

INFLUENCE OF PHENOL ON GLUCOSE DEGRADATION DURING SUPERCRITICAL WATER GASIFICATION

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Biomass is an ideal candidate for renewable energies and to decrease CO₂ emissions. Super Critical Water Gasification (SCWG) is a recent way of treatment still in development for wet biomass. Above its critical point water has particular properties and is able to convert wet biomass into gas, hydrogen particularly. In order to propose a general scheme of the SCWG for lignocellulosic biomass, the interactions between lignin and cellulose must be highlighted. Lignocellulosic biomass could be modelled with phenol (lignin) and glucose (cellulose). In a continuous reactor, the gasification efficiency of solutions containing phenol, glucose or the two compounds are realized in presence of an alkaline catalyser. The comparison of global parameter, such as Total Organic Carbon (TOC), the composition of liquid (glucose, phenol...), the volume and composition of gas phase (H₂, CO₂, CH₄...) showed that a small quantity of phenol in a glucose solution decreased dramatically the conversion efficiency of glucose.

INTRODUCTION

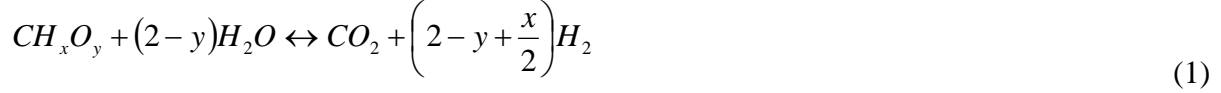
Nowadays, many researches are realized in the domain of the renewable or pseudo renewable energies: solar, wind, biogas, synthetic gas... in order to replace the fossil energies and decrease the carbon dioxide produced during the processing of fossil compounds. Taking into account these two points, biomass is an ideal candidate, showing a carbon dioxide balance quite null. Most of the techniques employed at the present are efficient with dry biomass (pyrolysis for example). On contrary, Super Critical Water Gasification (SCWG) is a recent way of treatment in development, which allows to use wet biomass, also with the natural water content of 80-90 %.

The principle is to convert wet biomass into gas, using high temperatures and pressures. Above the critical point (22.1 MPa and 374°C), water has particular properties and is able to convert carbon from biomass into methane and/or carbon dioxide. Hydrogen could be also transformed during this process into dihydrogen. At the present time, hydrogen seems to be the best energy vector because of its energetic potential and environmental compatibility, but it must be produced in a sustainable way. Different technologies for H₂ production are under development.

Above its critical point water is in a monophasic system [1], and its physico-chemical properties are modified compared to the liquid water [2, 3]. Generally, supercritical fluids are really interesting because they form an unique phase; their diffusivity is close to those of the gas and their density could be easily adjusted at the values desired [4]. The most important properties explaining the interest of the SCW are density, viscosity and the dielectric constant; SCW media are very reactive because they hydrolyse efficiently organic compounds [5-7]. At low densities SCW is a poor solvent for ionic species like inorganic salts [8], but it is completely miscible with many organic compounds and gases [7], allowing precipitation

process or homogenous reaction process. Reactions in supercritical water could be catalysed by acid or base [7, 9] or initiated by free radicals [10].

Biomass reacts with water and forms H_2 and CO_2 as main compounds, the global reaction of SCWG can be resumed by Equation 1. But other intermediary or concurrent reactions could take place; such as steam reforming, Water Gas Shift (2, WGS) and methanation.



All molecules of biomass cannot react with the supercritical water, even if water is really reactive, kinetics is a limitative factor. Sometimes, char and/or tar could be produced during the process [11]. Catalysts are used to increase kinetics and improve some reactions, as WGS by alkaline salts [11]. After cooling and depressuring liquid and gas phase are analysed. A short mass balance can be realised, leading to determine the performances of the reaction. Most of researches are published on the SCWG of glucose [10-15], which is an intermediate compound of cellulose decomposition. Some recent studies showed that the lignin seems to modify the conversion efficiency of the glucose solutions [16]. In order to propose a general scheme of the SCWG for lignocellulosic biomass, the interactions between these 2 compounds must be highlighted.

MATERIALS AND METHODS

Experiments were performed in a continuous tubular reactor built of Inconel 625. The dimensions were 18 m length, 1.6 mm of internal diameter and 6.35 mm of external diameter. The volume of the reaction zone is 36.19 mL. The temperature increase was assumed by an electrical device and controlled by a thermocouple on the external surface of the reactor. The GraphWorX32 of the Genesis32 Software supplied by ICONICS monitored the temperatures. The solution was feeding the reactor by a membrane pump, supplied by LEWA (Type EL1). After cooling, the product mixture was expanded to ambient pressure by a back-pressure regulator.

