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Research Article

Thermodynamic Analysis of Glycerol Steam Reforming

A thermodynamic analysis of steam reforming of glycerol using the stoichiometric method has been performed. Since the aim of this work is to study product distribution and coke formation in equilibrium, two different models have been proposed: (a) CO as primary product and (b) CO_2 as primary product. Moreover, substantial information regarding the behavior of the different reactions could be acquired. Product distribution at equilibrium has been investigated in a broad range of conditions: temperature (600–1200 K), water-to-glycerol feed molar ratio (0:1–10:1), and pressure (1–9 atm). Glycerol conversion results completely over the whole range of the mentioned conditions. Consequently, product distribution at equilibrium is determined by water gas shift (WGS) and methanation or methane steam reforming reactions. Finally, high temperatures and a high water-to-glycerol feed molar ratio favor hydrogen production and decrease both methane and coke.
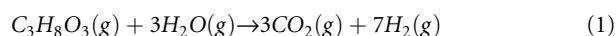
1 Introduction

Nowadays, production of biodiesel is increasing all over the world and it is predicted that biodiesel would make up as much as 20 % of all transportation fuel by 2020 [1]. Biodiesel is mainly produced by transesterification of plant and animal oils, with glycerol being the most important by-product of this process (10 wt %). The growth of biodiesel production is going to cause an excess of glycerol which is expected to flood the world market [2].

At the moment, glycerol of high purity is used in diverse industries, such as food, cosmetics, and pharmaceutical. Since it is really expensive to refine crude glycerol especially for medium- or small-sized plants [1], researchers are looking for alternative applications for this glut of glycerol. On the other hand, 95 % of hydrogen production is based on fossil fuel as feedstocks and it is mostly consumed in oil and petrochemical industries. Its demand has recently increased due to the new application of hydrogen as an energy vector, particularly as feed to fuel-cells. Therefore, producing hydrogen from glycerol has been proposed as a feasible option with the major advantage of being a carbon-neutral process with less impact on global climate [2].

In order to produce hydrogen from glycerol, two different options are studied. One of them, aqueous phase reforming of oxygenated hydrocarbons, has been proposed by the Dumesic group [3–12] and by Luo et al. [1]. The other option, glycerol steam reforming, has been studied by Czenik et al. [13] using crude glycerine over nickel-based catalysts. Similar studies have been performed by Adhikari et al. [2, 14, 15]. Also the use of noble metal catalysts and different supports for steam reforming of glycerol has been investigated [16–19].

The overall reaction of hydrogen production by steam reforming of glycerol is:

$$C_3H_8O_3(g) + 3H_2O(g) \rightarrow 3CO_2(g) + 7H_2(g) \tag{1}$$

However, steam reforming of glycerol involves complex reactions. As a result, several intermediate by-products are formed affecting the purity of the produced hydrogen. Furthermore, hydrogen production strongly depends on different operative conditions, such as water-to-glycerol feed molar ratio, temperature, and pressure. In addition, the deactivation of catalysts produced by coke formation can be minimized operating at a high water-to-glycerol feed molar ratio. Therefore, the first step to understand the effect of the mentioned variables on hydrogen production and coke formation is a complete thermodynamic study of the glycerol-water system.

Although several studies have been carried out on hydrogen production from glycerol, only Adhikari et al. [15, 20] have

Correspondence: Dr. Norma Amadeo (norma@di.fcen.uba.ar), Laboratorio de Procesos Catalíticos, Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad de Buenos Aires, Pabellón de Industrias, Ciudad Universitaria, 1428 Buenos Aires, Argentina.

done a thermodynamic analysis of the process by the non-stoichiometric method (minimization of Gibbs free energy). In their studies, Adhikari et al. have found that the best conditions for hydrogen production are temperatures higher than 900 K, atmospheric pressure, and a water-to-glycerol feed molar ratio of 9:1.

In this work, an analysis of steam reforming of glycerol is carried out applying the stoichiometric method, studying the effect of process variables, such as pressure, temperature, and water-to-glycerol feed molar ratio on product distribution and coke formation.

