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Optimization of Glycerol Gasification Process in Supercritical Water using Thermodynamic Approach

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Glycerol is a byproduct of biodiesel production. An alternative to use of this byproduct is the gasification with supercritical water (*SCWG*) for hydrogen generation. This work aims to analyze the conditions that enhance the formation of hydrogen using the response surface methodology in combination with optimization techniques. The results of the reaction in the equilibrium condition were obtained using Gibbs energy minimization method for isothermic systems and entropy maximization method for adiabatic systems. The proposed thermodynamic models were solved using GAMS 23.9.5 *software* in combination with CONOPT3 solver. As a result of the simulations, the final compositions of the gaseous phase and the thermal behavior for the operational conditions of the reaction are presented. The reaction was characterized by the formation of hydrogen, evaluating the temperature between 586.64 and 1259 K, pressures in the range of 216.36 to 283.64 bar and the glycerol / water molar ratio varying from 0.032 to 0.368 in the feeding according to the planning experimental. Higher hydrogen formation was observed for isothermic reaction conditions, indicating that glycerol *SCWG* was an endothermic reaction, this fact is justified by the results of adiabatic reactors. Hydrogen formation is mainly influenced by the effects of temperature and glycerol composition, reaching the maximum hydrogen formation (2.29 moles) operating in an isothermal manner for high temperatures (1123 K) and high glycerol/water ratios in the feed (0.368). For both results, the pressure pressure on the amount of internal hydrogen was not statistically significant at 95%.

1. Introduction

The conversion of biomass into energy, fuels or chemicals with high added value can be accomplished in a number of ways. Biochemical and thermochemical conversion routes are possible ways to obtain biofuels through the conversion of biomass. The thermochemical routes, such as gasification, pyrolysis and combustion, deal with the conversion of biomass into gases, either directly by burning or using chemicals as intermediates, these are more favorable because they present better efficiency in destroying organic compounds in less reaction time (Lachos-Perez et al. 2015). An alternative route for converting biomass into clean combustible gases is the gasification reaction with supercritical water (*SCWG*), this process has high levels of hydrogen formation with a high degree of purity and does not require the pre-drying treatment that would be necessary for the conventional gasification process (Freitas and Guirardello 2014).

The interest in using supercritical water as a reaction medium is in its transport and solubilization properties (Calzavara et al. 2005). Supercritical water has the viscosity of the gas phase and density of the liquid phase, approximately. The increase in temperature provides a decrease in its density, which causes the reduction of its dielectric constant, which causes water to behave similarly to a non-polar solvent, making it a good solvent for organic compounds (Houcinat et al. 2018).

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The gasification reaction with supercritical water has the advantage of a high rate of hydrogen formation, an effect resulting from the possibility of operating with biomass sources with a high moisture content. This trend ocourss because the addition of water that favors the displacement of the *water gas shift* reaction, thus generating more hydrogen.

Glycerol is a substrate of great potential for application in *SCWG*, since it is the by-product generated in greater quantity in the production of biodiesel, making up approximately 10% of the volume of biodiesel formed. The amount of this substance that forms as industrial waste is hardly fully utilized in traditional ways such as the production of cosmetics and animal feed (Castello and Fiori 2011). Through gasification, glycerol can be converted into hydrogen and other by-products.

This work uses the response surface methodology to verify the results of the glycerol *SCWG* simulations. The equilibrium compositions were obtained with the aid of the GAMS 23.9.5 *software*, using the Gibbs thermodynamic energy minimization and entropy maximization methods. This study aims to verify the operational conditions that maximize the formation of hydrogen throughout the glycerol *SCWG*.

