



# Supercritical Water Gasification of Glucose and Cellulose for Hydrogen and Syngas Production

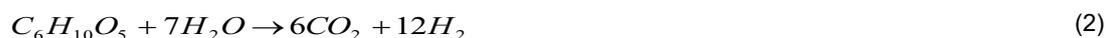
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Interests in large scale use of biomass for energy and in hydrogen production are motivated largely by global environmental issues. Generation of hydrogen and syngas from biomass using supercritical water gasification (SCWG) is an environmentally benign method to produce energy. In the present work the Gibbs energy minimization, at constant pressure ( $P$ ) and temperature ( $T$ ), and entropy maximization at constant  $P$  and enthalpy ( $H$ ), were utilized to calculate the equilibrium compositions and equilibrium temperatures for SCWG of glucose and cellulose. The effect of pressure, temperature and initial composition of reactants were evaluated. The problems were formulated as non-linear programs. The formulation used ensures finding the global optimal solution with no need initial estimate. The model predictions were compared with experimental and simulated data found in literature with a good agreement between them. In both SCWG processes, hydrogen production was favored in high temperatures and low molar compositions of glucose or cellulose in the feed. The effect of pressure was found to be irrelevant. Syngas with a  $H_2/CO$  molar ratio close to 2 (ideal for Fischer-Tropsch synthesis applications) are obtained with an addition of  $CO_2$  as a co-reactant. The calculated final temperatures were close to the initial temperature of the reaction in both systems thus, indicating low energy requirements for maintain these reactions, and in the reaction conditions analyzed here these systems can be considered safe. Both systems showed potential for application in hydrogen and syngas production.

## 1. Introduction

Interests in large scale use of biomass for energy and in hydrogen production are motivated largely by global environmental issues. Generation of hydrogen and syngas from biomass using supercritical water gasification (SCWG) is an environmentally benign method to produce energy, because in the SCWG process the biomass does not need to be dried with a high expenditure (Kruse, 2008, 2009). Furthermore, due to the rapid hydrolytic decomposition of carbohydrates and the good solubility of the intermediate products under reaction conditions, high gas yields are reached at comparably low temperatures with a very low formation of undesired products as coke. The main reactions in SCWG of glucose and cellulose are steam reforming of glucose (Eq. 1) and steam reforming of cellulose (Eq. 2).



In this paper we report the thermodynamic analysis of SCWG of glucose and cellulose, where Gibbs energy minimization (in conditions of constant pressure ( $P$ ) and temperature ( $T$ )) was employed to calculate equilibrium compositions and entropy maximization (at constant  $P$  and enthalpy ( $H$ )) was employed to determine the final temperature of these reactions. The effect of processes variables such as pressure, temperature and reactant composition was studied. The effect of a  $\text{CO}_2$  addition as a co-reactant was evaluated under improvement of syngas production.

## 2. Methodology

### 2.1. Equilibrium at constant $P$ and $T$ : formulation as a problem of minimization of Gibbs energy

The thermodynamic equilibrium condition for reactive multicomponent closed system, at constant  $P$  and  $T$ , with given initial composition, can be obtained by minimization of Gibbs energy ( $G$ ) of the system, given by:

$$\min G = \sum_{i=1}^{NC} n_i^g \mu_i^g + \sum_{i=1}^{NC} n_i^l \mu_i^l + \sum_{i=1}^{NC} n_i^s \mu_i^s \quad (3)$$

While satisfying the restrictions of non-negative number of moles of each component in each phase:

$$n_i^g, n_i^l, n_i^s \geq 0 \quad (4)$$

And the restriction of mole balances, given by atom balance for reactive systems:

$$\sum_{i=1}^{NC} a_{mi} \cdot (n_i^g + n_i^l + n_i^s) = \sum_{i=1}^{NC} a_{mi} \cdot n_i^0 \quad m = 1, \dots, NE \quad (5)$$

Since the system analyzed by the present work was at high pressure, the virial equations of state, truncated at second virial coefficient, were used to determine the fugacity coefficient. The second virial coefficient is calculated by the correlation of Pitzer and Curl which was modified by Tsionopoulos. The fugacity coefficient was determined by the following relation:

$$\ln \hat{\phi}_i = \left[ 2 \sum_j^m y_j \cdot B_{ij} - B \right] \frac{P}{R \cdot T} \quad (6)$$

