

# Study of the Hydrogen Potentiality from Supercritical Water Gasification of Different Biomasses: Thermodynamic Analysis and Comparison with Experimental Data

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Awareness of climate changes and large usage of fossil fuels have attracted more attention on the other sources of energy. Hydrogen is considered nowadays as an energy carrier of great interest. It is also used as chemical in different industrial sectors. Similarly, biomass has been taken into consideration with great interest for both energy and chemical productions, as an alternative to fossil sources: this is still a challenging topic, which industries and researchers are facing with.

Several technologies have been studied for the hydrogen production from biomass. Supercritical water gasification (SCWG) is a reaction of potential interest for biomass processing, particularly for biomass characterized by a high moisture content (typically more than 50 % by weight). This technology allows to obtain a rich hydrogen gas stream, with a low CO content. The reaction takes place above the water critical point, where chemical and physical properties of water are subjected to significant changes, which affect the reactivity of the system. Different authors have studied the SCWG reaction applied to different biomass materials. In this paper an analysis of the reaction performances with different models and real biomasses is presented, comparing the results with the ones found in literature (obtained by modelling and experimental). The hydrogen potential is studied using the Gibbs free energy minimization tool available in commercial process simulators, showing a good agreement between predictions and experimental results.

## 1. Introduction

Energy demand is projected to globally grow over the next twenty years (BP, 2012), with a progressive diversification of the energy mix. Global concern on climate changes and large usage of fossil fuels are driving the attention and the research efforts to boost the usage of alternative and more sustainable sources of energy. In this scenario H<sub>2</sub> is considered as an energy carrier of great interest. The use of this substance is not only limited to the production of energy, but it is also used in several industrial sectors (production of chemicals, oil refineries, food industry). Its global demand is expected to increase over the next six years (IHS, 2013). In the mean time, biomasses have been taken into consideration for both energy and chemical productions. H<sub>2</sub> can be produced from biomass in several ways.

Supercritical water gasification (SCWG) of biomass is a reaction of potential interest for biomass processing. It operates above the critical pressure of water (22 MPa) and allows to obtain high pressure gaseous streams with high H<sub>2</sub> content and low CO production. The properties and the reactivity of water over its critical point are completely different respect to the normal operating conditions (Serani et al., 2008). For example, above its critical point, the dielectric constant of water decreases and it becomes able to act as a solvent for hydrocarbons and other non-polar compounds which normally show a poor solubility in water. Heat transfer is favoured and mass transfer limitations are reduced (Serani et al., 2008). Moreover, the presence of moisture into the biomass feedstock favours the hydrolysis of the biomass into its main constituents and higher conversions can be reached with lower solid residues (Serani et al., 2008). The SCWG technology allows to produce H<sub>2</sub> at lower costs in comparison with other possible solutions (Shuit et al., 2009). It is suitable for the processing of high moisture content biomasses. At

equilibrium conditions the H<sub>2</sub> yield is the maximum achievable and the biomass is completely gasified. In this work the thermodynamics of the SCWG reaction is studied using a commercial simulator tool (Aspen Plus v7.3<sup>®</sup>), by means of the Gibbs free energy minimization approach. The obtained results are compared with experimental data for reactions with both model compounds, such as ethanol (Byrd et al. 2007a), glucose (Byrd et al., 2007b), glycerol (Byrd et al. 2008) and real biomass, such as corn starch (Antal et al., 2000). The gasification reaction is controlled by the kinetics and, at the process conditions, reactions are extremely fast. The thermodynamic constraints and their modelling for the SCWG process have to be known and well described to better define the operating conditions and understand their relative effects on the process performances. After a validation of the approach with experimental data, the methodology has been used to predict the hydrogen potential of two lignocellulosic biomasses which can be interesting for application (wood sawdust and willow wood). These two materials present similar characteristics but different moisture contents.