2. Methodology

2.1. Thermodynamic models

Under conditions of constant pressure (*P*) and temperature (*T*), the condition of thermodynamic equilibrium can be formulated as a problem of minimizing Gibbs energy. The total Gibbs minimization problem of the system can be described according to Equation 1.

$$\min G = \sum_{i=1}^{NC} \sum_{k=1}^{NF} n_i^k \mu_i^k \quad (1)$$

The system in the condition of Gibbs minimum energy must satisfy the condition of non-negativity of the number of moles (Eq.2) and the conservation of the number of atoms (Eq.3).

$$n_i^k \geq 0 \quad (2)$$

$$\sum_{i=1}^{NC} a_{mi} \left(\sum_{k=1}^{NF} n_i^k \right) = \sum_{i=1}^{NC} a_{mi} n_i^o, m = 1, ..., NE \quad (3)$$

Under constant pressure (*P*) and enthalpy (*H*) conditions, equilibrium can be determined by the maximum entropy (Rossi et al. 2011). An entropy maximization problem can be written according to Equation 4. The formulation of equilibrium as an entropy maximization problem is interesting for determining the system equilibrium temperature (T_{eq}) mainly in exothermic reactions (Freitas and Guirardello 2012).

$$\max S = \sum_{i=1}^{NC} \sum_{k=1}^{NF} n_i^k \overline{S}_i^k \quad (4)$$

In addition to the restrictions imposed on the system in the condition of minimum Gibbs energy, the maintenance of the enthalpy (Eq.5) of the system must be added as a restriction.

$$\sum_{i=1}^{NC} \sum_{k=1}^{NF} n_i^k \overline{H}_i^k = \sum_{i=1}^{NC} n_i^o \overline{H}_i^o = H^o \quad (5)$$

The Gibbs energy minimization methodology provides as a result the equilibrium compositions of a reaction system in a reactor operating in an isothermal way and the methodology of maximizing entropy represents the operation of an adiabatic reactor.

To obtain the fugacity coefficients of the system components, the equations of the virial truncated in the second term were used. The calculation of the second virial coefficient will be made using the correlation of Pitzer and Curl (1957) , modified by Meng et al. (2004) according to Equation 6.

$$\ln \hat{\emptyset}_i = \left[\sum_{j}^{m} y_i B_{ij} - B\right] \frac{P}{RT} \tag{6}$$

The methodology used in this work, using the virial equation to represent the non-ideality of systems of interest, has been used by our research group to verify SCWG from several sources of biomass and previous works from our research group present the validation of this methodology comparing the predictive capacity of the virial equation with experimental data. Freitas and Guirardello (2014) presentes a comparison between experimental and predicted data using the virial equation for glycerol SCWG showing good agreement.

The thermodynamic models covered in this work will be solved by the GRG (Generalized Reduced Gradient) search method, using the CONOPT 3 solver, in the GAMS software.

Table 1 shows the thermodynamic properties of the chemical components involved and considered as possible to form in the SCWG reaction of glycerol, over the simulations performed in the GAMS *software*.

Table 1: Thermodynamic properties of the chemical components used in the simulations

Component	$V_c\left(\frac{m^3}{kmol}\right)$	$P_c(bar)$	$T_c(K)$	ω
H_2O	0.056	220.600	647.300	0.344
$C_3H_8O_3$	0.264	75.000	850.000	0.513
O_2	0.073	50.400	154.600	0.222
H_2	0.064	13.000	33.000	0.000
N_2	0.089	34.000	126.200	0.038
CH_2O_2	0.125	58.100	588.000	0.316
CH_3COOH	0.171	57.900	594.500	0.445
CH_4	0.099	45.800	191.100	0.011
CH_3OH	0.118	81.000	512.600	0.565
C_2H_6	0.146	48.700	305.300	0.099
C_2H_6O	0.167	64.500	513.900	0.649
C_3H_8	0.200	42.500	369.800	0.152
C_4H_{10}	0.255	38.000	425.100	0.200
CO	0.058	64.800	180.000	0.582
CO_2	0.082	101.500	431.002	0.851

Font: Poling et al. (2001)

The SCWG reaction of different sources of biomass produces various components such as methanol, methane, ethanol, ethane and others besides hydrogen. It was chosen to analyze the formation of hydrogen in view of the fact that it presents a major part in the formation of the synthesis gas (syngas), in addition to being a product of high interest for application in the Fischer-Tropsch synthesis reaction to obtain fuels or for use direct into fuel cells.