### 2.2. Equilibrium at constant $P$ and $H$ : formulation as a problem of entropy maximization

The thermodynamic equilibrium condition for reactive multicomponent closed systems, at constant  $P$  and  $H$ , with given initial composition, can be obtained by maximization of the entropy ( $S$ ) of the system, with respect to  $n_i^k$ :

$$\max S = \sum_{i=1}^{NC} n_i^g \cdot S_i^g + \sum_{i=1}^{NC} n_i^l \cdot S_i^l + \sum_{i=1}^{NC} n_i^s \cdot S_i^s \quad (7)$$

While satisfying the same previous restrictions, given by equations (4) and (5). Usually, physical properties are given as functions of composition, pressure and temperature, not enthalpy. Therefore an additional restriction, referent to enthalpy balance, must be satisfied:

$$\sum_{i=1}^{NC} (n_i^g \cdot H_i^g + n_i^l \cdot H_i^l + n_i^s \cdot H_i^s) = \sum_{i=1}^{NC} (n_i^0 \cdot H_i^0) = H \quad (8)$$

Although the formulated problem is non-linear, the used methodology guarantees the global optimum, since in this case the problem is convex (White et al., 1958). The software GAMS<sup>®</sup> 23.1, (*General Algebraic Modeling System*) with the CONOPT2 solver executed in a Pentium III (512 MB, 900 MHz), was used in the resolution of the calculation problem of chemical and phase equilibrium; this software was previously used, in similar problems, with good results (Silva and Guirardello, 2010). A description of GAMS can be found in Brooke et al. (1998). The solid phase formed was considered as pure component. In this work, the thermodynamic analysis was carried out over the following variable ranges: pressure 250-350 atm, temperature 703.15-1073.15 K, and a feed concentration in mass percentage of glucose or cellulose of 2.5 to 20%.

### 3. Results and Discussion

#### 3.1. Comparison between simulated and experimental data

Figure 1 shows the comparison with simulated data present in the works of Voll et al. (2009) for the SCWG of glucose and cellulose using an ideal gas consideration and the data calculated by the present work using the virial equation of state to represent the vapor non-ideality and using an ideal gas formulation. The SCWG of glucose was performed in the following conditions: temperature between 903.15 and 1023.15 K, pressure of 280 atm and a feed concentration of glucose of 0.6 M. The SCWG of cellulose was performed with a constant pressure of 350 atm, a constant concentration of cellulose in the feed of 14 wt% and in a temperature range of 653.15 and 713.15 K. As can be seen in the Figure 1, the results calculated by the present work are in agreement with that found in the literature, for the glucose and cellulose.

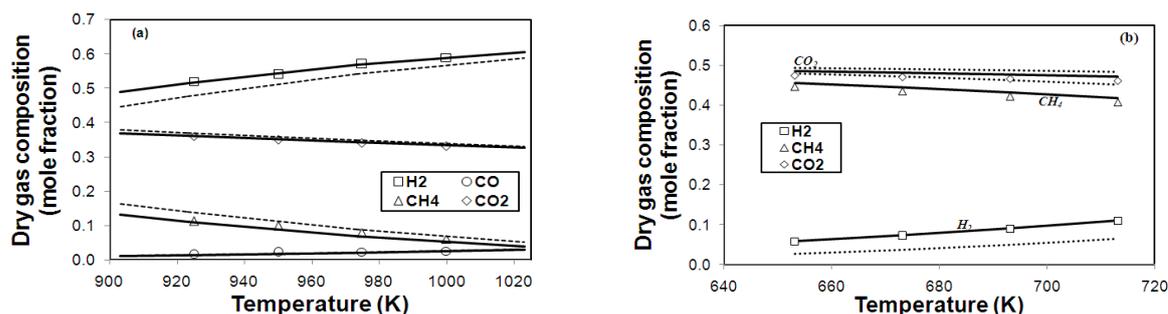


Figure 1. Comparison with simulated data obtained in the work of Voll et al. (2009) for the SCWG of glucose (a) and cellulose (b). Symbols: data obtained in the work of Voll et al. (2009), dashed lines: data calculated by the present work using the virial equation of state; solid lines: data calculated by the present work using the ideal gas formulation.

In the Figure 2 we can see the comparison with the experimental data of Byrd et al. (2007) for the SCWG of glucose.