## 2. Simulation approach

The Gibbs free energy minimization methodology allows to calculate species distribution with a non-stoichiometric approach. It does not require the description of a chemical equilibrium starting from a direct definition of the reactions involved in the process, but allows the determination of the equilibrium composition for a reactive systems by minimizing the Gibbs free energy at a given temperature and pressure (Eq (1)). The conservation of the number of atomic species in the molecules is satisfied (Eq (2)):

$$\min_{n_i} (G_{T,P}) = \min_{n_i} \left( \sum_{i=1}^{N_c} n_i \mu_i \right) \quad (1)$$

$$\sum_{i=1}^{N_c} a_{k,i} n_i = b_k^0 \quad (2)$$

where G is the Gibbs free energy of the system, T is the temperature and P is the pressure of the system, n is the number of moles of the i-specie,  $\mu$  is the chemical potential, N<sub>c</sub> is the number of components, a is the number of atoms of the k- element in the i-specie and b<sub>k</sub><sup>0</sup> is the initial number of atoms of the k- element.

To apply this method, the components of the system have to be defined (both reactants and products). The advantage of using this methodology for chemical equilibrium description in reactive systems is that possible errors, due to avoidance of important reactions in the scheme, are neglected (Castello and Fiori, 2011). This approach has already been used in literature (Castello and Fiori, 2011; Voll et al., 2009; Freitas and Guirardello, 2012; Langè and Pellegrini, 2013) to describe this reaction. In this work this methodology has been tested by means of the Gibbs free energy minimization tool available in a commercial process simulator (Aspen Plus<sup>®</sup>) with the Peng-Robinson equation of state for the gas phase fugacity. The obtained results have been checked against experimental data and results, obtained with the same approach, proposed in literature with different computational tools (Castello and Fiori, 2011; Byrd et al., 2008; Voll et al., 2009). To apply this methodology to real biomasses, the elemental composition of the compound has to be assigned to evaluate its thermodynamic properties (Aspen Plus<sup>®</sup>, 2010).

## 3. Model and real biomass description

To better assess the reliability of the model predictions, several model compounds have been considered. Experimental data for the SCWG reaction of ethanol (Byrd et al., 2007a), glucose (Byrd et al., 2007b) and glycerol (Byrd et al., 2008) have been used. In these works, the authors made experimental investigations to study the effect of temperature, pressure, reactor residence time and feed concentration on the gas product yields. The authors show that in few seconds the compound can be considered completely converted and results obtained are close to the theoretical ones predicted by equilibrium calculations (Byrd et al., 2008). In a second step, the methodology has been checked against an experimental test performed on corn starch (Antal et al., 2000), where the obtained experimental product gas yields were closer to the equilibrium ones. After this validation, calculations have been made on two different biomasses: wood sawdust and willow wood. The characterization of the three biomasses is reported in Table 1.

Table 1: real biomass characterization (ultimate and proximate analysis, dry basis)

Element [wt %]	Corn starch	Wood Sawdust	Willow Wood
C	42.7	45.97	49.9
H	6.2	5.13	5.9
O	50.9	48.53	41.8
N	0.1	0.12	0.61
S	0.1	0.24	0.07
Ash	0.1	0.6	1.71
Moisture	12.8	9.2	50.0
Fixed Carbon	12.6	16.4	16.07
Volatile Matter	87.3	83.0	82.22

The elemental analysis of corn starch has been taken from the work by Antal et al. (2000), except for the fixed carbon and the volatile matter content, which have been taken from the work by Brown (2003). The characteristics for the wood sawdust have been outsourced from the work by García et al. (2005). The composition of the willow wood biomass has been taken from the work by Jenkins et al. (1998), while its definition of the moisture content has been found in the work by Ledin (1996).

#### 4. Results and discussion

The results obtained for the validation of the adopted methodology with model compounds are reported in Figure 1, while the results for the application of the studied approach to real biomass are reported in Figure 2.