2   Methodology

Since the stoichiometric method was employed, a set of linearly independent reactions is necessary to describe the system. Based on several studies about glycerol steam reforming [2, 15, 18, 21–25], glycerol aqueous phase reforming [8], and ethanol steam reforming [26], the reaction between water and glycerol in the presence of a catalyst might involve the following chemical equations:

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \tag{2}$$

$$C_3H_8O_3 + H_2O \rightleftarrows 2CO_2 + CH_4 + 3H_2 \tag{3}$$
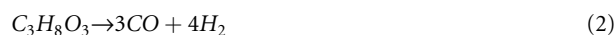
Carbon monoxide, considered as an intermediate product, might be consumed by the water gas shift (WGS) and methanation reactions as follows:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{4}$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \tag{5}$$

The thermodynamic data for these four reactions and for reaction (1) are presented in Tab. 1. Reactions (2) and (3) have higher equilibrium constants in the analyzed range of temperature. It can be seen that reaction (2) is endothermic while reaction (3) is slightly exothermic. WGS and methanation reactions present an exothermic behavior. Therefore, two models have been suggested for this study: model A which is comprehended by reactions (2), (4), and (5), and model B which includes reactions (3), (4), and methane steam reforming reaction instead of methanation reaction (5). Although product distribution in the equilibrium is independent of the used

Table 1. Thermodynamic data.

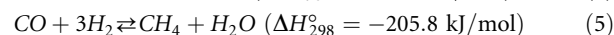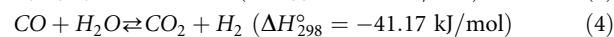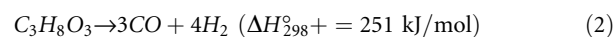|	$\Delta H^\circ_{(298\ K)}$ [kJ/mol]	$\Delta G^\circ_{(298\ K)}$ [kJ/mol]	$K_{(298\ K)}$
Reaction 1	127.71	–48.85	$3.66 \cdot 10^8$
Reaction 2	251.21	37.04	$3.22 \cdot 10^{-7}$
Reaction 3	–36.93	–162.15	$2.65 \cdot 10^{28}$
Reaction 4	–41.17	–28.63	$1.04 \cdot 10^5$
Reaction 5	–205.80	–141.93	$7.57 \cdot 10^{24}$

scheme, it is useful to study the extent of the reactions involved in each model. A similar study has been performed by Mas et al. for ethanol steam reforming [26].

An ideal gas mixture and a homogeneous system were assumed, except when coke formation was analyzed. Temperature and pressure ranges were established between 600 and 1200 K and 1 to 9 atm, respectively. The water-to-glycerol feed molar ratio ($r = mol_{H_2O}/mol_{C_3H_8O_3}$) ranges between 0:1 and 10:1 for model A and between 1:1 and 10:1 for model B.

3   Results and Discussion

One of the main advantages of performing the thermodynamic analysis of glycerol steam reforming by the stoichiometric method is that we can not only relate the acquired information to product distribution in equilibrium but also information regarding the behavior of the different reactions involved in the proposed reaction scheme. These might be useful in order to recommend the catalyst role required to minimize an undesired intermediate, such as methane.

3.1   Model A: CO as Primary Product

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \ (\Delta H^\circ_{298}+ = 251\ kJ/mol) \tag{2}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \ (\Delta H^\circ_{298} = -41.17\ kJ/mol) \tag{4}$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \ (\Delta H^\circ_{298} = -205.8\ kJ/mol) \tag{5}$$

In these reaction schemes the overall reaction results from the addition of reactions (2) and (4). In addition, since carbon monoxide and hydrogen are present in the reacting system, the methanation reaction should be considered.

For the analysis, 1 mol of glycerol and r moles of water were considered. The stoichiometric balance for this system is:

$$n_{C_3H_8O_3} = 1 - \xi_2$$
$$n_{H_2O} = r - \xi_4 + \xi_5$$
$$n_{CO_2} = \xi_4$$
$$n_{H_2} = 4\xi_2 + \xi_4 - 3\xi_5$$
$$n_{CO} = 3\xi_2 - \xi_4 - \xi_5$$
$$n_{CH_4} = \xi_5$$
$$n_T = 1 + r + 6\xi_2 - 2\xi_5$$

Equilibrium constants as a function of the mole number are:

$$K_2 = \frac{n_{CO}^3 n_{H_2}^4 P^6}{n_{C_3H_8O_3} n_T^6}$$

$$K_4 = \frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}}$$

$$K_5 = \frac{n_{CH_4} n_{H_2O} n_T^2}{n_{CO} n_{H_2}^3 P^2}$$

The mole number in the equilibrium of each component and the reaction extent for each reaction were obtained solving this algebraic equation system using the Newton Raphson

method. Reaction (1) is completely shifted to the products, the extent of this reaction being equal to 1 for all ranges of temperature and water-to-glycerol feed molar ratios studied.

