

## Thermodynamic Effect of Co-reactant Addition in the Supercritical Water Gasification of Biomass

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Due to the increasing price and decreasing amount of fossil fuels, energy obtained from biomass has received much attention in recent years. Biomass generally contains much water and they must be dried first to be used in conventional thermochemical gasification process. However, a large amount of energy is consumed when the biomass are dried. In order to avoid the drying process, hydrothermal gasification processes, like as supercritical water gasification (SCWG), has attracted more attention because water can be used as a reaction medium, so that wet biomass does not need in the dried to be processed. The SCWG is related to present large hydrogen yields, but the excess of water inhibits the carbon monoxide production in the system and thus the syngas production is very low. The use of co-reactants appears as a strategy to promote syngas production in SCWG processes. In this work optimization techniques are applied in the minimization of Gibbs energy and in entropy maximization to study the thermodynamic effect of the use of CH<sub>4</sub> and CO<sub>2</sub> as co-reactant in the SCWG of microalgae biomass (*Nannochloropsis sp.*) and sugarcane bagasse. The Virial equation of state was used to represent the non-ideality of the systems. Both problems were formulated as optimization problems (non-linear programming) and the software GAMS in combination with the CONOPT solver, were used to solve them. Syngas with a H<sub>2</sub>/CO molar ratio close to 2 (ideal for Fischer-Tropsch synthesis applications) was obtained with an addition of CO<sub>2</sub> 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.

### 1. Introduction

Harvesting energy from carbon neutral sources with simultaneous reduction of gas emissions to the environment is of even greater importance. It is expected that future energy use will have increased utilization of different energy sources mixes, including biomass, municipal solid wastes, industrial wastes, agricultural wastes and many other alternative sources.

Algae have been proposed as a biomass energy source for hydrogen and biofuel production. The photosynthetic efficiency of algae for converting atmospheric CO<sub>2</sub> into biomass is as much as ten times higher than that for terrestrial plants (Ross et al., 2009).

Sugarcane bagasse is the major by-product of the sugar cane industry. It contains about 50 % cellulose, 25 % hemicellulose and 25 % lignin. Due to its abundant availability, it can serve as an ideal substrate for microbial processes as well as energy conversion via combustion or gasification for the production of fuels and value added gases (Ahmed and Gupta, 2012).

The interest in supercritical fluids began in the late 1970s and remains today. This interest has also led to the usage of supercritical water for biomass conversion technologies such as supercritical water oxidation for waste treatment or supercritical water (SCW) gasification for biofuel production (Brunner, 2009). The SCWG is related to present large hydrogen yields, but the excess of water inhibits the carbon monoxide production in the system and thus the production of syngas is very low. The use of co-reactants appears as a strategy to promote syngas production in SCWG processes. In previously published works of our group the use of CO<sub>2</sub> and CH<sub>4</sub> co-reactants proved to be effective to promote the syngas production in

SCWG of glucose and cellulose (Freitas and Guirardello, 2012a) and in SCWG of microalgae biomass from *C. vulgaris* and *Spirulina sp.* (Freitas and Guirardello, 2013).

In this work, optimization techniques are applied in the minimization of Gibbs energy and in the entropy maximization to study the thermodynamic effect of CH<sub>4</sub> and CO<sub>2</sub> use as co-reactant in the SCWG of microalgae biomass (*Nannochloropsis sp.*) and sugarcane bagasse. 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 in combination with the CONOPT solver, were used to solve them.

## 2. Methodology

### 2.1. Gibbs energy minimization – Isothermic systems

The thermodynamic equilibrium condition for reactive multicomponent closed system, at constant pressure ( $P$ ) and temperature ( $T$ ), 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:

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

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

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

The Gibbs energy minimization was applied to evaluate the behaviour of SCWG systems as regards the composition of products for isothermic systems. Thus, the best operating conditions with respect to temperature, composition of biomass and co-reactants in the feed stream can be determined in order to obtain the highest syngas productivity.

### 2.2. Entropy maximization – Adiabatic systems

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

$$\max S = \sum_{i=1}^{NC} n_i^g S_i^g + \sum_{i=1}^{NC} n_i^l S_i^l + \sum_{i=1}^{NC} n_i^s S_i^s \quad (4)$$

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:

$$\sum_{i=1}^{NC} (n_i^g H_i^g + n_i^l H_i^l + n_i^s H_i^s) = \sum_{i=1}^{NC} (n_i^0 H_i^0) = H^0 \quad (5)$$

The entropy maximization method was applied to study the thermal characteristics of the SCWG systems in adiabatic systems. The thermal effect of co-reactants addition was analysed too, in order to determine the better thermal conditions in the SCWG systems.