In all experiments, $KHCO_3$ (Roth Company, 99.5% purity) was used as catalyser at 0.2 wt %. The pressure was kept constant at 25 MPa. The temperature was 400, 450 or 500°C. The flow rate was chosen between 0.9 and 3.8 $kg\ h^{-1}$ (corresponding residence time: 0.25 to 0.06 min). The concentration of glucose (Monohydrat, Merck) or phenol (Merck, 99% purity) was varied from 0.25 to 2 wt %.

After 30 and 60 minutes of stable state of the reactor, gas and liquid samples are taken for analysis. To compare the efficiency of the conversion, the only comparison of gas volume or liquid mass is not pertinent, particularly in case of different flow rate. In the outflow, a ratio between the volume of gas and the weight of the liquid was defined:

$$ratio = \frac{gas\ volume}{liquid\ weight} \text{ in } L\ kg^{-1} \quad (3)$$

The mineralization efficiency was estimated by measuring the Total Organic Carbon (DIMATOC[®] 2000). Residual phenols (phenol and based-phenol molecules) and glucose were also quantified in the liquid phase by using cuvette test from Dr Lange (LCK 346 Phenols) and a special enzymatic test and UV-method supplied by Roche. A Gas Chromatograph HP-6890A Series was used to analyse the gas, and the volume injected was 100 μL . Two columns (80/100 Hayesep and 60/80 Molesieve 5A) placed in series and two

kinds of detectors were employed for the gas quantification. A computer equipped with the ChemStation software monitored the system.

RESULTS

1. Glucose solutions

The influence of the glucose concentration was studied in the range of 0.25-2 wt % at 25 MPa, 500°C and with a flow rate of 1.385 kg h⁻¹ (residence time equals to 0.1624 min). Glucose was totally removed from the solution (<0.003 mg L⁻¹, not shown) meaning that molecules react completely with supercritical water in the operating conditions considered.

Fig. 1 shows that the ratio (Eq. 3) increases linearly with the concentration of glucose in the solution. Keeping the residence time and the catalyser amount constant, this evolution means that these two parameters are not limitative in the operating conditions. Moreover, it means that the gas volume increases with the increase of glucose concentration. The conversion efficiency is quasi the same for all experiments. The evolution of TOC and residual phenol of the liquid phase as function of glucose concentration is also linear (not shown). An increasing linear profile for the TOC indicates that mineralization of organic compounds is independent from the concentration in the investigated range. Moreover, the concentration of residual phenol, considered as intermediate product [10], increases with the concentration, meaning that the degradation mechanism seems to be similar in all cases.

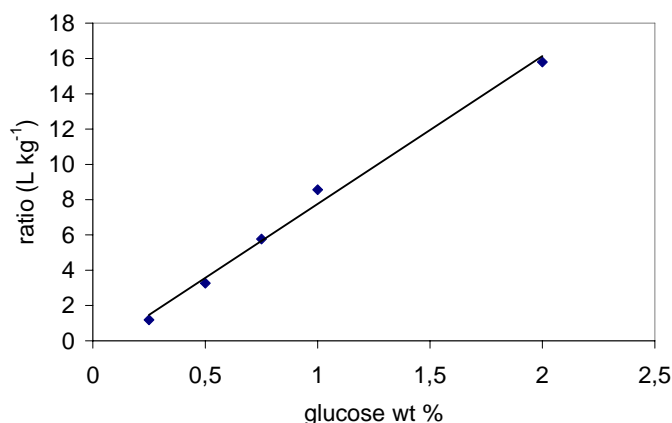


Figure 1: Influence of glucose concentration on the ratio during the SCWG at 500°C, 25 MPa and 1.385 kg h⁻¹.

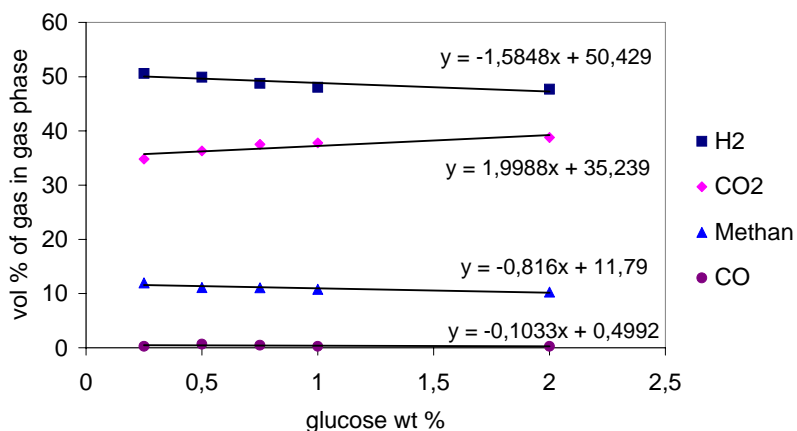


Figure 2: Influence of glucose concentration on gas composition during SCWG (500°C, 25 MPa, 1.385 kg h⁻¹).