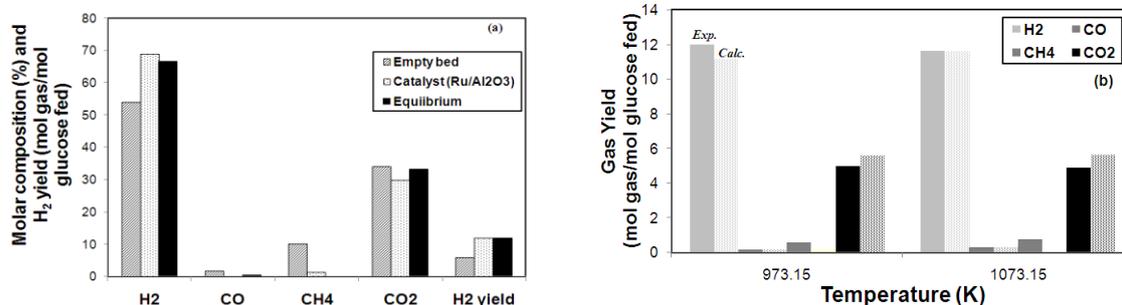


Figure 2. Comparison with experimental data obtained in the work of Byrd et al. (2007) for the SCWG of glucose.

The Figure 2 (a) show the comparison with the experimental data obtained with a constant temperature of 973.15 K (700 °C) with a pressure of 248 bar and a feed with 1 wt% of glucose, the experimental results are obtained with the catalytic bed empty and with a catalyst of Ru/Al<sub>2</sub>O<sub>3</sub>. In the Figure 2 (b), the results are explained as function of the temperature, for the temperatures of 973.15 K (700 °C) and 1073.15 K (800 °C). As can be seen, the calculated equilibrium compositions are closely of the experimental results obtained in the work of Byrd et al. (2007) for the SCWG of glucose.

### 3.2. Equilibrium compositions

#### 3.2.1. Temperature effect

In the Figure 3 (a) we can see the effect of the temperature over the SCWG of glucose and in the Figure 3 (b), we can see the same effect for the SCWG of cellulose, both simulations were performed at a constant pressure of 280 atm and a constant feed composition of glucose or cellulose of 5 wt%.

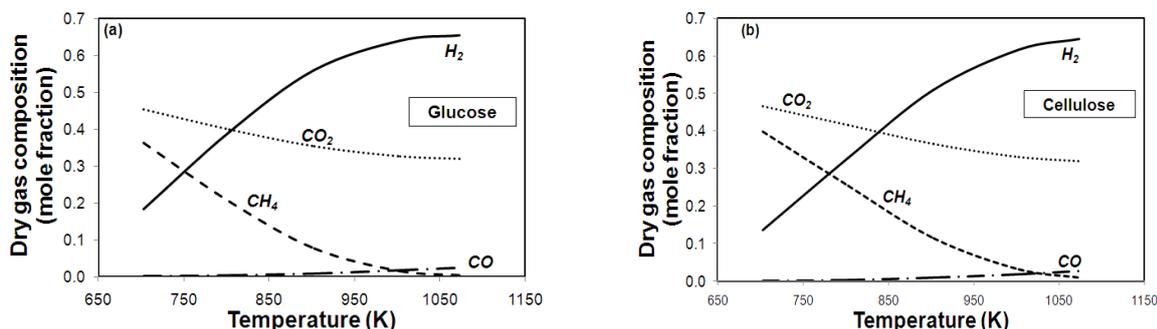


Figure 3. Dry gas molar compositions for the SCWG of glucose (a) and cellulose (b) as function of the reaction temperature.

For the analysis of Figure 3 (a) and (b), can be seen that SCWG of glucose and cellulose shows a similar equilibrium composition behavior, were H<sub>2</sub> production was favored in conditions of high temperature, the CO production showed to be not significant in the conditions analyzed here, similar behavior for the CO production were observed by Kruse (2008). In the conditions of low temperature the main components in the reactional systems are CO<sub>2</sub> and CH<sub>4</sub>, these behavior were observed by Kruse (2008) and Voll et al. (2009) too.

#### 3.2.2. Feed composition and pressure effect

The effect of the concentration of the glucose and cellulose in the feed were evaluated over the composition of H<sub>2</sub> in the product stream the results can be visualized in the Figure 4 (a).