### 2.3. Equation of state

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

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

Details about the formulation and solution of the optimization problems using the proposed approaches, as well as the validation of the models with experimental and simulated data can be found in Freitas and Guirardello (2012a, 2012b and 2013). The composition of biomass sources was obtained in the literature for microalgae *Nannochloropsis sp.* (Guan et al., 2012) and for sugarcane bagasse (Osada et al., 2012).

### 3. Results and discussion

The Gibbs energy minimization and entropy maximization models were previously validated with both experimental and simulated data for the SCWG of glucose and cellulose (Freitas and Guirardello, 2012a), in the SCWG of microalgae biomass (Freitas and Guirardello, 2013) and for the oxidative reforming of methane (Freitas and Guirardello, 2012b). In this work these models were applied in order to check the thermodynamic effect of the addition of CH<sub>4</sub> or CO<sub>2</sub> as co-reactant in the SCWG of microalgae *Nannochloropsis sp.* and sugarcane bagasse for isothermic (Gibbs energy minimization) and adiabatic (entropy maximization) systems.

#### 3.1. Thermodynamic effect of co-reactant addition in isothermic systems

In Figure 1 the composition of the main gaseous products are presented for the SCWG of microalgae *Nannochloropsis sp.* in Figure 1 (a) and for the sugarcane bagasse in Figure 1 (b), in both cases the temperature, the pressure and the inlet biomass composition are fixed in 1073.15 K, 260 bar and 15 wt%.

The co-reactants addition was analyzed in three different conditions 15, 25 and 35 wt%. The addition of CH<sub>4</sub> resulted in a significant increase in the H<sub>2</sub> production, mainly due to the increase in the H/C molar ratio in the feed stream. The highest concentrations of CH<sub>4</sub> were observed in the systems with CH<sub>4</sub> addition too; this behavior could be explained by the large amounts of CH<sub>4</sub> used in the feed stream. The behavior was very similar for both biomass sources analyzed. The production of CO was favored for the addition of both CH<sub>4</sub> and CO<sub>2</sub>, the use of CO<sub>2</sub> as a co-reactant resulted in the reduction of H<sub>2</sub> production, and large amounts of CO<sub>2</sub> were observed when this compound was used as a co-reactant.

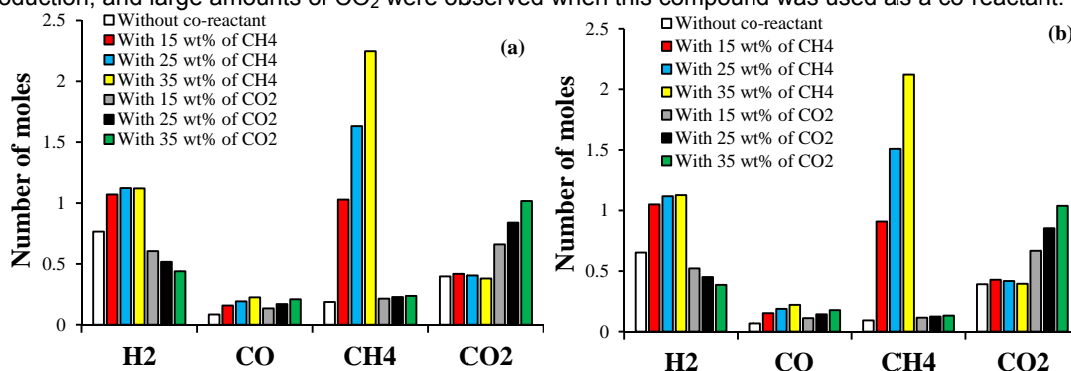


Figure 1. Effect of co-reactant addition on number of moles of main gaseous products: in the SCWG of (a) *Nannochloropsis sp.* and (b) sugarcane bagasse. Conditions: temperature: 1073.15 K; pressure: 260 bar; biomass composition: 15 wt%.

