

Use of the Surface Methodology in the Thermodynamic Evaluation of Glycerol Supercritical Water Gasification Systems

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There is strong interest in the use of glycerol, a by-product of the biodiesel production, as feedstock for hydrogen production through reforming processes such as the supercritical water gasification reaction (SCWG). In this work, the response surface methodology was applied to the results of glycerol SCWG simulations, with the aim of analysing the conditions which enhance hydrogen formation. The simulations were carried out with the aid of the software GAMS 23.9.5, through a non-stoichiometric thermodynamic model based on Gibbs energy minimization. Those simulations presented the final compositions of the gas phase for a range of operational conditions. The three variables whose influence was analysed were: temperature (from 617.16 K to 1182.84 K), pressure (from 231.72 to 288.28 atm) and initial quantity of glycerol (from 0.0189 to 0.2311 mol). Initially, three central composite rotational designs (CCRD) were done, each one with two independent variables and two levels for each of those variables. The statistical analysis of the results was done with the aid of the software TIBCO® STATISTICA™, which presented the response surfaces, in addition to the mathematical expressions of the obtained models and their respective coefficients of determination. It was verified that the influence of the pressure on the quantity of hydrogen produced was not statistically significant. On the other hand, the temperature and the initial amount of glycerol had strong influence on the hydrogen formation. There was continuous increase in the hydrogen production as the temperature was risen, and higher amounts of that product were obtained when greater initial quantities of glycerol were used. Those tendencies were present in the results of the three 2² designs. The maximum quantity of hydrogen (0.9365 mol) was obtained in the simulation in which the following values were used for the independent variables: 1100 K for the temperature, 260 atm for the pressure and 0.2 mol for the initial amount of glycerol.

1. Introduction

It is possible to obtain biofuels from biomass through biochemical and thermochemical conversion routes. Thermochemical routes are usually more advantageous because they are more capable of destroying organic compounds and less reaction time is required (Lachos-Perez *et al.*, 2015). Gasification, pyrolysis, liquefaction and combustion are some of the thermochemical conversion routes. Gasification technologies allow the conversion of biomass feedstocks to clean fuel gases. The gasification of wet biomass has an important disadvantage, which is the energy spending in the drying step. Supercritical water gasification is an option for hydrogen production in which the biomass drying is not necessary (Guan *et al.*, 2012).

Water is in the supercritical state when its temperature and pressure are higher than those of its critical point: 647 K and 220 bar, respectively. The interest in supercritical water as a reaction medium is due to its specific transport and solubilization properties (Calzavara *et al.*, 2015). Under supercritical conditions, there are significant changes in the physical properties of water: the dielectric constant, the thermal conductivity, the viscosity and the ionic product decrease, whereas there is only a slight reduction in density. Thus, the

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supercritical water has, approximately, the viscosity of the gas phase and the density of the liquid phase. That reaction medium works as a non polar homogeneous solvent, capable of dissolving organic compounds and gases. The low viscosity favours mass transfer and the density of a liquid improves solvation (Houcinat *et al.*, 2018). No other solvent presents more significant changes in its physical properties under supercritical conditions. The changes in the structure of water at high temperatures allows the formation of intramolecular and intermolecular hydrogen bonds, which are essential to obtain hydrogen from water.

Hydrogen is also produced through the water-gas shift reaction (simultaneous reaction that occurs during SCWG), in which water reacts with carbon monoxide to produce hydrogen and carbon dioxide. Other advantages of SCWG include the high rate of solids conversion (which results in lower levels of solid residues), the production of hydrogen at high pressures (reducing the amount of energy needed to pressurize the product gas), the use of a homogeneous reaction medium (reducing the resistance related to transport phenomena), the possibility of separating the carbon dioxide easily (due its much higher solubility in water at high pressures, in comparison to methane and hydrogen) and the shorter time required. The efficiency of biomass conversion through traditional methods decreases as the moisture content increases, whereas SCWG efficiency remains constant. Thus, it as an interesting option for wet biomass gasification (Freitas and Guirardello, 2014).

Glycerol is an interesting model compound for studies about SCWG because it is a by-product of biodiesel production. The huge amount of that substance that is formed as industrial waste is hardly fully used in traditional ways such as the production of cosmetics and animal feed (Castello and Fiori, 2011).