The methanation reaction extent in equilibrium is shown in Fig. 1 as a function of temperature and water-to-glycerol feed molar ratio. The reaction extent decreases as the temperature is increased, in agreement with exothermic reaction behavior. Considering the same temperature, the reaction extent decreases as r increases, due to the dilution effect caused in the system by the increase of the moles of water and by the fact that water is a product of the reaction. As a consequence the methanation reaction extent shifts to the reactants. Although the reaction extent reaches values close to zero, its value is always positive, hence the inverse reaction (methane steam reforming) does not take place in the studied range of temperature.
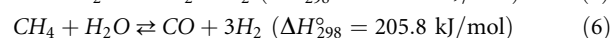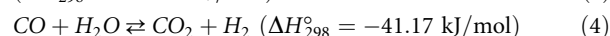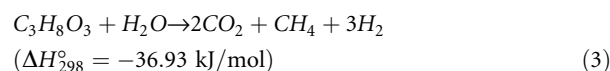
Regarding the WGS reaction extent, it results positive in the whole range of temperature and r analyzed, as shown in Fig. 2. Despite the fact that WGS is an exothermic reaction, its reaction extent presents a maximum with temperature. These maximum values shift to higher temperatures when the water-to-glycerol feed molar ratio is between 1 and 7, while for higher r-values the maximum moves towards lower temperatures. This behavior is a consequence of the competitive effect between reaction exothermicity and high values of water-to-glyc-

erol feed molar ratio. The existence of the competitive effect is evidenced when $r = 0$, since, as there is no competition between water and reaction exothermicity, the WGS extent does not present a maximum and decreases continuously with temperature.

From these results it can be concluded that the methanation reaction is predominant over the WGS reaction at low temperatures and low water-to-glycerol feed molar ratios. Similar results have been obtained by Fishtik et al. [27], who have performed a thermodynamic analysis for steam reforming of ethanol. They concluded that the WGS contribution is poor at low temperatures and low water-to-ethanol ratios, while its importance increased when temperature and water-to-ethanol ratio were increased.

3.2 Model B: CO$_2$ as Primary Product

Model B considered the following scheme of reaction:

$$C_3H_8O_3 + H_2O \rightarrow 2CO_2 + CH_4 + 3H_2$$
$$(\Delta H^\circ_{298} = -36.93 \text{ kJ/mol}) \quad (3)$$
$$CO + H_2O \rightleftarrows CO_2 + H_2 \ (\Delta H^\circ_{298} = -41.17 \text{ kJ/mol}) \quad (4)$$
$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \ (\Delta H^\circ_{298} = 205.8 \text{ kJ/mol}) \quad (6)$$

The overall reaction could be obtained for this model by addition of the three reactions. Methane steam reforming reaction has been considered instead of methanation reaction, since for this model methane is an intermediate product.

As in model A, the feed consists of 1 mol of glycerol and r moles of water. Then the stoichiometric balance is:

$$n_{C_3H_8O_3} = 1 - \xi_3$$
$$n_{H_2O} = r - \xi_3 - \xi_4 - \xi_6$$
$$n_{CO_2} = 2\xi_3 + \xi_4$$
$$n_{H_2} = 3\xi_3 + \xi_4 + 3\xi_6$$
$$n_{CO} = -\xi_4 + \xi_6$$
$$n_{CH_4} = \xi_3 - \xi_6$$
$$n_T = 1 + r + 4\xi_3 + 2\xi_6$$

Equilibrium constants are defined as follows:

$$K_3 = \frac{n^2_{CO_2} n_{CH_4} n^3_{H_2} P^4}{n_{C_3H_8O_3} n_{H_2O} n^4_T}$$
$$K_4 = \frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}}$$
$$K_6 = \frac{n_{CO} n^3_{H_2} P^2}{n_{CH_4} n_{H_2O} n^2_T}$$

For the glycerol steam reforming reaction (3) a similar behavior to that presented by the glycerol dehydrogenation reaction (2) in model A is observed, since it is completely shifted to the products, with an extent of reaction of one in the whole
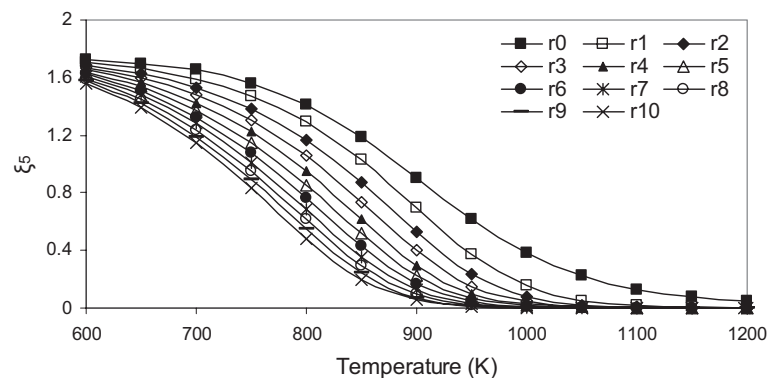