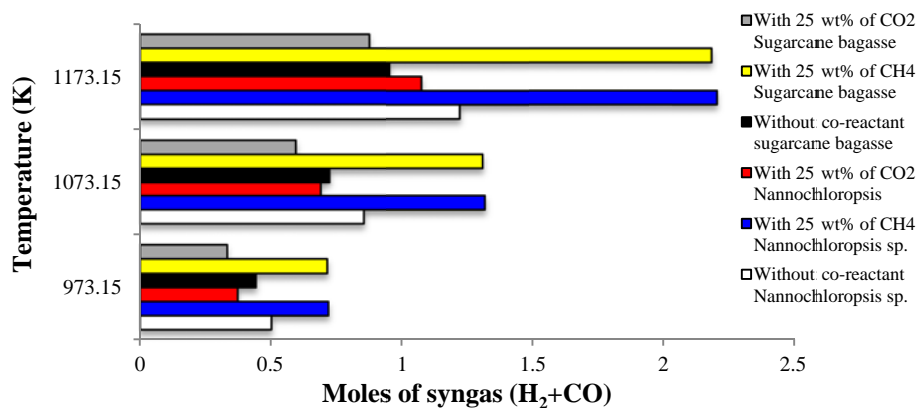


Figure 2. Effect of reaction temperature and co-reactants addition on syngas production in the SCWG of *Nannochloropsis sp.* and sugarcane bagasse.

The effect of temperature on syngas ( $H_2+CO$ ) production is presented in Figure 2. In this figure the addition of co-reactants were fixed at 25 wt% of  $CO_2$  or  $CH_4$ . The elevation of temperature resulted in the elevation of syngas production in all range and for all cases analyzed. Higher production of syngas can be explained by the higher reactivity of the systems in high temperature conditions. Analyzing both figures it is possible to verify that the addition of  $CH_4$  presented a significant increase in syngas production, but the syngas produced in this system presented a high  $H_2/CO$  molar ratio. In other way the addition of  $CO_2$  resulted in a reduction in the number of moles of syngas produced in the system but the syngas produced presented a  $H_2/CO$  ratio close to 2. In this way, the addition of  $CH_4$  showed to be interesting for systems that aims  $H_2$  production and the addition of  $CO_2$  proved to be interesting to produce syngas with a  $H_2/CO$  molar ratio close to 2, for further use in Fischer-Tropsch processes.

### 3.2. Thermodynamic effect of co-reactants addition in adiabatic systems

In Table 1, the effect of co-reactants addition was evaluated on equilibrium temperatures for the SCWG reactions at constant pressure (260 bar), initial temperature (973.15 K) and composition of biomass (15 wt%). In a General way, was possible to verify that for both substrates the addition of  $CH_4$  resulted in a small decrease in exothermic behavior of the system. The addition of  $CO_2$  showed an inverse behavior, i.e., the addition of  $CO_2$  resulted in a small increase in exothermic behavior of the system.

Table 1. Effect of co-reactant addition on equilibrium temperatures observed in the SCWG of microalgae *Nannochloropsis sp.* and sugarcane bagasse. Conditions: initial temperature: 973.15 K; Pressure: 260 bar and biomass concentration in the feed: 15 wt%.

Condition	Equilibrium temperatures (K)	
	<i>Nannochloropsis sp.</i>	Sugarcane bagasse
Without co-reactant	1044.91	1151.46
15 wt% $CH_4$	1010.07	1066.60
25 wt% $CH_4$	1003.96	1055.22
35 wt% $CH_4$	1001.65	1049.59
15 wt% $CO_2$	1058.39	1162.23
25 wt% $CO_2$	1064.88	1167.83
35 wt% $CO_2$	1069.72	1172.17

In Figure 3 the effect of initial temperature was analyzed at constant pressure (260 bar), composition of biomass (15 wt%) and co-reactant concentration (25 wt%). The SCWG of sugarcane bagasse presented a more significant exothermic behavior, within the range examined.  $CH_4$  addition resulted in a decrease in exothermic behavior and  $CO_2$  addition resulted in a small increase in the exothermic behavior of both systems. Still in Figure 3, it is possible to verify that in all range analyzed the elevation of initial temperature resulted in the elevation of equilibrium temperatures.

