de-carboxylation is an

2 important reaction for H_2 formation in SCWG.

3

4 **3.3 A possible reaction mechanism**

5 On the basis of the analysis of Section 3.2 and taking also into account the literature in the field [13,

6 30, 33], a simplified reaction mechanism for the degradation of glucose can be postulated. Such

7 mechanism is visually presented in Figure 7.

8

9 Figure 7

10

11 Glucose can be converted into smaller organic compounds through retro-aldol condensation. In this

12 way, erythrose and glycolaldehyde are formed. The former compound, which presents a furanic

13 ring, is the basis from which furfurals can be produced. The latter is a C_2 aldehyde, which can

14 undergo several reactions. First, it can be simply de-carbonylated into methanol. Another

15 possibility, which is common to many aldehydes in supercritical water, is represented by the

16 disproportionation reaction. Such reaction involves two aldehydes, one of which is reduced into the

17 corresponding alcohol and another one which is oxidized to the corresponding organic acid

18 (Cannizzaro reaction).

19 Glucose may also undergo isomerization into fructose, which can be dehydrated into 5-

20 Hydroxymethylfurfural (5-HMF), by losing three molecules of H_2O. Such pathway can lead to the

21 formation of heavy compounds, through chemical condensation. Another possibility is the

22 degradation of 5-HMF into levulinc acid and formic acid. From formic acid, H_2 and CO_2 can be

23 produced by thermal degradation, at the considered reaction conditions [31, 34].

24 Fructose can form two molecules of glyceraldehyde, a C_3 aldehyde. Also in this case, several

25 reactions are possible. First, glyceraldehyde can undergo de-carbonylation and subsequent thermal

26 degradation to give formaldehyde and methanol. Formaldehyde is quite unstable in supercritical

16

water at 400 °C and it can be completely converted into other compounds [35]: indeed,

formaldehyde was found here only in negligible amounts among the reaction products.

Formaldehyde can produce gases by direct conversion into CO and H_2. However, the main reaction

pathway of formaldehyde in supercritical water is represented by disproportionation. For the case of

formaldehyde, two possible disproportionation reactions are documented in the literature [36]. First,

the self-disproportionation of formaldehyde into methanol and formic acid, which is also known as

the Cannizzaro reaction:

$$2HCHO + H_2O \rightarrow CH_3OH + HCOOH \tag{6}$$

Another possible way is the cross-disproportionation between formaldehyde and formic acid, giving

methanol and CO_2:

$$HCHO + HCOOH \rightarrow CH_3OH + CO_2 \tag{7}$$
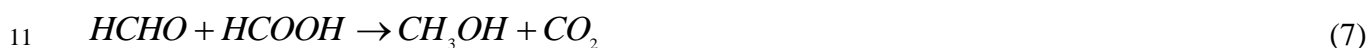
Morooka et al. [36] found that cross-disproportionation is the prevailing pathway at 400 °C.

However, both reactions lead to the formation of methanol, which was found to be the most

abundant reaction product in the present study, in particular during the first 60 s of operations (see

Figure 6d).

Considering Figure 7 and the reaction mechanisms above discussed, it is clear that many pathways

leading to the formation of methanol are possible. Methanol is a relatively stable product in

supercritical water at 400 °C; thus, once it is formed, it is hardly gasified. A possible explanation to

the fact that methanol concentration decreases in the second stage of gasification could be the

occurring of reactions involving other organics present in the liquid phase. Methanol could provide

methyl groups to other organics. Further research is needed to investigate about the interactions

between methanol and the other organic compounds at supercritical conditions.

Glyceraldehyde can also be dehydrated to form pyruvaldehyde and, hence, acetic acid. Acetic acid

is a relatively stable product at the considered reaction conditions [31]. From Figure 6e, it can be

clearly observed that acetic acid is produced in first stage of gasification, and its amount remains almost constant during the second stage.

Given the simplified reaction scheme of Figure 7, the role of phenol during gasification can be addressed. In Section 3.2 it was highlighted that large differences are encountered when comparing the trends of glycolic acid and methanol, whose formations are much more reduced for phenol containing mixtures in comparison with a feed with only glucose (Figures 6c and d). Conversely, a slight increase (in relative terms) in the production of 5-HMF is observed for the phenol-containing mixtures (Figure 6a). Looking at the reaction schemes here depicted, this implies that the introduction of phenol penalizes those pathways in which water is a reactant, such as the hydration of glyceraldehyde to glycolic acid, or the hydration of pyruvaldehyde to acetic acid. On the contrary, de-hydration reactions are favored.

A possible explanation could be that phenol reduces the availability of water molecules. Indeed, phenol needs a quite elevated number of water molecules in order to be solvated. Water is thus less available and this causes dehydration reactions to be favored. It is interesting to notice that such effect does not show a linear dependence on the amount of phenol loaded. As far as the reaction goes on, water is slowly made available to the reacting compounds. This can be observed looking at the different trends of glycolic acid, where a stable increase is observed in the longer times for the phenol-containing mixtures.

Another explanation could be that phenol as an acid influences the reaction pathways. Cannizzaro reaction and other reactions involving carbonyl-groups need strong bases in water at ambient conditions, and they occur without any addition or with weak acids at hydrothermal conditions [37]. Phenols are weak acids at ambient conditions, while they become stronger at increased temperatures [37]. On the other hand, together with other acids, like acetic acid, a buffer system might be formed. Up to now, not enough knowledge exists about these systems and their consequences on chemical reactions for a precise evaluation of the effect on the observed results.

For this discussion is relevant that, at 400 °C and 25 MPa, there are still ionic reactions in the solution. A discussion only based on free-radical reactions, like in [20], is therefore not useful for the present case.

4. Conclusions

In the present work, mixtures of glucose and phenol as model compounds of biomass constituents were gasified in supercritical water at 400 °C and 25.0 MPa. Liquid and gaseous products were sampled and characterized. The results clearly show that the addition of phenol reduces the gas yield obtainable from the feedstock. However, as far as the production of gases is concerned, the inhibitory effect of phenol was relatively low. In other words, when phenol-containing mixtures are utilized, gas yields are lower mainly because the amount of glucose fed is lower. The role of phenol seems more active when the liquid products are considered. Here, phenol interferes with the mechanism of glucose degradation, by favoring the pathways involving de-hydration reactions. Further research should be conducted in order to understand in a detailed way how such inhibition takes place.

The performed tests also highlighted that, at 400 °C, the SCWG of glucose/phenol mixtures at 5 wt. % takes place over two distinct stages: the former, with a duration of 40-60 s, where a fast gas formation occurs; the latter, for longer residence times, where gas yields are practically unchanged and mainly reactions in the liquid phase occur. The reactions taking place in the second stage should deserve more attention and further research in the future. An interesting issue could be the investigation of the fate of methanol, which is an abundant product at hydrothermal conditions, and whose degradation kinetics in SCWG has been already investigated [38]. Trying to enhance methanol degradation into gaseous products rather than liquid intermediates could be crucial for the overall efficiency of biomass SCWG.

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