Figure 1. Methanation reaction extent vs. temperature at different r-values. Model A.
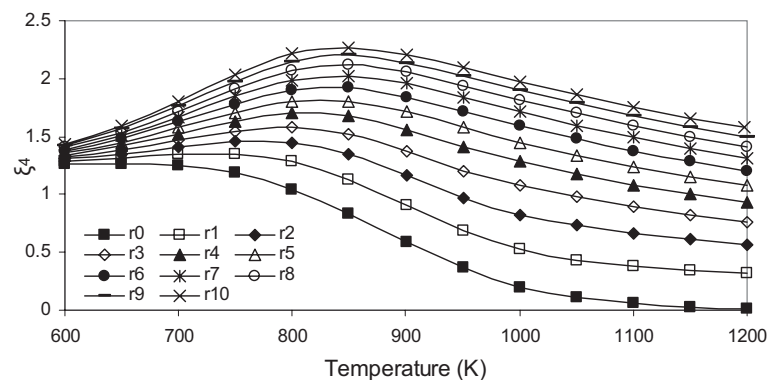

Figure 2. Extent of WGS reaction vs. temperature at different r-values. Model A.

range of temperature and water-to-glycerol feed molar ratio studied.

The ethane steam reforming reaction extent is shown in Fig. 3, as a function of temperature for different water-to-glycerol feed molar ratios. The behavior observed is opposite to that exhibited in model A by the methanation reaction, where the reaction extent diminished with temperature. For this model, the reaction extent takes negative values at low temperatures and moves to positive values as the temperature increases, reaching the constant value of 1 at temperatures higher than 1050 K for all water-to-glycerol feed molar ratios used. As expected, the reaction extent increases with temperature for every r-value, in agreement with the endothermic behavior of the methane steam reforming reaction. Considering the same temperature, the reaction extent increases as the water-to-glycerol feed molar ratio is increased due to the dilution effect caused by the increase in moles of water. Negative values of the reaction extent imply that at temperatures lower than 850–725 K, for $r = 1$ and $r = 10$, respectively, the inverse reaction, namely the methanation reaction, takes place.

Concerning the WGS reaction, its reaction extent follows the same trend of that registered in model A, even though reaction extents are displaced in one unit to lower values. The reaction extent takes negative values in a wide range of temperature and water-to-glycerol feed molar ratios (Fig. 4). Evidently, at low temperatures for each mole of CO_2 produced via reaction (3) approximately half of it reacts to produce carbon monoxide which is then consumed via methanation. While r-values are lower or equal to 6, the WGS reaction extent is negative in the range of temperature analyzed, suggesting that parts of the carbon dioxide and hydrogen produced by reaction (3) are consumed by the inverse WGS. From $r = 7$, the WGS reaction extent takes positive values in a range of intermediate temperatures (around 800 K), which is widened as r increases. Under these conditions, the carbon monoxide produced by methane steam reforming is consumed to give dioxide via WGS, whereas, at high temperatures for the whole range of r, inverse WGS proceeds with methane steam reforming.
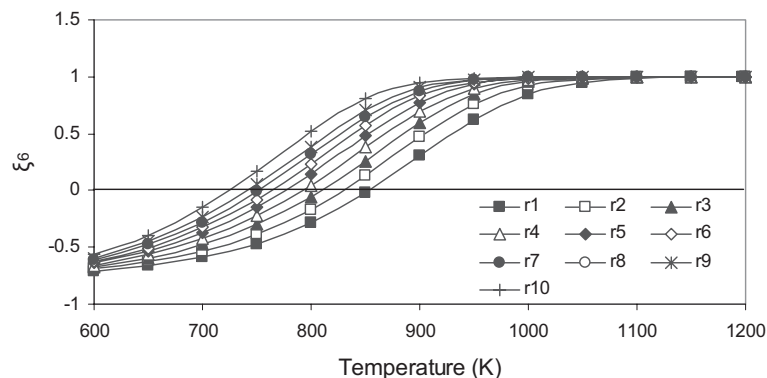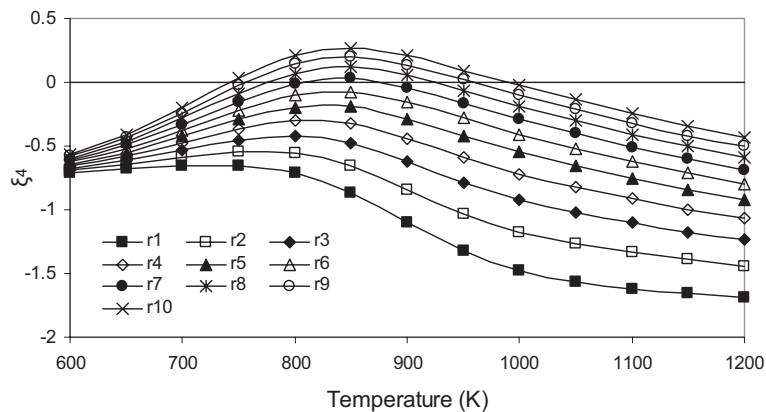