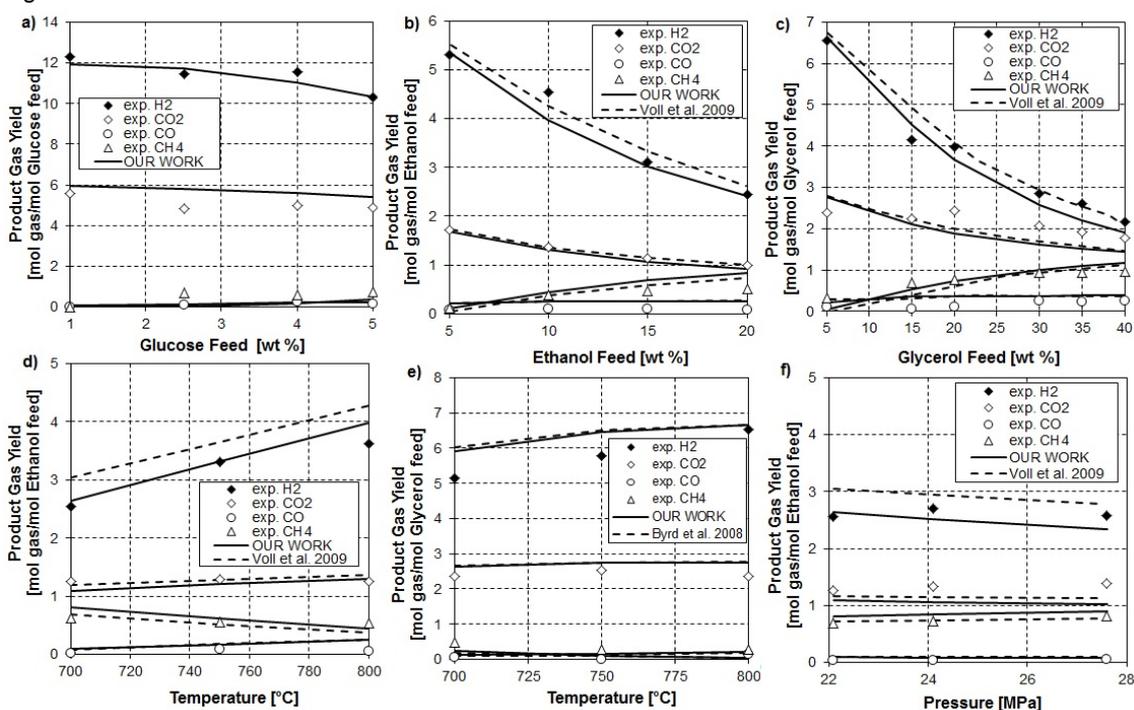


Figure 1: results obtained on model compounds (experimental data by Byrd et al., 2007a; Byrd et al., 2007b; Byrd et al., 2008) and comparison with other modelling works (Byrd et al., 2008; Voll et al., 2009). Effect of the feed concentration a), b) and c); effect of the temperature d) and e); effect of the pressure f)

The obtained results show a good agreement between the approach used in this work and the experimental data. A good correspondence exists also with other modelling results available in literature. The results obtained in this work for model compounds show a better agreement with experimental data than the ones obtained by Voll et al. (2009) for the calculated H<sub>2</sub> yields. The SCWG reaction is endothermic and occurs with an increase in the moles number. For this reason the hydrogen yield decreases as pressure is increased and is favoured by a temperature increase. An increase of the feed concentration tends to decrease the H<sub>2</sub> and CO<sub>2</sub> yields, but favours the formation of methane with no

significant changes in the carbon monoxide production, which remains at low levels. A temperature increase yields to a higher  $H_2$  production and inhibits the formation of  $CH_4$ .

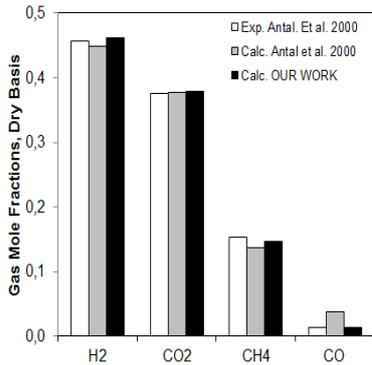


Figure 2: results obtained on corn starch (Antal et al., 2000). Comparison among Antal et al. (2000) experimental data and modelling and results obtained in this work

The results obtained with the modelling of corn starch SCWG are in good agreement with experimental data. For this reason the model has been applied to two different kinds of lignocellulosic biomasses (wood sawdust and willow wood), to predict their  $H_2$  potential. Results are reported in Figures 3-4.