There is strong interest in hydrogen nowadays because it is a renewable and clean energy source. Renewable energy became more important because of the climate change which results from the carbon dioxide emissions to the atmosphere, the increase in energy demand and the volatility of the prices of conventional energy sources because of political factors (Lachos-Perez *et al.*, 2015). Hydrogen is a fuel with high energy content (141,8 MJ/kg) and diverse application possibilities (Ahmed *et al.*, 2012). Conventional hydrogen production processes have important disadvantages: water electrolysis has very high costs, methanation with the aid of micro-organisms has a very slow reaction rate and low efficiency. Thus, SCWG is an option with better efficiency and selectivity (Freitas and Guirardello, 2013).

It is possible to use mathematical models to study the physical and chemical phenomena that occur in the gasification reactor. Large scale SCWG experiments are often very expensive, so modelling and simulation are very useful to better understand that. There two possible approaches for the development of the SCWG thermodynamic model: stoichiometric and non stoichiometric. It is needed to know which reactions occur in the system to develop a stoichiometric model. That approach has the advantage of allowing the contribution of each reaction to be identified. In the non stoichiometric approach, it is only needed to know which chemical compounds may be present in the products, and then the principle of Gibbs energy minimization is used to determine their distribution. It a very flexible approach and prevents the neglect of important reactions (Castello and Fiori, 2011).

In this work, the response surface methodology was applied to the results of glycerol SCWG simulations, with the aim of analysing the conditions which enhance hydrogen formation. The simulations were carried out with the aid of the software GAMS 23.9.5, through a non-stoichiometric thermodynamic model based on Gibbs energy minimization. Those simulations presented the final compositions of the gas phase for a range of operational conditions. The three variables whose influence was analysed under hydrogen formation were: temperature (from 617.16 K to 1182.84 K), pressure (from 231.72 to 288.28 atm) and initial quantity of glycerol (from 0.0189 to 0.2311 mol).

2. Methodology

2.1 Thermodynamic model

The thermodynamic calculations were performed in this work by the use of a Gibbs energy minimization model, formulated as a non-linear programming in the software GAMS 23.9.5. This model is based in the fact that, at constant pressure (P) and temperature (T), with given initial composition, can be obtained by direct minimization of Gibbs energy, considering only the formation of a fluid phase and the possibility of solid carbon formation, can be represented by:

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

while satisfying the restrictions of non-negative number of moles of each component in each phase, given by:

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

In addition, the restriction of mole balances, given by atom balance for reactive systems was used in this work to consider every possible reaction in SCWG systems during the simulations, this restriction is given by:

$$\sum_{i=1}^{NC} a_{mi}(n_i^f + n_i^s) = \sum_{i=1}^{NC} a_{mi}n_i^0 \quad (3)$$

Since the system analysed 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:

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

Details about this thermodynamic formulation, as well as the validation of this model with experimental data, can be found in previous works of our research group for similar systems in Freitas and Guirardello (2012) and in Freitas and Guirardello (2014). A Total of 16 output compounds were selected as representative of the main compounds, which can be found in the output stream of SCWG reactive systems. These compounds were selected based on previous works that studied the SCWG reaction found in the literature (Guan et al., 2012).

2.2 Statistical analysis

In this work, the response surface methodology was applied to the results of glycerol SCWG simulations, with the aim of analyzing the conditions which enhance hydrogen formation.

The three variables whose influence the hydrogen formation and was analyzed in this work were: temperature (from 617.16 K to 1182.84 K), pressure (from 231.72 to 288.28 atm) and initial quantity of moles of glycerol (from 0.0189 to 0.2311 mol). The number of moles of water in the feed was fixed at 5 mols for all performed simulations. Initially, three central composite rotational designs were done, each one with two independent variables and two levels for each of those variables as presented in Tables 1-3. The statistical analysis of the results was done with the aid of the software TIBCO® STATISTICA™, which presented the response surfaces for the total number of moles of hydrogen produced.