2.2. Statistical analysis

The statistical treatment of the results presented in this work was done with the aid of the TIBCO® STATISTICA™ *software*, using the response surface methodology applied to the results of the simulations made in GAMS for the glycerol *SCWG*. The reaction was characterized for the formation of hydrogen by evaluating temperatures between 586 and 1259 K, pressures in the range of 216.36 to 283.64 bar and the glycerol/water molar ratio varying from 0.032 to 0.368 in the feeding (ranges determined by the planning carried out in the STATISTICA *software*).

3. Results and discussion

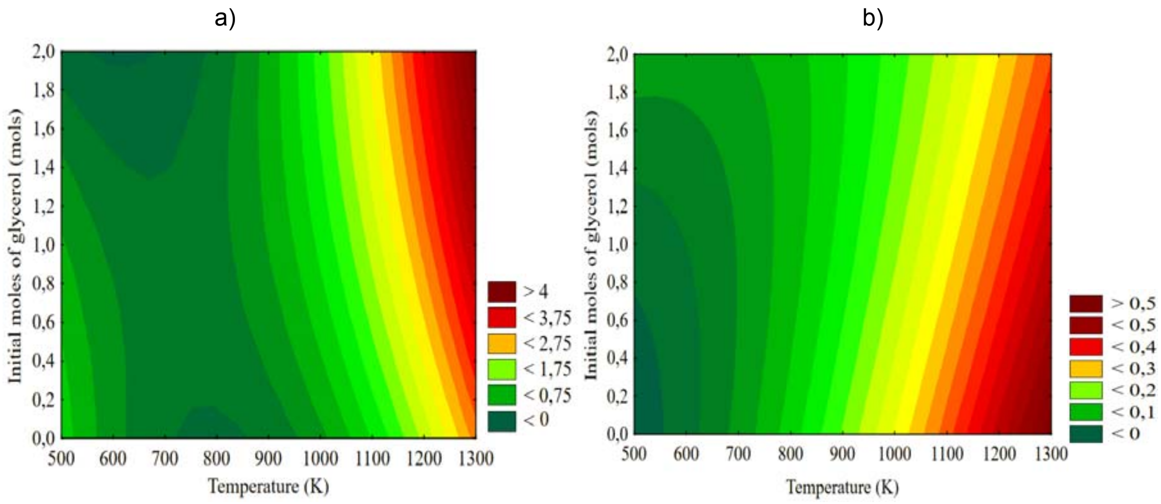
The results of Table 2 were obtained through simulations made in the GAMS *software* using methods of Gibbs energy minimization and entropy maximization for hydrogen formation during the reaction and the system equilibrium temperature (T_{eq}), for the conditions established in the planning matrix provided by the STATISTICA *software*. For both methodologies, the results presented in Table 2 indicate that the formation of hydrogen is favored with the increase in temperature. The yield of hydrogen production increases with increasing temperature, mainly above 873 K, similar results have been reported by Withag *et al.* (2012).

It is possible to conclude that lower rates of hydrogen formation are observed with the increase in system pressure, however, this difference has an insignificant value, at a 95% confidence level (F test). Similar results for temperature and pressure effects are reported in the literature for the glucose and cellulose *SCWG* reaction (Freitas and Guirardello 2012). Figure 1 presents the results for the effects of temperature and glycerol feeding under the formation of hydrogen throughout the reaction for Gibbs energy minimization and entropy maximization method by fixing the pressure at 250 bar.