Figure 4. WGS reaction extent vs. temperature at different r-values. Model B.

From the obtained results and considering that methane is an undesired subproduct of the reforming of glycerol since it competes with hydrogen production, the following suggestions may be made:

- If CO is a primary product (model A), a catalyst that prevents methanation reaction is required in order to diminish methane formation.
- If CO_2 is a primary product (model B), a catalyst that favors the methane reforming reaction is required.

3.3 Product Distribution

Product distribution in equilibrium is independent of the chosen reaction scheme. Hydrogen and carbon monoxide yields ($y_i = n_i/n_{C_3H_8O_3}$) as a function of the temperature for different water-to-glycerol feed molar ratios (r), are demonstrated in Figs. 5 and 6, respectively. Results show that the hydrogen yield increases with the increase of r due to the rise of the H/C ratio in agreement with the results reported by Adhikari et al. [20] and Vagia and Lemonidou [28]. Nevertheless, it must be noted that an excess of water in the feed has a negative effect on the energy consumption. The increase in the number of moles of hydrogen is less marked as r increases (see Fig. 5). For each r-value, except for $r = 0$, there is a temperature at which the hydrogen yield reaches a maximum value. Adhikari et al. [20] reported that only for r higher than 6:1 the hydrogen yield presented a maximum. These maxima shift to lower temperatures as r increases, so for each r-value there is an optimal operation temperature at which hydrogen production is maximized. For instance, when $r = 10$ and the temperature is 926 K, 6.07 moles of hydrogen are obtained which is slightly lower than the stoichiometric maximum of 7 moles of hydrogen per mol of glycerol. In addition, the carbon monoxide yield decreases as r increases and considering an r-value it grows with temperature (see Fig. 6). The carbon dioxide yield in the equilibrium follows the same trend as the WGS reaction extent with temperature for different r-values (Fig. 1). At
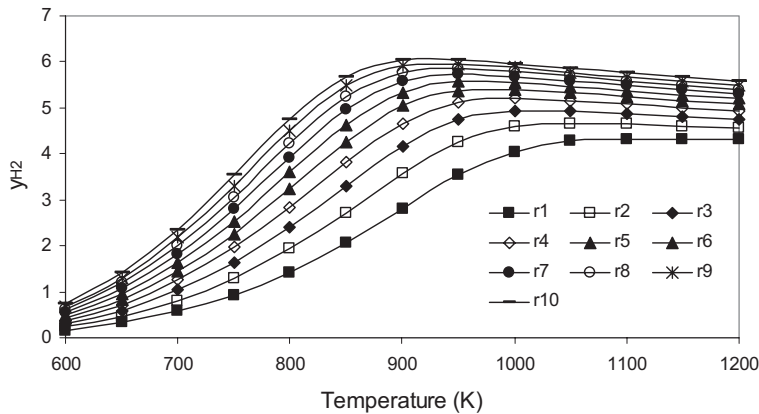

Figure 3. Extent of methane steam reforming reaction vs. temperature at different r-values. Model B.

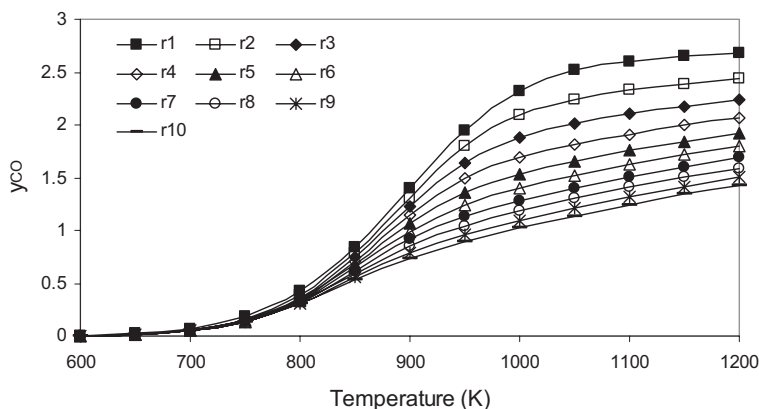**Figure 5.** Hydrogen yield in equilibrium at different *r*-values.