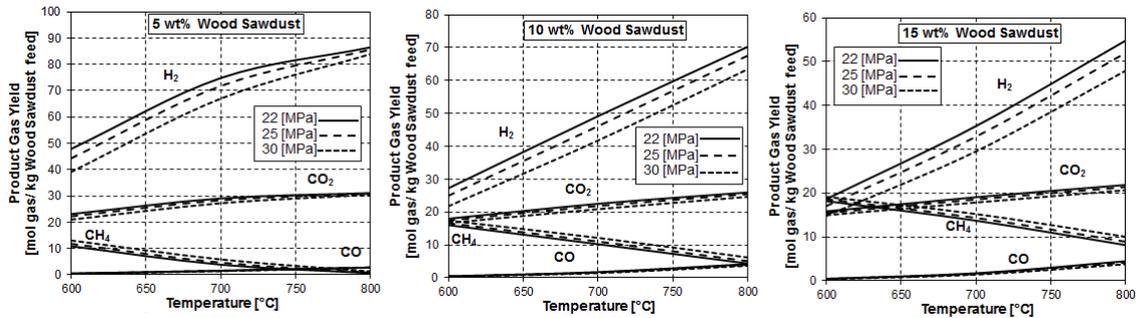


Figure 3: product gas yields for the SCWG of wood sawdust at temperatures between 600 °C and 800 °C, 22 MPa, 25 MPa and 30 MPa and at different feed concentration (5 wt %, 10 wt % and 15 wt %)

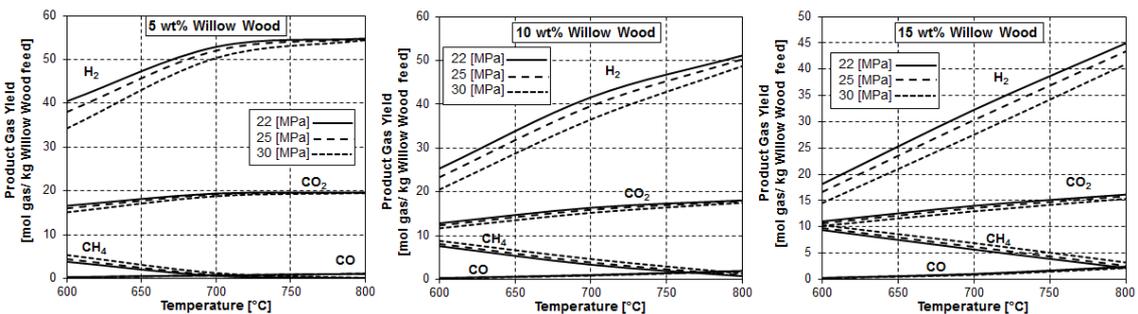


Figure 4: product gas yields for the SCWG of willow wood at temperatures between 600 °C and 800 °C, 22 MPa, 25 MPa and 30 MPa and at different feed concentration (5 wt %, 10 wt % and 15 wt %)

The results obtained for the wood sawdust and willow wood SCWG show similar trends and they are in accordance with the results obtained with model compounds. Product gas yields increase with temperature and decrease with pressure. An increment of the initial feed concentration tends to limit the equilibrium gas yields. The  $H_2$  potentiality is good, but the two biomasses show some differences.

From the biomasses characterization (Table 1), it can be outsourced that the two lignocellulosic materials present similar elemental content, except for moisture. Moreover, the willow wood presents slightly higher content of  $H_2$  and lower content of  $O_2$ . To better understand the differences in product yields, the results

obtained at 800 °C, 22 MPa (where the H<sub>2</sub> yields are higher in the studied operating conditions range) and different initial biomass concentrations have been analysed in terms of mol kg<sup>-1</sup> of initial biomass and mol kg<sup>-1</sup> of dry initial biomass. Results obtained are shown in Figure 5.

