

Thermodynamic Analysis of Supercritical Water Gasification of Microalgae Biomass for Hydrogen and Syngas Production

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Supercritical water gasification (SCWG) is an alternative thermochemical technology for the conversion of wet biomass in a high heat value product gases, such as syngas and hydrogen. Algal biomass has been suggested as one promising option to produce biomass for use as fuels and chemical feedstocks with high area-specific yields. In this study, the thermodynamic analysis of SCWG of microalgae biomass (*C. vulgaris* and *Spirulina Sp.*) for hydrogen and syngas production was presented. The effects of pressure (240-300 bar), initial temperature (703.15-1103.15 K), microalgae concentration (5-20 wt%) and co-reactant addition (CO₂ and CH₄) were evaluated with respect to production and final characteristics of the products. The formation of coke and the energetic characteristics of the SCWG were discussed. The analysis was conducted using two non-stoichiometric thermodynamic models, based on Gibbs energy minimization and entropy maximization methods. The virial equation of state was used to represent the non-ideality of the system. Both problems were formulated as optimization problems (non-linear programming) and the software GAMS 23.2.1 in combination with the CONOPT solver, were used to solve them. The results obtained were compared with previously published experimental and simulated data obtained in the literature, with good agreement between them. The syngas production was low for all conditions tested, but the addition of a CO₂ and CH₄ as a co-reactant proved to be effective way to increase the syngas production with a H₂/CO molar ratio close to 2 (ideal for Fischer-Tropsch applications). The SCWG presents exothermic behavior for low initial temperatures. In the region of high initial temperatures the systems showed to be less exothermic.

1. Introduction

Biomass can be converted into gas for further application, such as hydrogen for fuel cell systems or syngas for application in fuel production through Fischer Tropsch synthesis. In a general way, this is the scope of biomass gasification. Conventional thermochemical processes of biomass (for example pyrolysis or gasification) utilize dry biomass as feedstock. Hydrothermal processes (processes in an excess of water at high temperature and pressure are used) opens up the opportunity to process biomass with the natural water content. In hydrothermal gasification processes the biomass does not need to be dried with a high-energy expenditure. Also, hydrothermal gasification can lead to low tar and char formation and high hydrogen yields because water serves as both a reactant and reaction medium (Kruse, 2008).

In this context the supercritical water gasification (SCWG) of biomass appears, as a promising technology for the production of hydrogen and other useful gases from wet biomass, because of the remarkable characteristics of the supercritical water ($T_C = 647$ K, $P_C = 221$ bar) with respect to its density, dielectric constant, ion product, viscosity, diffusivity, electric conductance, and solvent ability compared to ambient water. These processes present high efficiencies and can be adapted for many biomass sources (Savage, 2000).

The literature is scarce of works that use thermodynamic analysis in SCWG of real biomass compounds. Thus, in this study, the thermodynamic analysis of SCWG of microalgae biomass (*C. vulgaris* and *Spirulina Sp.*) for hydrogen and syngas production was presented. The effects of pressure (240-300 bar), temperature (703.15-1103.15 K), microalgae concentration (5-20 wt%) and co-reactant addition (CO₂ and

CH₄) were evaluated. The formation of coke and the energetic characteristics of the SCWG were discussed too.

2. Methodology

2.1. Gibbs energy minimization: Equilibrium at constant pressure (P) and temperature (T)

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:

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

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

$$n_i^g, n_i^l, n_i^s \geq 0 \quad (2)$$

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

$$\sum_{i=1}^{NC} a_{mi} (n_i^g + n_i^l + n_i^s) = \sum_{i=1}^{NC} a_{mi} n_i^0 \quad m = 1, \dots, NE \quad (3)$$

Since the system analyzed by the present work was at high pressure, the virial equations of state (EoS), truncated at second virial coefficient, were utilized to determine the fugacity coefficient. The second virial coefficient is calculated by the correlation of Pitzer and Curl (1957), which was modified by Tsonopoulos (1974). The fugacity coefficient was determined by the following relation:

$$\ln \hat{\phi}_i = \left[2 \sum_j^m y_j B_{ij} - B \right] \frac{P}{RT} \quad (4)$$

2.2. Entropy maximization: Equilibrium at constant pressure (P) and enthalpy (H)

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 :

$$\max S = \sum_{i=1}^{NC} n_i^g S_i^g + \sum_{i=1}^{NC} n_i^l S_i^l + \sum_{i=1}^{NC} n_i^s S_i^s \quad (5)$$