Figure 6. Carbon monoxide yield in equilibrium at different *r*-values.

$$2CO \rightleftarrows CO_2 + C \; (\Delta H^{\circ}_{298} = -172.45 \; \text{kJ/mol}) \quad (7)$$

$$CH_4 \rightleftarrows H_2 + C \; (\Delta H^{\circ}_{298} = 745.2 \; \text{kJ/mol}) \quad (8)$$

$$CO + H_2 \rightleftarrows H_2O + C$$
$$(\Delta H^{\circ}_{298} = -131.28 \; \text{kJ/mol}) \quad (9)$$

$$CO_2 + H_2 \rightleftarrows 2H_2O + C$$
$$(\Delta H^{\circ}_{298} = -90.12 \text{kJ/mol}) \quad (10)$$

Reaction (6), known as the Bouduard reaction, has the lowest free energy of formation. Therefore, this reaction is chosen to perform the analysis of the effect of coke formation over product distribution in equilibrium. The Bouduard reaction must be added to one of the two models formerly studied. In particular, we considered Model A and the Bouduard reaction.

Since the aim is to analyze the effect of coke formation over product distribution, the Bouduard reaction (7) is included in the reaction scheme. This reaction is chosen as representative, since the obtained results are independent of the chosen reaction.

Model A and Bouduard reaction

The following reactions are considered:

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \quad (2)$$
$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (4)$$
$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \quad (5)$$
$$2CO \rightleftarrows CO_2 + C(s) \quad (7)$$

The stoichiometric balance results:

$$n_{C_3H_8O_3} = 1 - \xi_2$$
$$n_{H_2O} = r - \xi_4 + \xi_5$$
$$n_{CO_2} = \xi_4 + \xi_7$$
$$n_{H_2} = 4\xi_2 + \xi_4 - 3\xi_5$$
$$n_{CO} = 3\xi_2 - \xi_4 - \xi_5 - 2\xi_7$$
$$n_{CH_4} = \xi_5$$
$$n_T = 1 + r + 6\xi_2 - 2\xi_5 - \xi_7$$
$$n_C = \xi_7$$

The equilibrium constants for reactions (2), (4), and (5) were given before, while the equilibrium constant for reaction (7) is:

$$K_7 = \frac{a_C n_{CO_2} n_T}{n_{CO}^2 P}$$

The Bouduard reaction extent vs. temperature for different water-to-glycerol feed molar ratios is presented in Fig. 7. It can be noted that the possibility of coke formation is higher at low *r*-values. When *r* = 0, coke formation is possible in the entire temperature range, while for *r* = 4 or higher coke formation is not possible in the whole range of studied temperatures.
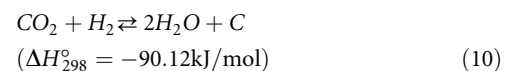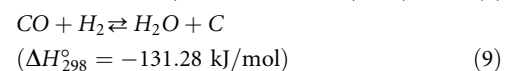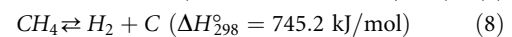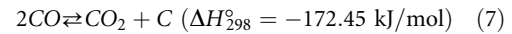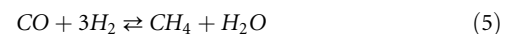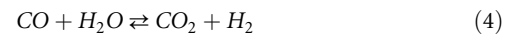
low temperatures (*T* = 600 K) the carbon dioxide yield tends to a constant value (approximately 1.3) which is almost the same for the *r*-values. Carbon dioxide moles increase with temperature until they reach a maximum value which increases as *r* increases. It can be concluded that carbon dioxide production is favored by the increase of the water-to-glycerol feed molar ratio, in agreement with the observed trend in the WGS reaction extent.

As already mentioned, methane competes with hydrogen by hydrogen atoms, consequently it is useful to analyze the methane behavior at equilibrium. Its production decreases with both, temperature and water-to-glycerol feed molar ratio, and its value tends to zero at temperatures higher than 1000 K for all *r*-values, following the same behavior as the methanation reaction extent.

3.4 Coke Formation

In order to analyze coke formation from the thermodynamic point of view, elemental carbon in the graphitic form is considered, hence, its free energy of formation (ΔG_f) and vapor pressure are zero in the studied range of temperature.

