CHEMICAL ENGINEERING TRANSACTIONS

VOL. 37, 2014

Guest Editors: Eliseo Ranzi, Katharina Kohse- Höinghaus
Copyright © 2014, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-28-0; **ISSN** 2283-9216

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

DOI: 10.3303/CET1437038

Hydrogen Production from Supercritical Water Gasification of Different Biomass Materials: Thermodynamic Behavior

Antonio C. D. Freitas, Reginaldo Guirardello*

School of Chemical Engineering, University of Campinas (UNICAMP), Av. Albert Einstein 500, 13083-852, Campinas-SP, Brazil
guira@feq.unicamp.br

In this paper, optimization techniques were applied in the characterization of the thermodynamic behavior of Supercritical Water Gasification (SCWG) of different biomass sources, like as ethanol, glycerol, lignin, microalgal biomass (*Nannochloropsis sp.*) and sugarcane bagasse. For this, the Gibbs energy minimization (at constant pressure and temperature) and entropy maximization (at constant pressure and enthalpy) methods were applied in combination with the Virial equation of state, using non-linear programing. The problems were solved in the software GAMS using the CONOPT solver. The effect of modifications in biomass source was analyzed on H_2 production and on the thermal behavior of the SCWG systems. High H_2 production was observed for all substrates and the highest productions were observed for the SCWG of ethanol at isothermic conditions. The entropy maximization has shown that, with the exception of the SCWG of ethanol, all other SCWG presented autothermal behavior for initial temperatures below 1100 K. However, at adiabatic conditions the highest productions of H_2 were observed for the SCWG of glycerol, mainly due to high exothermic behavior of this system. With the results, it is possible to conclude that all biomass sources tested presented potential for application in H_2 production.

1. Introduction

Energy shortage and environmental pollution are two main challenges we have to deal with in the future. With the increasing consumption of fossil fuels, much research is focused on renewable sources of energy like as solar and biomass. Biomass has received a great deal of attention as a new source for clean energy production mainly because it is renewable, alternative and producing lesser carbon dioxide than fossil fuels.

Gasification is an effective thermochemical route to convert carbon-containing feeds into hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). The resulting gas, called syngas, can be combusted to produce heat, energy or be applied in the production of methanol and synthetic liquid fuels using Fischer-Tropsch processes.

Supercritical water gasification (SCWG), in which supercritical water is not only a solvent for organic materials but also a reactant, is one of the applications for producing fuel gas from organic sources. Organic compounds, like as glycerol (Castello and Fiori, 2011), microalgae biomass (Freitas and Guirardello, 2013), glucose (Freitas and Guirardello, 2012a), cellulose (Freitas and Guirardello, 2012a) and many other substrates were examined as feedstock for SCWG in recent years. The reaction temperature required for non-catalytic complete gasification of biomass, in supercritical water (SCW), is about 873 K (600 °C) that is much lower than the reaction temperature of the conventional thermo-chemical gasification processes for hydrogen production (Lu et al., 2011).

In this paper, optimization techniques were applied in the characterization of the thermodynamic behavior of Supercritical Water Gasification (SCWG) of different biomass sources, like as ethanol, glycerol, lignin, microalgal biomass (*Nannochloropsis sp.*) and sugarcane bagasse. For this, the Gibbs energy minimization (at constant pressure and temperature) and entropy maximization (at constant pressure and enthalpy) methods were applied in combination with the Virial equation of state, the problems are formulated as optimization problems (non-linear programing).

Please cite this article as: Daltro de Freitas A.C., Guirardello R., 2014, Hydrogen production from supercritical water gasification of different biomass materials: thermodynamic behavior, Chemical Engineering Transactions, 37, 223-228 DOI: 10.3303/CET1437038

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:

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

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

$$n_i^g, n_i^l, n_i^s \geq 0 \tag{2}$$

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

$$\sum_{i=1}^{NC} a_{mi}\left(n_i^g + n_i^l + n_i^s\right) = \sum_{i=1}^{NC} a_{mi} n_i^0 \qquad m = 1,...,NE \tag{3}$$

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 :

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

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:

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

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:

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

2.4. Model implementation

The software GAMS (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 possibility of a solid phase formation was considered to represent the production of solid carbon in the system (solid carbon was represented as a pure component). These methodologies and considerations were applied in previous works of our research group with good predictive results for similar systems like as SCWG of glucose and cellulose (Freitas and Guirardello, 2012 a), microalgae biomass (Freitas and Guirardello, 2013) and oxidative reforming of methane (Freitas and Guirardello, 2012b).