While satisfying the same previous restrictions, given by equations (2) and (3). 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:

$$\sum_{i=1}^{NC} (n_i^g H_i^g + n_i^l H_i^l + n_i^s H_i^s) = \sum_{i=1}^{NC} (n_i^0 H_i^0) = H^0 \quad (6)$$

2.3. Model implementation

The software *GAMS*[®] 23.2.1, (*General Algebraic Modeling System*) with the *CONOPT* solver was used in the resolution of the combined chemical and phase equilibrium problem. A description of *GAMS* software can be found in Brooke et al. (1998). The solid phase formed was considered as solid carbon (pure component). These methodologies and considerations were applied in previous works of our research group with good predictive results (Freitas and Guirardello, 2012 a, b).

Microalgae biomass was modelled as a pseudo-component in the system, whose chemical formula is $C_a H_b O_c N_d$. The coefficients a , b , c and d were obtained in the literature for both microalgae's analysed here and the values of these constants were presented in Table 1.

A Total of 16 output compounds were selected as representative of the main compounds, which can be found in the output stream of these reactive systems. These compounds were selected based in

experimental works found in the literature. The complete list of output compounds, along with their critical parameters, is reported in Table 2.

Table 1. Coefficients of molecular formula for microalgae biomass analysed.

Microalga	a	b	c	d	Source
<i>Spirulina sp.</i>	1.00	1.87	0.59	0.13	Castello and Fiori (2011)
<i>Chorella vulgaris</i>	1.00	2.07	0.63	0.14	Chakinala et al. (2010)

General formula: $C_aH_bO_cN_d$.

Table 2. Chemical compounds considered in the simulations and your thermodynamic properties.

Compound	Chemical formula	T_c (K) ¹	P_c (bar) ¹	V_c (m ³ /kmol) ¹	ω (-) ¹
Water	H ₂ O	647.3	220.0	0.056	0.348
Hydrogen	H ₂	33.0	13.0	0.064	0.000
Methane	CH ₄	191.1	45.8	0.099	0.013
Carbon dioxide	CO ₂	304.2	73.9	0.094	0.420
Carbon monoxide	CO	133.0	35.0	0.093	0.041
Oxygen	O ₂	154.6	50.4	0.073	0.022
Ethane	C ₂ H ₆	305.4	48.2	0.148	0.105
Propane	C ₃ H ₈	369.9	42.0	0.200	0.152
Ethylene	C ₂ H ₄	283.1	50.5	0.124	0.073
Propylene	C ₃ H ₆	369.9	45.4	0.182	0.143
Methanol	CH ₃ OH	512.6	80.13	0.116	0.559
Nitrous oxide	N ₂ O	309.6	72.4	0.098	0.161
Ammonia	NH ₃	405.6	113.5	0.072	0.250
Nitric oxide	NO	180.0	64.8	0.058	0.607
Nitrogen dioxide	NO ₂	431.0	101.0	0.169	0.860
Nitrogen	N ₂	126.2	33.9	0.086	0.040

¹Source: Poling et al. (2000).

3. Results and discussion

3.1. Gibbs energy minimization

3.1.1. Model validation

The Gibbs energy model predictions were compared with experimental data obtained in the work of Chakinala et al. (2010) for the SCWG of *Chlorella vulgaris* with Ru/TiO₂ [E] metallic catalyst. The experiments were conducted at 600 °C (873.15 K), 240 bar, with 2 minutes of reaction time and 7.3 wt% of microalgae feed concentration.

The Gibbs energy model was run at the same conditions in which the experiments of Chakinala et al. (2010) were performed. The comparison between the simulations and experimental results were presented in the Figure 1 (a). This figure shows the agreement between experimental data for Ru/TiO₂ [E] catalyst obtained in the work of Chakinala et al. (2010) and the virial and ideal models predictions. The ideal model considers the ideality of the system, which, mathematically, means that the fugacity coefficient of the system is equal to unit ($\hat{\varphi} = 1$).

In order to compare the results calculated using the proposed approach with the values found in literature, the mean relative error (MRE) was used, according to equation 7.

$$MRE = \frac{1}{NPE \cdot NCE} \cdot \sum_j \sum_i \left| \frac{x_{j,i}^{literature} - x_{j,i}^{simulated}}{x_{j,i}^{literature}} \right| \quad (7)$$

Where NPE is the number of experimental points, NCE is the number of components for each experimental point, $x_{j,i}^{simulated}$ is the value calculated by the present work and $x_{j,i}^{literature}$ is the experimental value obtained in the literature.