Table 2: Experimental design and results of simulations of hydrogen formation and equilibrium temperature of the system fixing the water supply to 5 moles and varying the conditions of temperature, pressure and glycerol composition in the system feed

			minG	*maxS*	
Temperature (K)	Pressure (bar)	Glycerol (moles)	H_2 (moles)	H_2 (moles)	T_{eq} (K)
723.000	230.000	0.500	8.62E-02	6.13E-02	687.340
723.000	230.000	1.500	1.19E-01	6.39E-02	661.290
723.000	270.000	0.500	7.48E-02	5.68E-02	687.680
723.000	270.000	1.500	1.05E-02	5.92E-02	661.500
1123.000	230.000	0.500	1.48E+00	3.30E-01	972.730
1123.000	230.000	1.500	2.29E+00	2.61E-01	836.980
1123.000	270.000	0.500	1.38E+00	3.07E-01	973.680
1123.000	270.000	1.500	2.11E+00	2.42E-01	837.630
586.641	250.000	1.000	1.25E-02	2.73E-02	607.930
1259.359	250.000	1.000	3.90E+00	3.90E-01	987.450
923.000	216.364	1.000	6.57E-01	1.58E-01	780.070
923.000	283.636	1.000	5.53E-01	1.39E-01	780.980
923.000	250.000	0.159	3.83E-01	1.85E-01	876.040
923.000	250.000	1.841	7.48E-01	1.31E-01	739.630
923.000	250.000	1.000	6.00E-01	1.48E-01	780.570
923.000	250.000	1.000	6.00E-01	1.48E-01	780.570

The results presented in Figure 1 indicate greater efficiency of the Gibbs energy minimization methodology when compared to the entropy maximization for hydrogen formation. Under conditions of temperature equal to 923K, pressure equal to 250 bar and molar ratio of glycerol/water equal to 0.2 in the feed, the values of gas formation found were 0.60032 and 0.14783 moles of H_2, respectively for each method. This result indicates a better operationalization of the reactors in isothermal mode in comparison to adiabatic reactors, being still a proof of the endothermic behavior of this reaction.



a) b)

Figure 1: Hydrogen formation along the glycerol SCWG using Gibbs energy minimization methodologies (a) and entropy maximization (b)

Figure 2 shows the system equilibrium temperature as a function of the biomass concentration to be fixed at 250 bar. The results indicate that a glycerol *SCWG* presents a slightly endothermic behavior for both conditions analyzed. For this reason, a glycerol *SCWG* presents better rates of H_2 formation operating in isothermal reactors, as the temperature support offered by the system compensates for the endothermic effect of the reaction. This behavior is an indication that the reactions that result in the formation of hydrogen during a glycerol SCWG are mostly endothermic, probably associated with the glycerol decomposition routes.