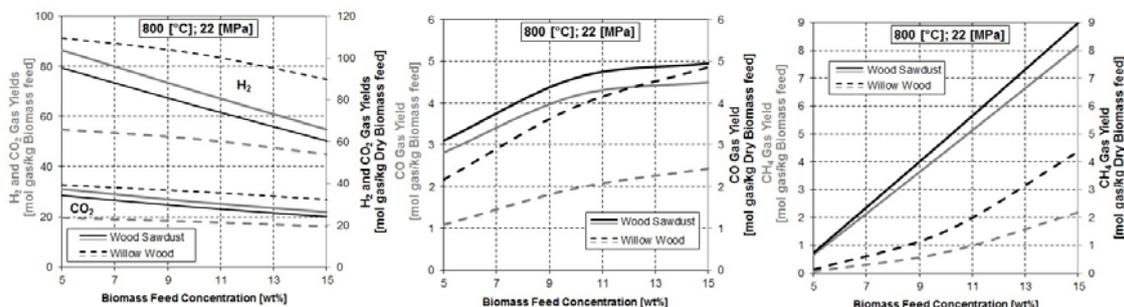


Figure 5: comparison among product gas yields in mol kg<sup>-1</sup> of biomass feed (grey lines) and mol kg<sup>-1</sup> of dry biomass feed (black lines) obtained by the SCWG of wood sawdust (solid lines) and willow wood (dashed lines) at 800 °C, 22 MPa and different initial biomass concentration

The results show that a higher biomass moisture content decreases the product gas yields (mol kg<sup>-1</sup> of biomass feed), but if the yields are calculated on the dry biomass basis the ones obtained for willow wood are higher than the ones obtained with wood sawdust. Moreover, a biomass with a higher H<sub>2</sub> and a lower O<sub>2</sub> contents can lead to significantly higher H<sub>2</sub> yields, without relevant differences in the CO<sub>2</sub> ones. To better investigate this aspect, simulations of SCWG at 800 °C and 25 MPa and 5 wt % initial feed concentration have been performed, considering model compounds (such as methanol, glucose, glycerol, methane, ethane, propane, ethylene and formaldehyde) to investigate the relative effect of the O/C and H/C ratios of the feedstock on the product gas yields. Results are summarized in Figure 6.

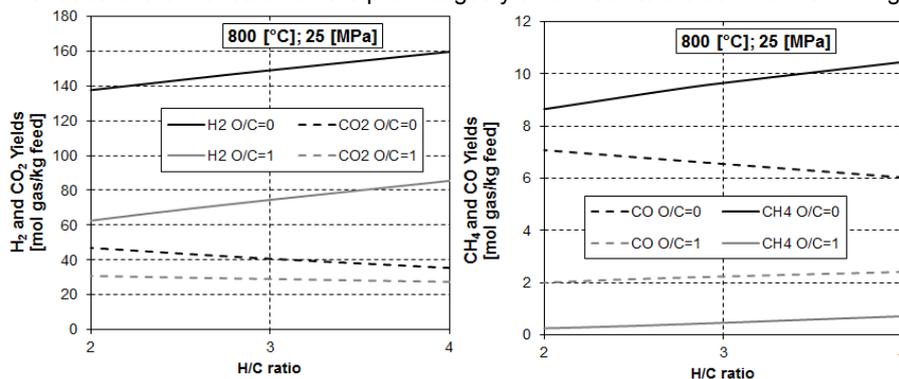


Figure 6: product gas yields as a function of H/C and O/C ratios obtained at 800 °C, 25 MPa and 5 wt % initial feed concentration, for different model compounds

At higher O/C ratios of the initial feed, the product H<sub>2</sub> yields are sensibly lower, while the CO<sub>2</sub> ones are not particularly different. The H<sub>2</sub> yields increase with the H/C ratio. This confirms the results obtained from the comparison of the product yields obtained with wood sawdust and willow wood biomasses.

## 5. Conclusions

The Gibbs free energy minimization approach with the Peng-Robinson equation of state has been tested and validated against experimental data on both model and real biomass compounds. The results obtained show a good agreement between predictions and experimental data. The methodology has been used to evaluate the performances and the H<sub>2</sub> potential of the SCWG reaction of lignocellulosic biomasses (wood sawdust and willow wood), which are commonly available in different countries of Europe and/or United States. The analysis has been carried out considering different possible operating conditions. For the considered biomasses, the predictions of the theoretical yields at thermodynamic equilibrium are in good agreement with the ones obtained for model compounds. Moreover, the effects of the biomass composition on the produced gas well match the theoretical ones.

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