The agreement is found to be very good with MRE of 0.807 for Virial equation model and MRE of 1.086 for ideal system consideration.

Figure 1 (b) shows the comparison between the simulated data from Castello and Fiori (2011) and the simulations performed by the present work using the proposed virial model. The simulations were performed at the following conditions: feed concentration of 60 wt% of *Spirulina sp.*, pressure of 250 atm

and temperatures between 700 and 1400 K. Those authors used a model of Gibbs energy minimization in combination with the Peng Robinson EoS. The Figure shows that the model proposed by this work using the virial EoS presents good agreement with the model developed using the Peng Robinson EoS.

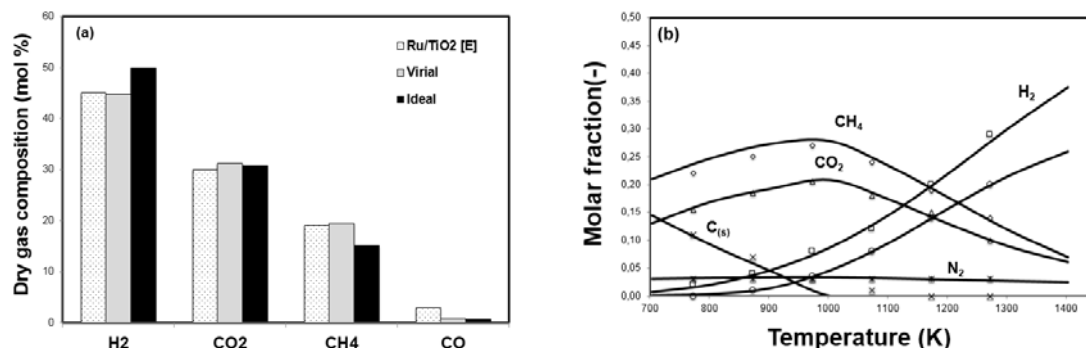


Figure 1. (a) Comparison between experimental data obtained in the work from Chakinala et al. (2010) for the Ru/TiO₂ [E] catalyst and the predictions obtained using the proposed Virial model and the ideal system consideration ($\hat{\phi}=1$). (b) Model validation with simulated data from Castello and Fiori (2011); solid line: simulations of the present work using the virial model; Symbols: simulations of Castello and Fiori (2011) using Peng Robinson EoS.

In general, it is possible to state that the Gibbs energy minimization technique combined with Virial equation of state provide results which are in good accordance with experimental and simulated data from literature, therefore, the proposed model is a valuable tool for predicting the thermodynamic behavior of SCWG reactive systems.

3.1.2. Pressure and temperature effects

Figure 2 (a) shows the H₂ compositions as a function of the temperature of the reaction for the SCWG of microalgae biomass, at constant pressure (250 bar) and composition of biomass in the feed (15wt%). The increase of the reaction temperature plays a favorable role in hydrogen formation. The hydrogen composition in product stream was greater for *C. vulgaris* microalgae biomass.

In the Figure 2 (b) the effect of the pressure increasing was presented, the simulations were performed at constant temperature (873.15 K) and microalgae composition (10 wt%). Figure 2 (b) shows that modifications in the system pressure have no significant effect on the formation of H₂ in the system.

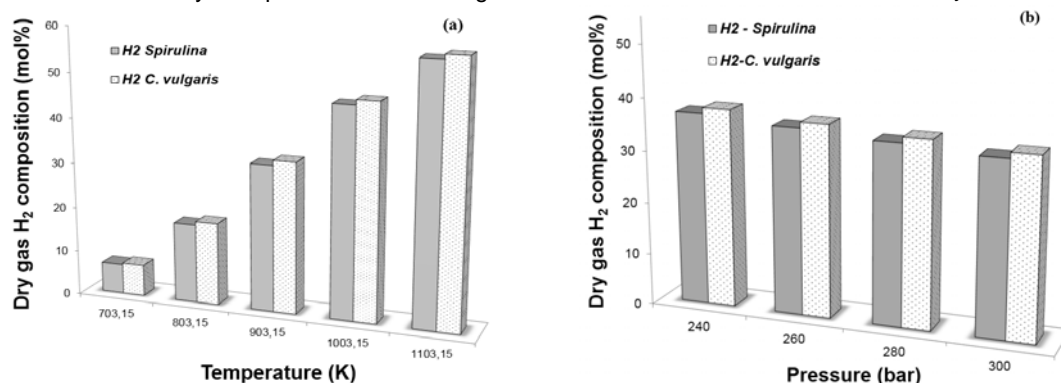


Figure 2. Effects of temperature (a) and pressure (b) under H₂ formation in SCWG of microalgae biomass.