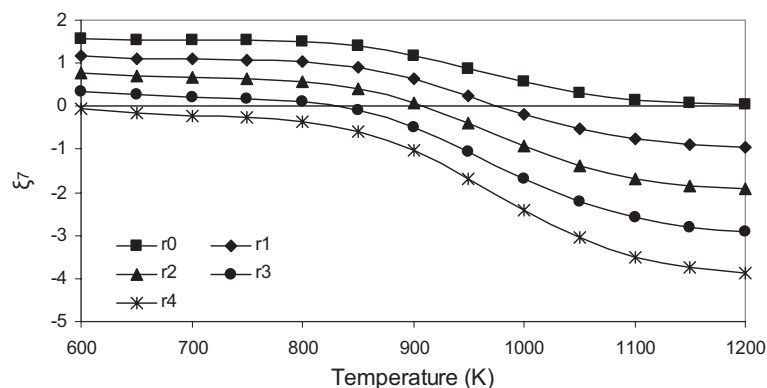Possible reactions of coke formation are:

Figure 7. Extent of reaction (6) vs. temperature at different *r*-values. Model A.

It can be noted that only when $r = 0$ the reaction extent has positive values in the whole range of temperatures. For all *r*-values, the reaction extent decreases with the increase of temperature. As the water-to-glycerol feed molar ratio increases, the Bouduard reaction extent decreases and takes negative values at lower temperatures. For *r* higher or equal to 4, coke formation is not possible in the whole range of temperatures considered in this work.

Finally, Fig. 8 shows the range of conditions under which coke formation is feasible. It can be concluded that coke formation can be avoided by working at high temperatures and high water-to-glycerol feed molar ratios, in agreement with Adhikari et al. [20].

3.5 Pressure Effect

With the aim of studying the effect of pressure on product distribution, the pressure range of 1 to 9 atm was examined. Considering the hydrogen yield, it decreases when the pressure of the system is increased. The maximum hydrogen yield with temperature moves towards higher temperatures when pressure increases. At high temperatures, moles of hydrogen in equilibrium tend to the same value (5.06 moles H_2) for different pressure values.
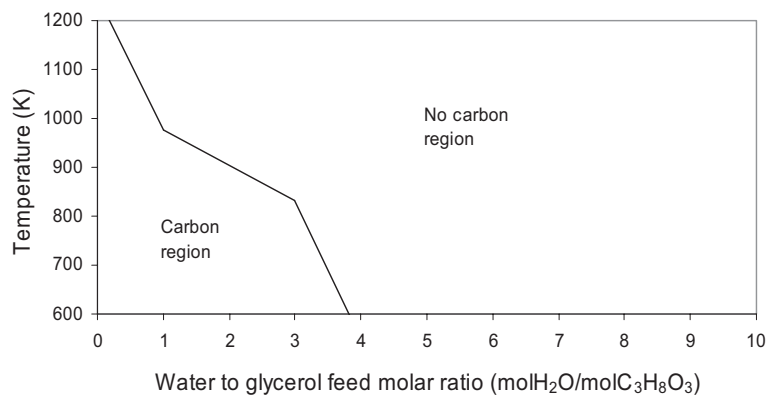

Figure 8. Range of conditions for carbon formation.

At higher pressures, a higher temperature is necessary for the disappearance of methane at the equilibrium (Fig. 9). This conduct could be explained by the methanation reaction, which occurs with a reduction of the total mole number. As a consequence, an increase in pressure shifts this reaction to product formation, increasing the yield of methane in the equilibrium.

From hydrogen and methane behavior with pressure it can be concluded again, that at high temperatures the WGS reaction is predominant over the methanation reaction. Hydrogen and methane moles reach constant values for all pressures at high temperature, in agreement with the fact that the WGS reaction is independent of the pressure.

Pressure effect over coke formation is shown in Fig. 10. As mentioned before, model A is considered for the analysis with the Bouduard reaction, since this behavior is independent of the chosen reaction for coke formation and of the chosen model.

A slight decrease in coke formation is observed for temperatures lower than 900 K as pressure increases. On the contrary, at temperatures higher than 900 K, coke formation is favored when pressure increases. Even at higher pressure the temperature range in which coke formation is feasible is significant.

Coke behavior with pressure could be explained by the fact that the most probable coke formation reactions are (6) and (8) which are exothermic and in which a contraction in the number of moles from reactants to products is produced. As a consequence, the exothermic character of the reactions is predominant over the contraction effect at low temperatures (<900 K), therefore, coke formation decreases with pressure. At high temperatures, the contraction effect is more important than the exothermic behavior, so coke formation increases with pressure at a given temperature.