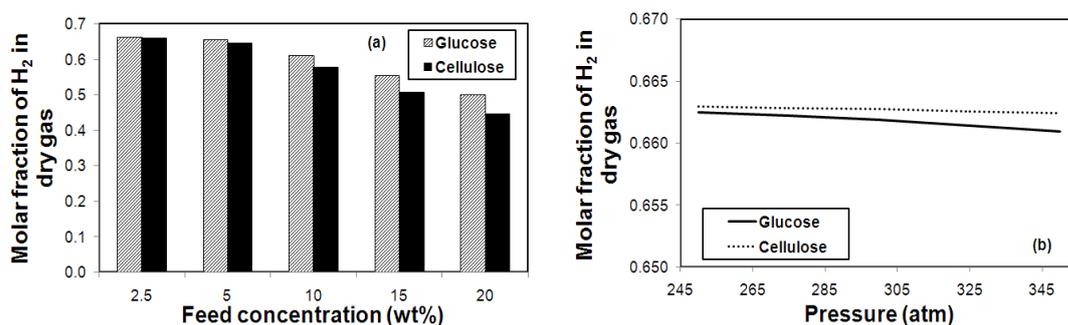


Figure 4. (a) Effect of the concentration of glucose and cellulose over the H<sub>2</sub> production in the SCWG processes for a constant temperature of 1073.15 K and a constant pressure of 280 atm; (b) Pressure effect under H<sub>2</sub> production in SCWG of glucose and cellulose for a constant temperature of 1073.15 K and a constant feed composition of 2.5 wt% of glucose or cellulose.

The simulations of both systems (SCWG of glucose or cellulose) were performed at constant temperature of 1073.15 K and at a constant pressure of 280 atm. As can be seen in the Figure 4, in the lower concentrations of glucose and cellulose were obtained the major concentrations of H<sub>2</sub> in the product stream, these behavior was observed in the work of Voll et al. (2009) too. The H<sub>2</sub> production is greater for the glucose systems. The pressure effect showed to be irrelevant under the hydrogen molar composition in dry gas for both SCWG processes, this behavior can be seen in the Figure 4 (b) similar behaviors were observed for the others systems components.

### 3.2.3. Effect of CO<sub>2</sub> addition as a co-reactant under hydrogen and syngas production

The production of CO in this type of reforming process showed to be insignificant (see topic 3.2.1). As a strategy for the improvement the CO production, the CO<sub>2</sub> was used as a co-reactant. The effect of CO<sub>2</sub> addition under the H<sub>2</sub> and syngas (H<sub>2</sub>+CO) production and under the H<sub>2</sub>/CO molar ratio of the product can be seen in the Figure 5, for a system with constant temperature of 1073.15 K and constant pressure of 280 atm. The concentration of glucose and cellulose was also constant in 5 wt%.

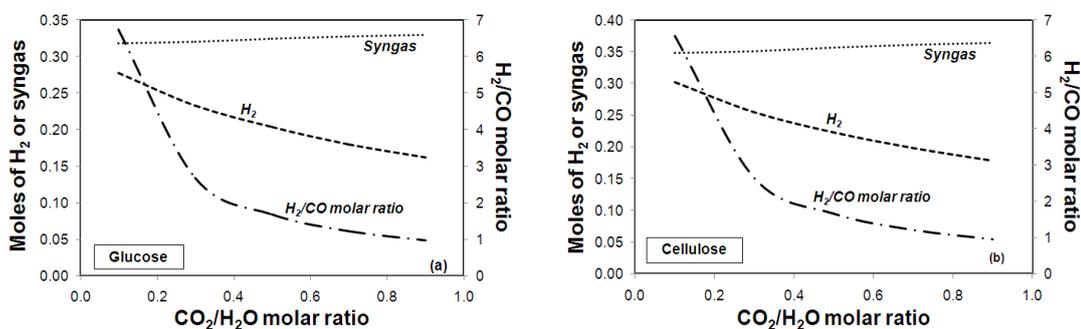


Figure 5. Effect of CO<sub>2</sub> addition over H<sub>2</sub> and syngas production and H<sub>2</sub>/CO molar ratio for glucose (a) and cellulose (b) SCWG.