In a general way, conditions of high temperature and low pressures results in high H₂ formation, this behavior was observed in other works of the literature for model compounds and real biomass materials (Freitas and Guirardello, 2012a).

3.1.3. Microalgae concentration and co-reactants addition effects

Figure 3 presents the effect of feed concentration under dry gas molar composition for SCWG of microalgae biomass. Figure 3 (a) presents the results for SCWG of *C. vulgaris* and Figure 3 (b) presents the results for SCWG of *Spirulina sp.*, both systems presented similar behavior as expected.

In general, the elevation of the feed concentration, results in decreased production of H_2 . The production of CH_4 significantly increased at the same conditions. The CO_2 concentration remains practically constant throughout entire range of initial compositions analyzed. The nitrogenous compounds formed don't show significantly concentrations of nitrogenous oxides. Nitrogen (N_2) was the main nitrogen compound produced, however, small amounts of NH_3 were observed too. CO formation was low throughout all composition range analyzed.

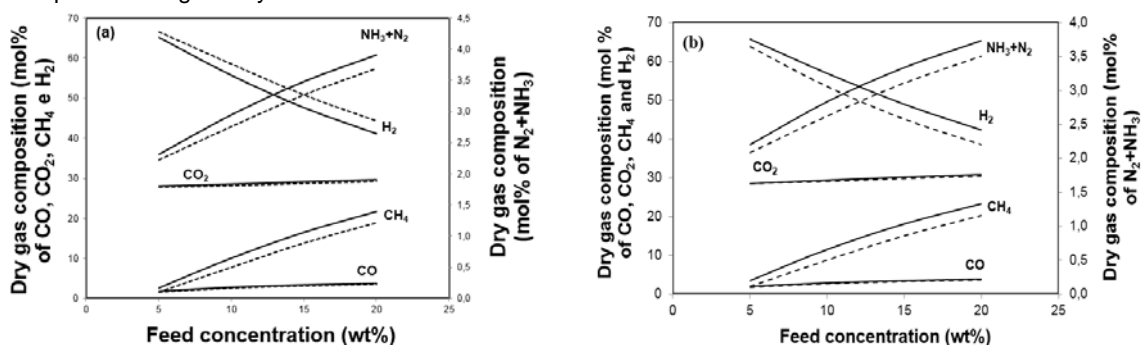


Figure 3. Effect of feed concentration under dry gas molar composition for SCWG of (a) *C. vulgaris*; (b) *Spirulina sp.* Symbols: Solid line – Virial equation model; dashed line – ideal formulation ($\phi = 1$).

Figures 4 (a) and (b) shows the effect of CO_2 and CH_4 addition as a co-reactant in SCWG, under number of moles of H_2 produced and under H_2/CO molar ratio obtained in the product, as a function of the feed concentration of microalgae. The co-reactants (CO_2 or CH_4) were added with a molar ratio of 2:1 in relation of the microalgae. This molar ratio was selected based on previous analyzes.

The addition of CO_2 and CH_4 results in decreased H_2/CO molar ratios, but H_2/CO ratio closer to 2 (ideal molar ratio for Fischer Tropsch applications) was obtained only with CO_2 addition in regions of high biomass concentration (see Figure 4 (b)). This behavior was observed for SCWG of glucose (as model compound) when CO_2 was added in the system, in a previous published work (Freitas and Guirardello, 2012a). The addition of CH_4 presents another interest effect: the formation of H_2 increased significantly when CH_4 was used in the feed as a co-reactant (see Figure 4 (a)). In none of the simulations performed, the formation of solid carbon was observed.