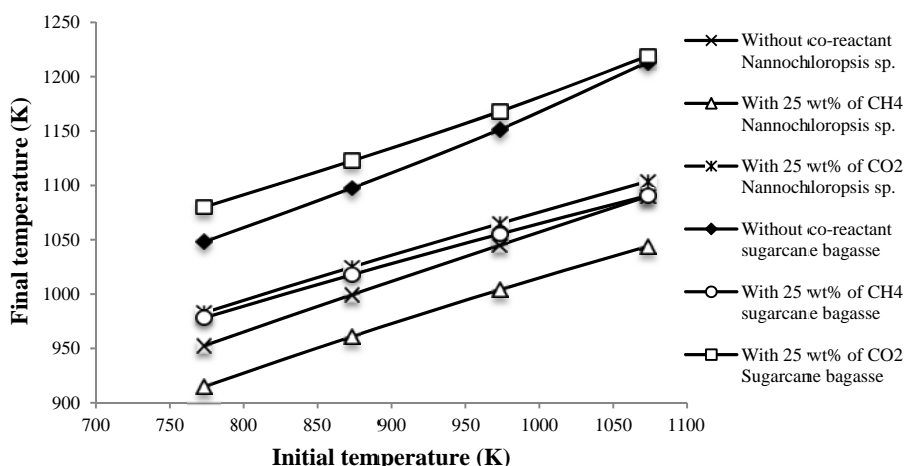


Figure 3. Effect of initial temperatures and co-reactants addition on equilibrium temperatures in the SCWG of *Nannochloropsis sp.* and sugarcane bagasse.

Figure 4 shows the moles of syngas produced as function of the initial temperature of reaction. In the simulations the pressure, the composition of biomass in the feed and the amount of co-reactant added to the system were fixed at 260 bar, 15 wt% and 25 wt%, respectively. The syngas production was favored by elevations in the initial temperature. The use of  $CH_4$  as a co-reactant resulted in significant increase in  $H_2$  production. Similar results were observed when co-reactants were used in the SCWG of glucose,

cellulose and microalgae biomass from *C. vulgaris* and *Spirulina sp.* (Freitas and Guirardello, 2012a, 2013). With the elevation of H<sub>2</sub> production the use of CH<sub>4</sub> as a co-reactant resulted in a product that still remains with a high H<sub>2</sub>/CO molar ratio.

The use of CO<sub>2</sub> as a co-reactant resulted in a decrease in the total syngas production, but this syngas presented a low H<sub>2</sub>/CO molar ratio, which provides that this syngas could be used in further Fischer-Tropsch synthesis reactions. Similar results were observed in the SCWG of glucose and cellulose (Freitas and Guirardello, 2012a) and in SCWG of biomass from *C. vulgaris* and *Spirulina sp.* (Freitas and Guirardello, 2013).

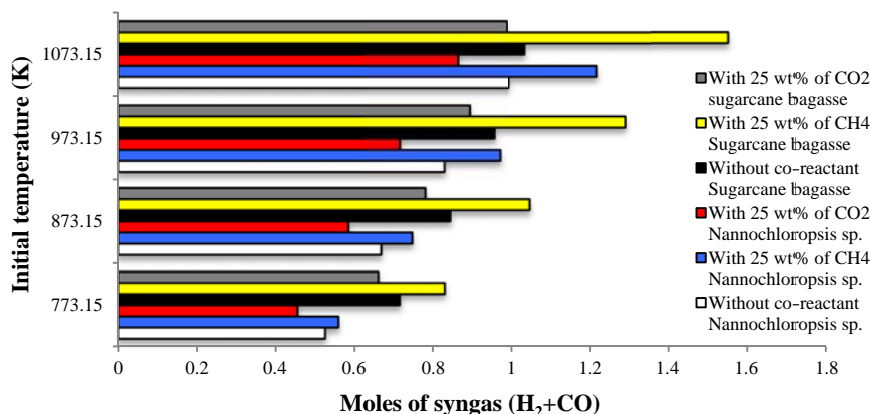


Figure 4. Effect of initial temperature and co-reactant addition on syngas production in the SCWG of *Nannochloropsis sp.* and sugarcane bagasse.

As the H<sub>2</sub>/CO molar ratio was an important factor for further use of the syngas, a detailed study of this factor was presented in Figure 5. Figure 5 presents the H<sub>2</sub>/CO molar ratio obtained in the product as a function of initial temperature of reaction; these simulations were performed at constant pressure (260 bar) and biomass composition (15 wt%) the use of CH<sub>4</sub> and CO<sub>2</sub> as co-reactants were considered in a range of 15-35 wt%.