Table 1: Absolute and coded values for temperature and pressure considered on first CCRD 2²

Temperature	Coded values	-1.414	-1	0	1	1.414
	Absolute values (K)	617.157	700	900	1100	1182.843
Pressure	Coded values	-1.414	-1	0	1	1.414
	Absolute values (bar)	231.715	240	260	280	288.284

Table 2: Absolute and coded values for temperature and initial number of moles of glycerol used in the feed considered on second CCRD 2²

Temperature	Coded values	-1.414	-1	0	1	1.414
	Absolute values (K)	617.157	700	900	1100	1182.843
Initial moles of glycerol	Coded Values	-1.4142	-1	0	1	1.4142
	Absolute values (mols)	0.019	0.050	0.125	0.200	0.231

Table 3: Absolute and coded values for pressure and initial number of moles of glycerol used in the feed considered on third CCRD 2²

Pressure	Coded values	-1.414	-1	0	1	1.414
	Absolute values (bar)	231.716	240	260	280	288.284
Initial moles of glycerol	Coded Values	-1.4142	-1	0	1	1.4142
	Absolute values (mols)	0.019	0.050	0.125	0.200	0.231

3. Results and discussion

Figure 1 presents the response surfaces obtained by the simulated results obtained in software TIBCO® STATISTICA™, for the three factorial designs 2² presented in Tables 1-3. Figure 1 (a) present the results for the effects of pressure and temperature under the total number of moles of H₂ produced, for these simulations, the initial amount of glycerol in the feed was fixed at 0,125 mols. Evaluating Figure 1 (a) it is possible to verify that the value of the response in moles of H₂ shows a continuous growth as the reaction

temperature increases. The influence of pressure is less significant. From the statistical point of view, only the linear factor for temperature showed significance through the 95% confidence (test F). Similar results for temperature and pressure effects are reported in the literature for the SCWG reaction of different biomass sources, like as microalgal biomass (Freitas and Guirardello, 2013) and glucose/cellulose (Freitas and Guirardello, 2012).