The biomass was represented as pseudo-components with the following general formula: $C_aH_bO_cN_d$. The coefficients a, b, c and d were obtained in the literature for all biomass materials 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 on experimental and simulation works that studied the SCWG reaction found in the literature (Guan et al., 2012).

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

Substrate	***a***	***b***	***c***	***d***
Ethanol	2.00	6.00	1.00	0.000
Glycerol	3.00	8.00	3.00	0.000
Lignin[1]	42.39	45.46	12.15	0.000
Nannochloropsis sp.[2]	23.00	38.00	10.00	3.000
Bagasse[3]	3.69	6.00	3.08	0.028

General formula: $C_aH_bO_cN_d$. [1]Osada et al. (2004); [2]Guan et al. (2012); [3]Osada et al. (2012).

3. Results and discussion

3.1. Model validation

The validation was performed using simulated and experimental data obtained in literature in comparison with the simulations performed using the proposed virial model. The objective of the validating the model is to verify the predictive ability of the model against experimental data obtained in the literature and verify the ability of the virial equation in represent the non-idealities of the studied systems.

The Gibbs energy minimization predictions were compared with both experiments and simulations obtained in the work of Osada et al. (2012). Osada and coworkers studied the SCWG of sugarcane bagasse on activated carbon and titania-supported ruthenium catalysts. Their experiments were performed at the following conditions: reactant, 0.1 g; catalyst, 0.30 g; reaction temperature, 673 K; water density, 0.33 $g.cm^{-3}$ (pressure of 30.0 MPa) and reaction time of 15min; their simulations were performed using the Software *CHEMKIN III*. Their simulations and the simulations performed by the present work were performed at the same conditions of the experiments and all results are presented in Figure 1.

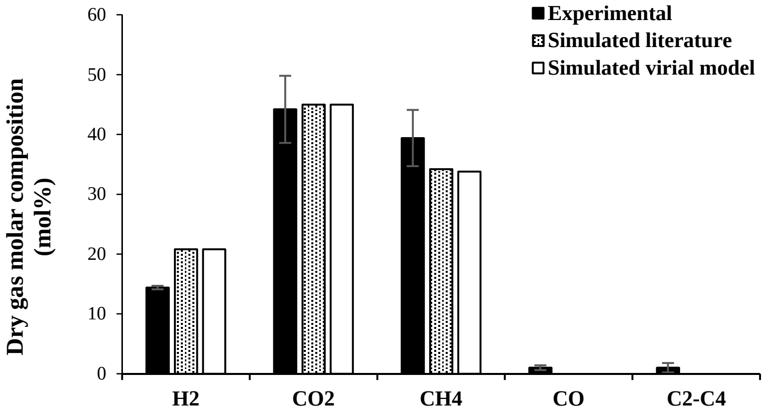

Figure 1. Comparison between simulated and experimental data from Osada et al. (2012) for the SCWG of sugarcane bagasse.

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. Similar results are observed in previous papers for different sources of biomass like as glucose and cellulose (Freitas and Guirardello 2012a) and microalgae biomass (Freitas and Guirardello, 2013). In the following sections, the effect of changes on the biomass source was studied on hydrogen production and on the thermal behavior of the systems.

3.2. Gibbs energy minimization – isothermic systems

Figure 2 (a) presents the number of moles of the main gaseous products for the different biomass substrates evaluated in the SCWG reaction. The simulations were performed at the following conditions: 15 wt%, 973.15 K and 280 bar. The Ethanol presented the highest production of H_2 in number of moles, however high production of CH_4 was also observed in this system.

High production of hydrogen was also observed in all other analyzed biomass substrate and the lower production of CH_4 was observed in the SCWG of glycerol, all SCWG technologies showed low production of CO on conditions where the reactions were analyzed. For almost all systems, the main compounds observed are H_2 and CO_2. The highest production of CO_2 was observed in the SCWG of Lignin.

The formation of ethane, propane, methanol and Ethanol was not observed in significant amounts on conditions in which the SCWG were analyzed for any of the tested substrates. Solid carbon was not observed in any simulation.