As can be seen, the use of CO<sub>2</sub> as a co-reactant was very effective in improve the production of CO, thus reducing the H<sub>2</sub>/CO molar ratio of product stream. We can note the H<sub>2</sub> production decreases with increasing in the CO<sub>2</sub>/H<sub>2</sub>O molar ratio. For example for a CO<sub>2</sub>/H<sub>2</sub>O molar ratio of 0.4075 the syngas produced in the cellulose SCWG process has a H<sub>2</sub>/CO molar ratio of 2.00 (ideal for Fischer-Tropsch application), and in that conditions, the moles of CO<sub>2</sub> in the feed are 2.1507 and the CO<sub>2</sub> in the outlet stream are 2.2139 moles. As we can see, the number of moles of CO<sub>2</sub> produced is small, so the CO<sub>2</sub> can be separated from the products of interest (CO and H<sub>2</sub>) and re-used as a co-reactant.

### 3.3. Equilibrium temperatures

Figure 6 depicts the final temperatures in the glucose (a) and cellulose (b) SCWG processes as a function of the feed concentration of glucose and cellulose with initial temperatures in the range of 703.15–1073.15 K, for 280 atm pressure. These calculations were performed using the entropy maximization method.

It can be seen from Figure 6 that, for an initial temperature of 703.15 K the equilibrium temperature is higher than the initial temperature for both SCWG processes, while for an initial temperature of 1073.15 K the equilibrium temperature is lower than the initial for the glucose (see Figure 6 (a)) and higher than the initial for the cellulose (see Figure 6 (b)). As we can see in the Figure 6 (a) and (b) the addition of glucose or cellulose causes an increase in the final temperatures of the systems. For a feed concentration of cellulose of 2.5 (wt%), the equilibrium temperature is 759.97 K for an initial temperature of 703.15 K, and 1092.31 K for a feed concentration of 20 (wt%). For the glucose in the same conditions, the final temperatures are 703.62 K (2.5 wt%) and 783.61 K (20 wt%). Therefore, under these operating conditions this reacting system can be considered safe.

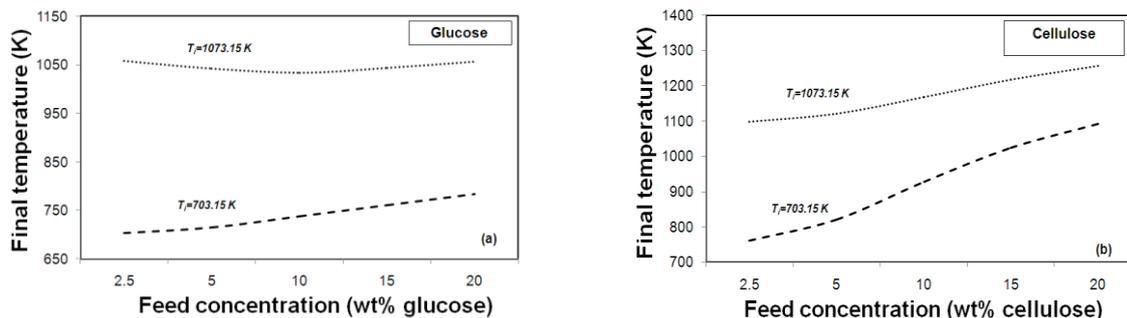


Figure 6. Equilibrium temperatures for the SCWG of glucose (a) and cellulose (b).

#### 4. Conclusion

The methodology used in this work was shown to be reliable for thermodynamic analysis of SCWG of glucose and cellulose. The results were compared with simulated and experimental data with a good agreement between them. Low feed concentrations of glucose or cellulose allied with high temperatures of reaction increased the efficiency of hydrogen production for all the studied cases. The proposed strategy of use  $\text{CO}_2$  as a co-reactant proved to be interesting to promote the CO production and using this strategy, the production of syngas from SCWG of biomass showed to be possible.

The results obtained using the entropy maximization showed that the reaction presents autothermal behavior for the cellulose SCWG reaction in the temperature range analyzed here. For the SCWG of glucose, for initial temperature of 703.15 K the reaction showed an autothermal behavior, for initial temperature of 1073.15 K, the reaction showed to be slightly endothermic.

The methodologies applied in the software GAMS<sup>®</sup>23.1, and solved with the solver CONOPT2, proved to be quick and effective in the resolution of the proposed problems, with computational time inferior to 1 s in all cases analyzed.

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