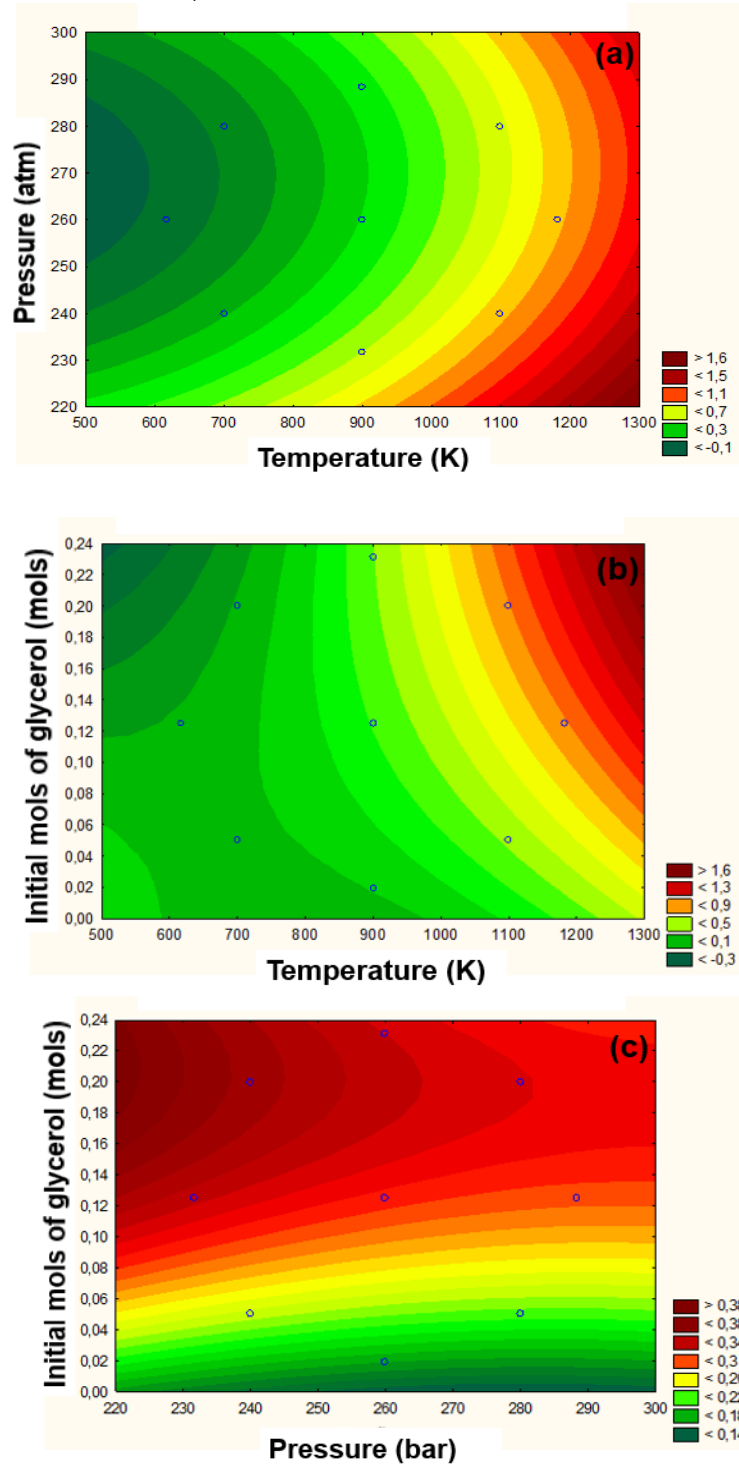


Figure 1. Obtained response surfaces for (a) temperature and pressure effects; (b) initial mols of glycerol and temperature effects; (c) initial mols of glycerol and pressure effects under total moles of hydrogen produced for SCWG of glycerol.

Figure 1 (b) presents the results for the effects of temperature and number of moles of glycerol in feed. As expected, it was found that the point at which the response reaches its maximum value is that at which the combination of the maximum values of the two independent variables analyzed occurs. The analysis of the graph reinforces the conclusion that the value of the amount of hydrogen produced increases sharply and continuously as the values of the experimental conditions in question become higher. Statistical analysis showed that both factors presented statistical significance at a 95% confidence level. Significance was also observed for the quadratic factor of temperature and for the cross-factor temperature x initial mol of glycerol.

In Figure 1 (c) the results for the evaluation of the effects of pressure and initial composition on the H₂ production by the SCWG reaction of the glycerol can be observed. Evaluating the results presented in Figure 1 (c), it can be verified that, as observed in the results presented in Figure 1 (a), that the pressure did not present significant effect on H₂ production. Thus, more evidence was obtained that the pressure does not affect the production of hydrogen from the glycerol SCWG in a relevant way. The initial mol of glycerol in the feed presented statistical significance at 95% confidence, both for the linear variable and for the quadratic variable.

Here is important to emphasize that during the simulations, the formation of ethane, propane, methanol and Ethanol was not observed in significant amounts, the formation of solid carbon was not observed in any of performed simulation as well, indicating that SCWG reaction, under the conditions under it was evaluated in this work, shows high substrate conversions, with low presence of intermediate compounds when the system reaches equilibrium.

Figure 2 shows the isolated effects of the variables pressure, temperature and initial composition of glycerol in the reactor feed. Figure 2 (a) shows the results for the initial composition of glycerol in the feed on the formation of hydrogen.