4 Conclusions

In this work, a thermodynamic analysis of hydrogen production from glycerol steam reforming using the stoichiometric method has been performed. Independently of the reaction system considered, glycerol conversion is complete in the equilibrium, which means that either glycerol dehydrogenation reaction or glycerol steam reforming reaction totally proceeds to products. In both models analyzed, equilibrium product distribution is determined by WGS and methanation reactions. Regarding the WGS reaction, a competition between reaction exothermic behavior and high water-to-glycerol feed molar ratios occurs, and as a consequence the reaction extent presents a maximum as a function of temperature for the different *r*-values. When considering the methanation reaction, a dilution effect caused by an excess in the moles of water has to be considered since this excess produced a decrease in its reaction extent while these conditions favored the
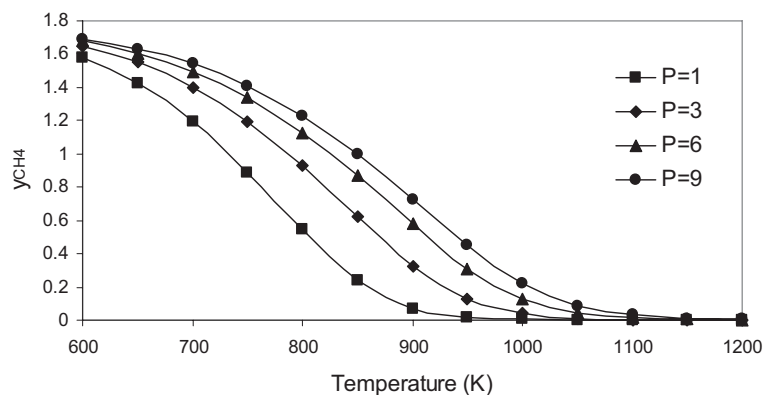
Figure 9. Methane yield vs. temperature at different pressures (atm). $r = 9{:}1$.
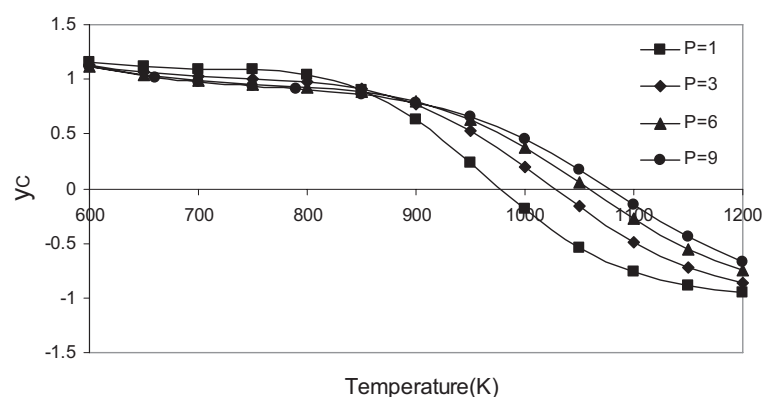

Figure 10. Coke yield vs. temperature at different pressures (atm). $r = 1{:}1$.

methane steam reforming reaction. In agreement with Fishtik et al. [27] we concluded that at low temperature the methanation reaction is predominant over the WGS reaction. On the contrary, at high temperatures WGS predominates, since at high temperatures moles of hydrogen converge to a constant value for different pressures, meaning that at high temperatures the product distribution is not affected by the pressure. It is evident from these results that one of the main advantages of performing the thermodynamic analysis by the stoichiometric method is the fact that substantial conclusions regarding the behavior of the different reactions involved can be achieved.

If the aim of glycerol steam reforming is hydrogen production, then the reaction should be carried out at high temperatures and high water-to-glycerol feed molar ratios. These operation conditions favor hydrogen production and decrease both, methane and coke formation. In addition, carbon monoxide production is favored at high temperatures and low water-to-glycerol feed molar ratios. The dilution effect in carbon monoxide moles due to an excess in water moles has to be considered when different catalysts are being compared, since wrong conclusions might be reached.

Finally, the pressure effect on product distribution in equilibrium has been analyzed. An increase in the pressure favors the methane yield while hydrogen production decreases. Concerning coke formation, at low temperatures (<900 K) and increasing pressure coke formation slightly decreases, while this behavior is exactly the opposite when the temperature is higher than 900 K.

Symbols used

K_j	equilibrium constant of j reaction
n_i	mole number of i species
nT	total mole number
r	water-to-glycerol feed molar ratio
ξ_j	extent of j reaction
ac	coke activity
yi	yield of i species defined as n_i/n_{C3H8O3}°

Subscripts

i	species
j	reaction

Superscript

$^{\circ}$	initial

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