The total volume of gas increases with the glucose concentration, but the tendencies of the individual components are more contrasted. Fig. 2 represents the volume percentage of the main gas (H_2 , CO_2 , CH_4 and CO) in the total volume as function of glucose concentration. The volumic composition of the gas is about 50% H_2 , 40% CO_2 , 10% CH_4 and 1% CO . Hydrogen is the main compound in the gas phase. Of course, the presence of the catalyser decreases the amount of CO , so the WGS reaction is promoted. Fig. 2 shows that, when glucose concentration increases, the proportion of H_2 slightly decreases and the proportion of CO_2 slightly increases. This phenomenon could be due to a difference between the kinetics of the reactions.

2. Phenol solutions

The influence of flow rate (or residence time) for phenol solutions was studied for the same operating conditions. A 1 wt % phenol solution corresponds to 10 g L^{-1} of phenol. Fig. 3 shows that the conversion of phenol is not really efficient (under 50%). On contrary to glucose solutions, the reactivity of phenol in supercritical water is low. For all the parameters: TOC, phenol and ratio, the curve profiles as function of residence time presents an abrupt increase or decrease between the lower residence time and the second one, then the values for the next points are quite similar.

In view to determine if the thermal transfer influences the reactivity, the influence of temperature was studied. Insert in Fig. 3 represents, for lowest residence time, the residual phenol as function of reactor temperature. The quantity of phenols decreases when the temperature increases. It means that higher temperatures promote the reactivity of phenols in supercritical water. The difference of efficiency between 450°C and 500°C is not negligible, so temperature must be homogenous in the reactor.

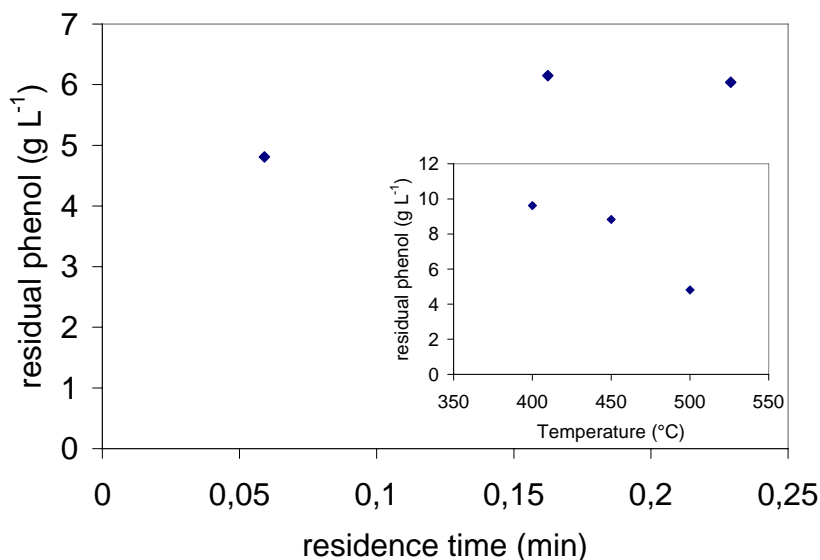


Figure 3: Influence of residence time on the residual phenol during the SCWG (500°C , 25 MPa, 1 wt % phenol).
Insert: Influence of temperature on the residual phenol for a residence time of 0.06 min.

3. Glucose and phenol solutions

At first, the objective was to check if the phenol influenced glucose reactivity. The ratio for the solutions containing only one compound (1 wt %) was compared to this of mixture solutions (1 wt % of each compound). With this kind of representation, phenol will have no influence on glucose degradation and mutually if the values for the mixture are the sum of the

two other values. The ratio is represented for the 3 solutions on Fig. 4 for 3 different flow rates. On Fig. 4 the ratio for the mixtures increases with the flow rate. But, the ratio obtained for a mixture is not the sum of the two other values corresponding to only one compound. If each compound reacts independently with supercritical water, the global value should be close to the sum of the two values. The results obtained through Fig. 4 mean that the phenol has an influence on the glucose conversion and precisely on the quantity of gas produced.