Figure 2 (b) presents the effect of the biomass concentration on the feed stream on H_2 production. Increasing the biomass concentration in the feed showed a slight decrease in the H_2 production, although this behavior was not pronounced, it was observed in all range of biomass concentration and for all biomass materials analyzed by the present work. The highest production of hydrogen was observed in the SCWG of ethanol for all range of reactants composition evaluated. The highest production of H_2 in the SCWG of ethanol can be explained by the highest H/C ratio observed in ethanol molecule, this elevated ratio results in high H_2 production for this substrate when compared with others.

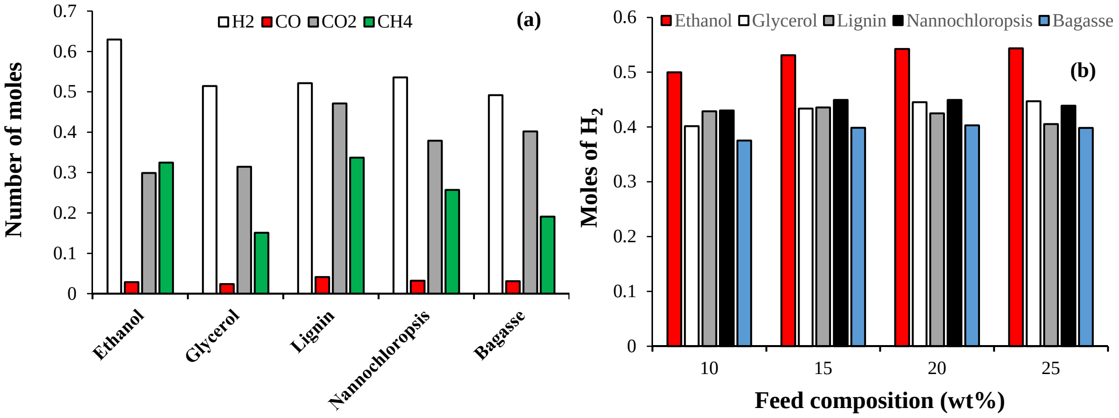

Figure 2. (a) Production of gaseous products in SCWG of different sources of biomass; Conditions: 280 bar 973.15 K and 15 wt%; (b) effect of feed composition on H_2 production; conditions: 280 bar and 973.15 K.

3.3. Entropy maximization – adiabatic systems

Figure 3 presents the effect of initial temperature of the reaction on the equilibrium temperature for all substrates evaluated. The simulations were performed using the previously presented entropy maximization approach, in conditions of constant pressure (280 bar) and constant feed composition (15 wt%), the initial temperature was evaluated between 700 and 1,200 K.

The elevation of the initial temperature in the SCWG resulted in the elevation of the final temperature in all systems. Glycerol and sugarcane bagasse presented autothermal behavior in all range of temperatures analyzed. Lignin and microalgae *Nannochloropsis sp.* showed autothermal behavior only for temperatures below to 1,100 K; above that the reactions presented a slightly endothermic behavior. Ethanol presented a similar thermic trend but for temperatures below 1,000 K. Above this temperature the reaction presented a more pronounced endothermic behavior.

Figure 4 (a) presents the comparison between all substrates evaluated at the same initial temperature; this figure reinforces the behavior observed in Figure 3, Glycerol, Lignin, Nannochloropsis and bagasse presented autothermal behavior and the ethanol presented endothermic behavior for an initial temperature of 1,000 K, at constant pressure (280 bar) and initial composition (15 wt%).

Figure 4 (b) presented the hydrogen production at the same reaction conditions used in Figure 4 (a). The hydrogen production presented an interesting behavior when compared with the results observed for the Gibbs energy minimization approach.

The Gibbs energy minimization considers an isothermic system and with this consideration, the highest production of hydrogen was observed in the SCWG of ethanol, but when the entropy maximization approach (that considers an adiabatic system) was used, the ethanol presented the lowest hydrogen production among all substrates analyzed.

This behavior can be explained by the thermal characteristics of the reactions. The SCWG of ethanol presented endothermic behavior, and because of this, the equilibrium temperatures of reaction were lower and the production of H_2, which depends on high temperatures to occur, is hampered. The effects of thermal characteristics of these systems are better discussed in Figure 5.