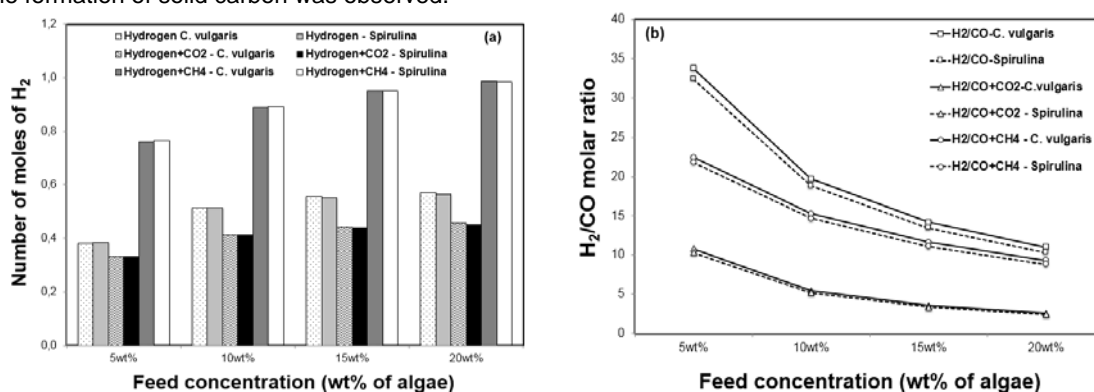


Figure 4. Effect of CO_2 and CH_4 addition under number of moles of hydrogen (a) and H_2/CO molar ratio (b) in the SCWG of *C. vulgaris* and *Spirulina sp.*

3.2. Entropy maximization: thermal effects

In the Figures 5 (a) and (b) were presented the results obtained using the entropy maximization method. In the Figure 5 (a), the effect of feed concentration under the equilibrium temperatures was presented for two initial temperatures (873.15 and 1073.15 K) for both microalgae's. In a general way was observed that in

all conditions the systems presented exothermic behavior, but for high initial temperature this trend was less pronounced. Similar results were observed for the SCWG of glucose and cellulose in Freitas and Guirardello (2012a).

Figure 5 (b) shows the effect of the initial temperature under H_2 formation for the two microalgae's analyzed. As can be seen, the increase in the initial temperature results in an increase in the formation of H_2 . In a general way the equilibrium temperatures and H_2 formation was higher for SCWG of *C. vulgaris*.

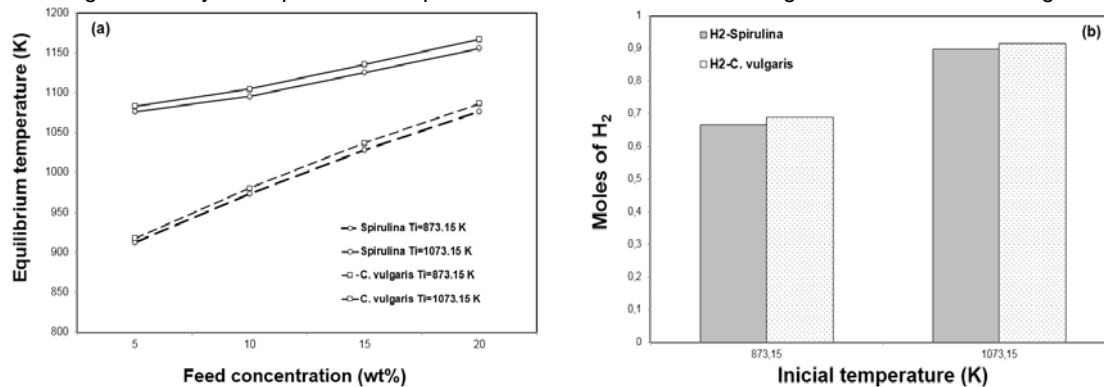


Figure 5. (a) Effect of feed concentration under the equilibrium temperatures for SCWG of *C. vulgaris* and *Spirulina* sp. at 873.15 K (dashed line) and 1073.15 K (solid line) of initial temperature; (b) Effect of initial temperature under H_2 formation for SCWG of *C. vulgaris* and *Spirulina* sp. (15wt%).

4. Conclusion

The methodologies proposed in this work showed to be reliable for thermodynamic predictions in SCWG reactive systems for real biomass compounds. The predictions presented good agreement with experimental and simulated data from literature. The methodologies used and applied in the software GAMS[®]23.2.1, and solved with the solver CONOPT proved to be quick and effective in the resolution of the proposed problems, with computational time inferior to 1 s in all cases analyzed. Microalgae biomass proved to be a viable source for hydrogen production. The syngas production with a H_2/CO molar ratio close to 2 was possible only with co-reactant additions. All reactions presented a slightly exothermic behavior.

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