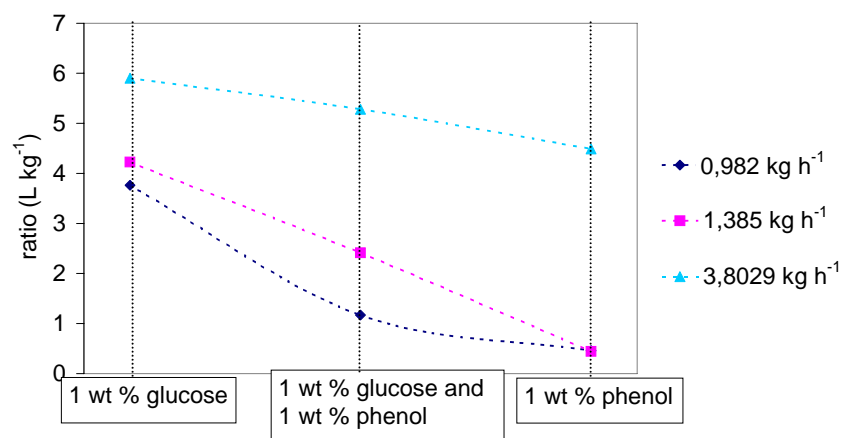


Figure 4: Influence of phenol on the ratio for 3 flow rates during the SCWG at 25 MPa, 500°C.

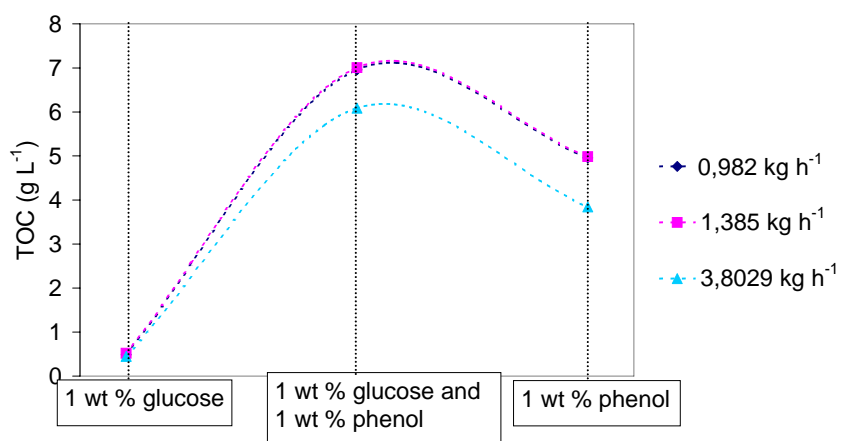


Figure 5: Influence of phenol on TOC values for 3 flow rates during the SCWG at 25 MPa, 500°C.

Gas quantity is not the only one parameter affected by the presence of phenol: TOC and residual phenol values for the mixtures are higher than the sum of them corresponding to the solutions of one compound. Fig. 5 shows the case of the TOC evolution as function of the composition and for three different flow rates. For glucose solutions of 1 wt % the TOC is very low. On contrary for 1 wt % phenol solutions, the TOC in the liquid phase is higher. If the TOC for the mixture was simply the sum of the 2 other values, the TOC would be only a little bit higher than the value for phenol solution. As seen on Fig. 5, TOC values for the mixtures are really higher, whatever the flow rate; it also means that phenol modifies glucose degradation. Moreover, the results are quite similar for the two lower flow rates; as noticed for phenol solutions.

Other experiments were realised with various compositions of the mixture solutions considering a total weight of organic compounds equal to 2%. These results (not shown) indicated that a small quantity of phenol had a strong influence on the behaviour of the solution (TOC and residual phenol). For example, the ratio value was 16 for a 2 wt % glucose solution and 13 for a solution composed by 1.95 wt % of glucose and 0.05% of phenol.

Adding a little amount of phenol (0.05%) values of TOC and residual phenol increase rapidly. It confirms that phenol influences the conversion of glucose molecules in supercritical water.

CONCLUSION

SCWG of glucose and/or phenol in diluted solutions was studied in a continuous reactor (25 MPa and 500°C). The comparison realised between solutions of only one component and mixtures showed that the presence of phenol, even in a small amount in a glucose solution, influences the conversion efficiency. Phenol seems to influence the conversion of glucose solution into hydrogen and particularly the total volume of gas. However, volume of gas is not the only one parameter affected by the presence of phenol, the TOC and residual phenols of the liquid phase are also influenced in presence of phenol.

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