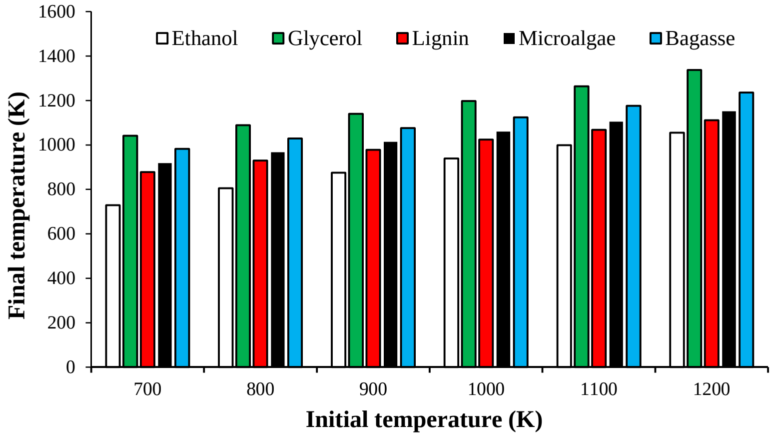

Figure 3. Effect of initial temperature on the final temperatures. Conditions: 15 wt% and 280 bar.

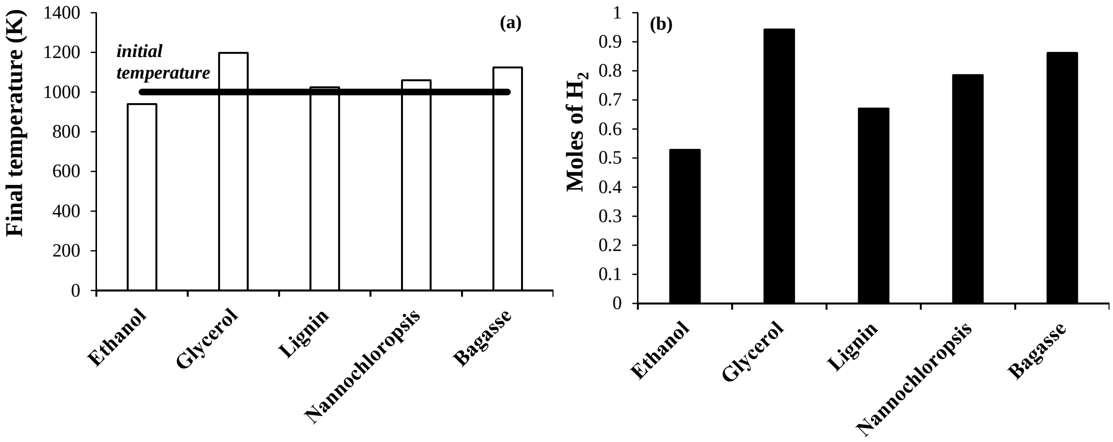

Figure 4. (a) Final temperature for all substrates analyzed and (b) hydrogen production for all substrates analyzed. Conditions: 1,000 K, 15 wt% and 280 bar.

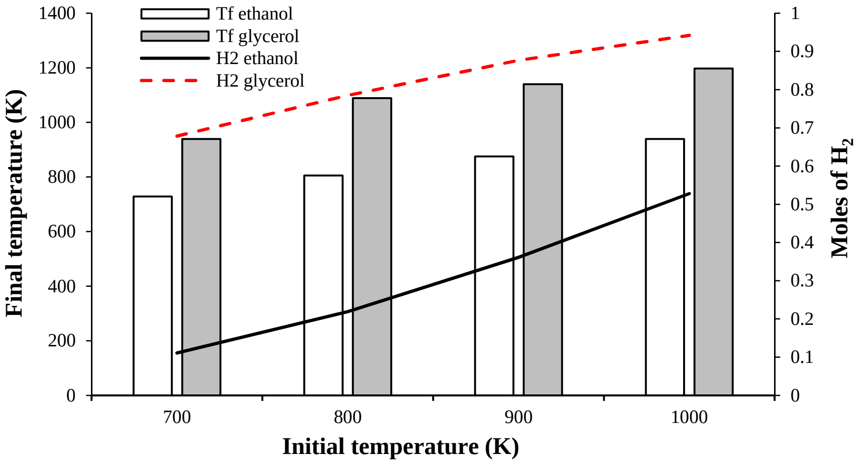

Figure 5. Final temperatures and H_2 production for the SCWG of glycerol and ethanol as function of initial temperature; conditions: 15 wt% and 280 bar.