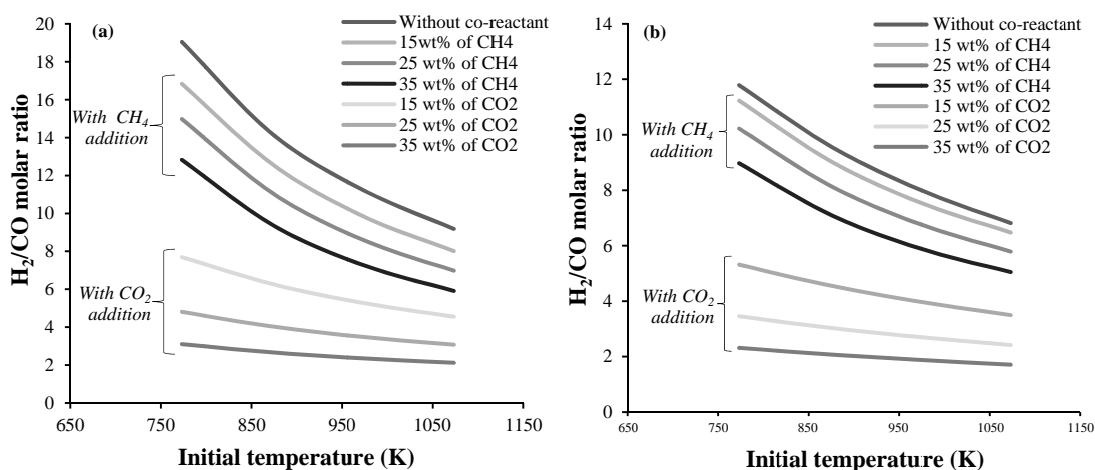


Figure 5. Effect of initial temperature of reaction on H<sub>2</sub>/CO molar ratio observed in the product for (a) microalgae *Nannochloropsis sp.* and for (b) Sugarcane bagasse.

Analyzing Figure 5 it is possible to verify that the addition of both CH<sub>4</sub> and CO<sub>2</sub> resulted in the reduction of the H<sub>2</sub>/CO molar ratio obtained in the product stream, but H<sub>2</sub>/CO molar ratios close to 2 was observed only with the addition of CO<sub>2</sub> with 25 and 35 wt% for both substrates (Figure 5 (a) for *Nannochloropsis sp.* and Figure 5 (b) for Sugarcane bagasse). The increase in the concentration of co-reactant in the feed resulted in reductions in the H<sub>2</sub>/CO molar ratio in all range of composition analyzed. Another interesting fact to be emphasized is that the addition of CO<sub>2</sub> even at the lowest concentration analyzed (15 wt%) had lower H<sub>2</sub>/CO molar ratios than when the highest CH<sub>4</sub> concentration (35 wt%) was used as co-reactant.

The elevation of the initial temperature resulted in reductions on the H<sub>2</sub>/CO molar ratio observed in all conditions analyzed, molar ratio close to 2 was observed in systems with CO<sub>2</sub> addition with 25 and 35 wt%. Modification of the biomass source showed a significant effect on the H<sub>2</sub>/CO molar ratio observed in the product stream, the sugarcane bagasse had lower H<sub>2</sub>/CO molar ratios in all conditions analyzed. This behavior can be visualized comparing Figures 5 (a) and (b).

The use of co-reactants proved to be an effective way to improve syngas production in the SCWG of different biomass sources. The use of CO<sub>2</sub> was more suitable for the production of syngas mainly because the syngas produced presented H<sub>2</sub>/CO molar ratio very close to 2, which is the ideal molar ratio for further use in Fischer-Tropsch synthesis reactions. The addition of CH<sub>4</sub> presented a significant increase in the H<sub>2</sub> production in the systems. This was the same behavior observed in the studies performed for isothermic systems. The addition of co-reactants did not modify significantly the thermal behavior of the studied systems under the conditions evaluated.

#### 4. Conclusion

The Gibbs energy minimization and entropy maximization methods, applied in the software *GAMS* 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.

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 in all conditions analyzed. The addition of CH<sub>4</sub> showed to be interesting for systems that aims H<sub>2</sub> production and the addition of CO<sub>2</sub> (with 25 and 35 wt%) proved to be interesting to produce syngas with a H<sub>2</sub>/CO molar ratio close to 2, for further use in Fischer-Tropsch processes. The addition of co-reactants did not modify significantly the thermal behavior of the studied systems under the conditions evaluated.

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