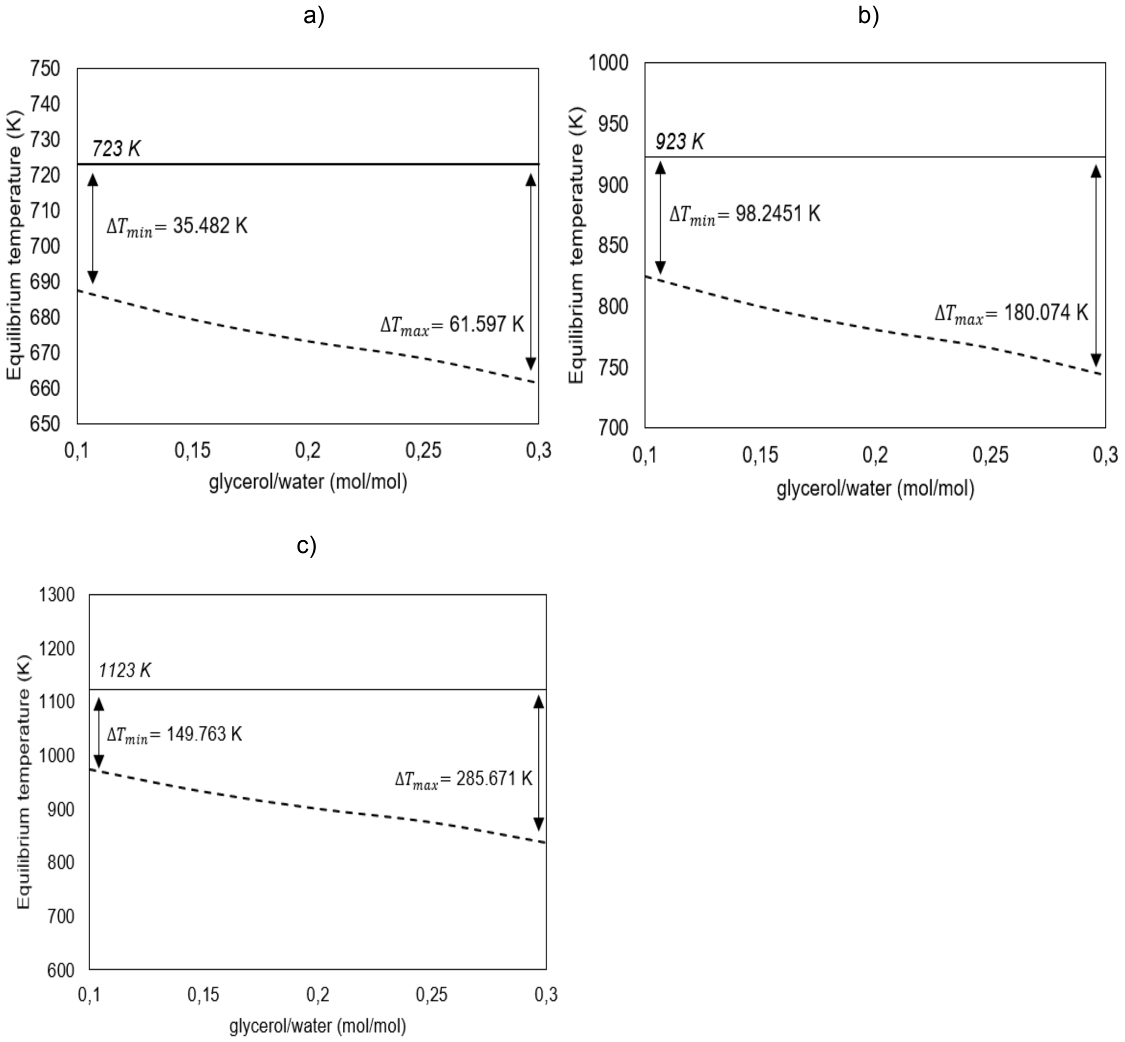


Figure 2: Equilibrium temperature as a function of the biomass concentration (a: 723 K; b: 923 K; c: 1123 K)

4. Conclusions

The Gibbs energy minimization and entropy maximization methods proved to be efficient for solving the equilibrium calculations during SCWG of glycerol. The thermodynamic models solved in the GAMS 23.9.5 *software* with the aid of the CONOPT solver are presented as a quick and effective way to solve the proposed thermodynamic problems, with computational time less than 1 second in all cases prevented by this work.

The temperature and composition of glycerol in the feed have a major influence on the formation of hydrogen throughout the reaction. Conversely, pressure is not significant under this result, at a level of 95% statistical confidence. The results indicate that the highest hydrogen formation rates are obtained during a glycerol SCWG when the system is conditioned at constant temperatures, which means, when an equilibrium condition is solved as a Gibbs energy minimization problem. This result is justified by the endothermic behavior of the glycerol SCWG when the isothermal reactor provides the thermal support favoring the formation of products throughout the reaction, compensating for its endothermic effect.

Under similar conditions of pressure, temperature and glycerol composition in the reactor supply, the results of hydrogen formation obtained by the Gibbs energy minimization methodology are on average 63.82% higher than the results obtained by the entropy maximization methodology for the formation of this product, indicating better operationalization of the reactors in isothermal mode compared to adiabatic reactors for an SCWG glycerol.

In an isothermal reactor, higher rates of hydrogen (2.29 moles) are formed during the SCWG reaction of glycerol when the system is conditioned to the high temperatures (1123K) and high glycerol/water ratios in the feed (0.368). Thus, the glycerol SCWG reaction proved to be an effective route for the production of hydrogen.

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