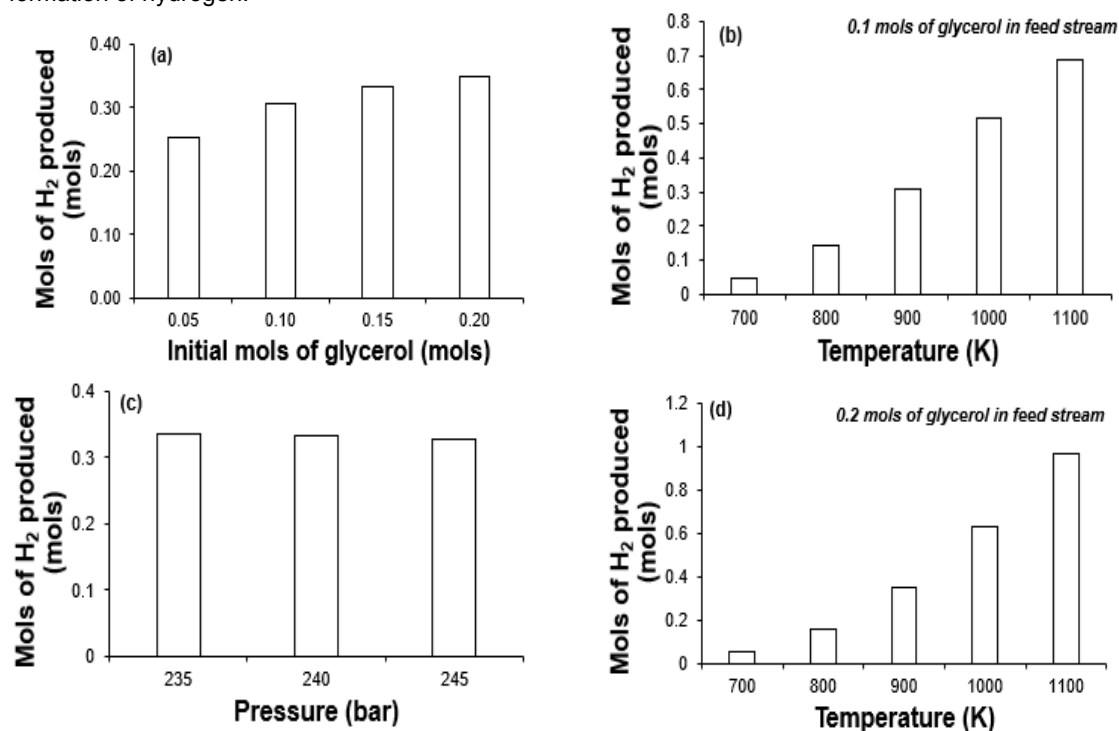


Figure 2. Isolated effects of the studied variables (a) initial composition of glycerol at constant pressure (240 bar) and temperature (900 K); (b) temperature at constant pressure (240 bar) and initial mols of glycerol (0.1 mols); (c) pressure at constant temperature (900 K) and initial mols of glycerol (0.15 mols); (d) temperature at constant pressure (240 bar) and initial mols of glycerol (0.2 mols).

Evaluating Figure 2 (a) it is possible to verify that increasing the concentration of glycerol in the feed results in increased productions of H₂. In Freitas and Guirardello (2013), when studying the SCWG of the microalgal biomass, a decrease in the formation of H₂ was observed with the increase of the amount of biomass in the feed stream of the reactor, this behavior is contrary to the observed in the simulations performed by the present work. This behavior can be explained by the high molar ratio of hydrogen present in the glycerol molecule (Houcinat et al., 2018).

In Figures 2 (b) and (d) the effects of reaction temperature are presented for 0.1 mol of glycerol in the feed and for 0.2 mol of glycerol in the feed, respectively. The observed effects are similar for the two temperatures evaluated, higher H₂ yields for higher reaction temperatures, with an approximately linear trend. Although higher amounts of H₂ have been produced when higher amounts of glycerol were used in the feed (see the results in Figure 2 (d)).

Figure 2 (c) shows the results for the effect of the pressure. As described in the results presented in Figure 1, the pressure had negligible effects on the formation of H₂ by the SCWG of the glycerol, maintaining at constant levels the remaining properties. Similar results, for pressure behavior, are reported by Castello and Fiori (2011), who also evaluated the SCWG reaction of glycerol.

4. Conclusions

The Gibbs energy minimization methodology, considering a system at constant pressure and temperature, proposed and developed in this work showed to be reliable for thermodynamic predictions in SCWG systems of glycerol. The thermodynamic model applied in the software GAMS 23.9.5 and solved with the solver CONOPT proved to be quick and effective in the resolution of the proposed thermodynamic problems, with computational time inferior to 1 s in all cases analysed by this work.

It was verified that the influence of the pressure on the quantity of hydrogen produced was not statistically significant at a 95% confidence level. On the other hand, the temperature and the initial amount of glycerol had strong influence on the hydrogen formation during SCWG of glycerol. There was continuous increase in the hydrogen production as the temperature was risen, and higher amounts of that product were obtained when greater initial quantities of glycerol were used as well. Those tendencies were observed in the results of the three 2² designs studying the statistic effects of the main reaction variables for all performed simulations. Statistically significant variations were observed for temperature and glycerol initial feed composition at a 95% confidence level. The maximum quantity of hydrogen (0.9365 mol) was obtained in the simulation in which the following values were used for the independent variables: 1100 K for the temperature, 260 atm for the pressure and 0.2 mol for the initial amount of glycerol, indicating that the glycerol SCWG reaction has good applicability for H₂ production.

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