Figure 5 presents the effect of initial temperature on the final temperatures and H_2 production for the SCWG of ethanol and glycerol; these substrates are selected as representative because they represent the extreme points regarding the thermal characteristics for SCWG of all considered substrates.

The highest H_2 production was observed in the SCWG of glycerol mainly due to high exothermic behavior presented in this reaction. It is observed in Figure 5 that the production of H_2 is directly related with the equilibrium temperatures, mainly because the reactions related with H_2 production are endothermic and therefore, needs high temperatures to be favored. This explains the lower production of H_2 for the SCWG of ethanol once this reaction showed endothermic behavior in almost all range of initial temperature analyzed. The highest exothermic behavior observed for the SCWG of glycerol can be explained by the high O/C ratio observed in the molecule of this substrate in comparison with the other tested substrates.

4. Conclusions

The methodologies proposed in this work showed to be reliable for thermodynamic predictions in SCWG systems of real biomass compounds. The predictions presented good agreement with experimental and simulated data from literature for the SCWG of sugarcane bagasse. The methodologies used and 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 effect of modifications in biomass source was analyzed on H_2 production and on the thermal behavior of the reactions. High H_2 production are observed for all substrates and the highest productions were observed for the SCWG of ethanol for isothermic systems. The entropy maximization has shown that, with the exception of the SCWG of ethanol, all other SCWG reactions presented autothermal behavior in almost all range of temperature and initial composition analyzed. However, at adiabatic conditions the highest productions of H_2 were observed for the SCWG of glycerol, mainly due to the exothermic behavior of this system. With the results, it is possible to conclude that all biomass materials tested presented potential for application in H_2 production.

Acknowledgements

The authors gratefully acknowledge the financial support from FAPESP – Fundação de Amparo à Pesquisa de Estado de São Paulo (Process 2011/20666-8) and CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil.

References

Brooke, A., Kendrick D., Meeraus A., Raman R., 1998, GAMS- A User's Manual. In GAMS Development Corp.: Washington, DC, USA.

Castello D., Fiori L., 2011, Supercritical water gasification of biomass: Thermodynamic constraints. Bioresource Technology, 102 (16), 7574-7582.

Freitas A.C.D., Guirardello R., 2013, Thermodynamic Analysis of Supercritical Water Gasification of Microalgae Biomass for Hydrogen and Syngas Production. Chemical Engineering Transactions, 32, 553-558, DOI: 10.3303/CET1332093

Freitas A.C.D., Guirardello R., 2012a, Supercritical Water Gasification of glucose and cellulose for hydrogen and syngas production. Chemical Engineering Transactions, 27, 361-366, DOI: 103303/CET1227061

Freitas A.C.D., Guirardello R., 2012b, Oxidative reforming of methane for hydrogen and syngas production: Thermodynamic Equilibrium analysis. Journal of Natural Gas Chemistry, 21, 571-580.

Guan Q., Savage PE., Wei C., 2012, Gasification of alga Nannochloropsis sp. In supercritical water. The Journal of Supercritical Fluids, 61, 139-145.

Lu Y.J., Zhao L., Guo L.J., 2011, Technical and economic evaluation of solar hydrogen production by supercritical water gasification of biomass in China. Int J Hydrogen Energy, 36, 14349–14359.

Osada M., Sato T., Watanabe M., Adschiri T., Arai K., 2004, Low-temperature catalytic gasification of lignin and celullose with a ruthenium catalyst in supercritical water. Energy & Fuels, 18, 327-333.

Osada M., Yamaguchi A., Hiyoshi N., Sato O., Shirai M., 2012, Gasification of sugarcane bagasse over supported ruthenium catalysts in supercritical water. Energy & Fuels, 26, 3179-3186.

Pitzer K.S., Curl R.L., 1957, The volumetric and thermodynamic properties of fluids. III. Empirical equation of the second virial coeficient. J. Am. Chem. Soc., 79, 2369-2370.

Tsonopoulos C., 1974, An empirical correlation of second virial coefficients. AIChE Journal, 20, 263-272.